This book contains extended abstracts of papers presented at the 6th International Conference on Nuclear and Radiochemistry (NRC 6), held from 29 August to 3 September 2004 in Aachen, Germany. It comprises in a compact form some of the recent advances in all branches of this broad and interdisciplinary field. An account of fundamental studies on nuclear reactions, actinides and transactinides is followed by a description of recent developments in radioanalytics and nuclear technology. The applications of radiochemistry in both energy and non-energy related research areas are discussed, with particular reference to nuclear fuel cycle, life sciences, geological and environmental sciences, and industry.
Syed M. Qaim and Heinz H. Coenen (Editors)

Advances in Nuclear and Radiochemistry

Extended Abstracts of Papers presented at the Sixth International Conference on Nuclear and Radiochemistry (NRC-6), 29 August to 3 September 2004, Aachen, Germany

In Cooperation with
University of Cologne, GDCh, FECS,
OECD-NEA and IAEA
Foreword

This book contains extended abstracts of papers presented at the 6th International Conference on Nuclear and Radiochemistry (NRC 6), held from 29 August to 3 September 2004 in Aachen, Germany. The conference was in a series of meetings held every four years in Europe to discuss the latest developments in all branches of chemically oriented nuclear sciences. The scientific responsibility of NRC 6 was entrusted to the Institute of Nuclear Chemistry of the Forschungszentrum Jülich. The scientific programme was established by the Local Organising Committee (LOC) in close consultation with the International Advisory Committee (IAC). It consisted of 13 invited talks, 64 oral contributions and 201 poster presentations. The extended abstracts given in this book were authored by 975 scientists from 42 countries of the world.

The NRC 6 was organised by the Forschungszentrum Jülich in cooperation with the University of Cologne, the Fachgruppe Nuklearchemie of the Gesellschaft Deutscher Chemiker (GDCh), the Federation of European Chemical Societies (FECS), the OECD - Nuclear Energy Agency (OECD-NEA) and the International Atomic Energy Agency (IAEA).

The conference was broad-based and this book comprises in a compact form a variety of reports on recent advances in all areas of the interdisciplinary field of radiochemistry. An account of fundamental studies on nuclear reactions, actinides and transactinides is followed by reports on recent developments in radioanalytics and nuclear technology. The applications of radiochemistry in both energy and non-energy related research areas are discussed, with particular reference to nuclear fuel cycle, life sciences, geological and environmental sciences, and industry. In short this book reflects the new trends in radiochemical research on a global scale.

The preparation of this book demanded appreciable reviewing, editing and technical efforts. We are grateful to the members of the two committees for their strong support during the review process. In particular we thank our colleague B. Scholten for assistance in editorial work and the authors for their precious contributions and their cooperation in the preparation of the final manuscripts.

Jülich, Germany
August 2004

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Heinz H. Coenen
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1. Fundamental Nuclear Chemistry
   (nuclear reactions, radioactive decay)

2. Actinides

3. Transactinides

4. Radioanalytics
   (nuclear and non-nuclear methods)

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   (techniques, cross sections, radionuclide production)

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XXXI
1. Fundamental Nuclear Chemistry
PROSPECTS FOR INVESTIGATION OF SUPERHEAVY ELEMENTS AT FLNR

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In fusion reactions of doubly magic $^{48}$Ca with actinide isotopes one can approach a region of superheavy compound nuclei which are predicted to be stabilized by the influence of the N=184 spherical shell. The significant mass excess of $^{48}$Ca allows one to form relatively cold compound nuclei at energies close to the fusion barrier ("warm" fusion), thus a maximum yield for the 3n- and 4n-evaporation channels is expected. The experiments on the synthesis of superheavy nuclei in $^{48}$Ca-induced reactions started at the FLNR in 1998 using VASSILISSA and the gas-filled recoil separators. During the past five years new $\alpha$-decaying and spontaneously fissioning nuclei in a wide range of $Z$ and $N$ were produced and studied. There are many arguments for assigning the observed decays to the heaviest isotopes of Rf, Db, Bh, Hs, Mt, Ds and to the isotopes of new elements 111 + 116 and 118 [1-4] (Fig. 1).

![Diagram](image)

Fig. 1. Possible location of the new isotopes synthesized in $^{48}$Ca induced reactions on the chart of nuclides.

All observed decay chains after sequential $\alpha$-decays ended in spontaneous fission with TKE $\approx$200 MeV and according to existing systematics must be related to the decay of rather long-lived nuclei ($T_{1/2}$ $\approx$10$^4$-1000 s) with $Z \geq 106$, which are the "children" or "grandchildren" of heavier nuclei.

Applying the basic rule of Geiger-Nuttall, which connects the $\alpha$-decay energy $Q_\alpha$ with the half-life $T_{1/2}$, one can conclude that we observe decays of nuclei with large atomic numbers.
Z=108 118. A significant increase in the lifetimes of the heaviest isotopes with $Z=110$ and 112 with respect to that of $^{231}110$ and of $^{27}112$ produced in “cold” fusion reactions, by a factor of $=10^9$, can be considered as an indication of the presence of a closed neutron shell at higher neutron numbers. Comparing the half-lives in the sequence of isotopes with $Z=114$, 116 and 118 one can suppose that $Z=114$ is probably a proton shell.

There are indications that this shell is a spherical one. The observation of spontaneous fission of $^{264}118$ can indicate that we are approaching the border of the region of stability by the high $Z$ side.

From Fig. 1 one can see that the new isotopes populate an isolated island, which has no connection with the region of known nuclei. Thus the analysis of generic decay links and cross-bombardments data are insufficient for their unambiguous identification.

The capability for on-line mass determination of complete fusion reaction products is essential for the identification of new isotopes. For this purpose behind the separator VASSILISSA a mass analyzer based on a dipole magnet was installed [5]. The upgraded set-up was used to verify the results of the previous experiments on the synthesis of heavy isotopes of element 112 in the $^{48}Ca+^{238}U$ reaction. The limits of $280 \leq A \leq 286$ for the masses of the observed spontaneously fissioning nuclei were determined [6]. In the future the use of calorimetric detectors at the focal plane can significantly improve the accuracy of mass measurements.

The use of other methods of identification requires an increase in the yield of superheavy elements in experiments.

A direct solution could be found by increasing the beam intensity. The rotating anode target equipped with a beam wobbling and a gas cooling systems can accept the beam power up to 500 W/cm$^2$, it corresponds to $=2\times10^{13}$ Ca ions/s (the gain factor is $=50$). The problems are the construction of such an accelerator, radiation safety and the projectile material consumption.

For the relatively long-lived (T$_{1/2}$ $\geq$ 1 s) isotopes with $Z=108 \div 114$ produced in $^{48}Ca$-induced reactions, quasi-on-line mass separation or chemical separation can be employed. In that case there is no need to conserve kinematic characteristics of reaction products, thus a target up to 3 ng/cm$^2$ in thickness can be used (the gain factor is $=10$ at the same beam intensity). The acceptability of the projectile beam power is not limited in these experiments. One can, for example, perform irradiation of horizontal or inclined rotating melted targets.

The properties of the elements with $Z=112\div120$ are predicted to be similar to those of volatile elements Hg $\div$ Ra, thus a separator of the ISOL-type can be employed for precise measurements of masses and investigation of properties of super heavy elements. The ISOL-type mass analyzer “MASHA” [7] is now under testing. In experiments with a plasma ion source the mass resolution $\Delta m/m$ of $=3\times10^{-5}$ was achieved for Kr, Xe and Hg isotopes.

First experiments on the chemical isolation and identification of element 112, produced in the reaction $^{238}U(^{48}Ca,3n)$ were performed using gas transportation. These experiments pointed to the “noble gas - like” rather than “Hg-like” behavior of element 112 [8,9].

It seems realistic that the production rate of superheavy nuclei may reach several atoms per hour, provided all possible improvements are realized. In this case one can consider the use of ion traps, x-ray or $\gamma$-spectroscopy.

The heaviest target which can be used in practice is a $^{240}$Cf one. Thus $=294$ 118 is the heaviest nuclide which can be produced in fusion reactions with $^{48}Ca$. In experiments at the CORSET + DEMON set-up it was found that the fusion-fission cross sections for the compound nuclei produced in reaction with $^{48}Ca$ and $^{24}Fe$ ions depended only slightly on reaction partners (the factor of 4–5). This fact is to be of great importance for planning new experiments on the synthesis of superheavy nuclei with $Z>114$ [10].
The experiments were carried out in the framework of a large collaboration with LLNL (Livermore), USA; GSI (Darmstadt) and TU (Munich), Germany; RIKEN, Wako-shi, Japan; Comenius University (Bratislava), Slovakia; Universita di Messina, Italy; IPN (Orsay), France; PSI and University of Bern, Switzerland; INP (Krakow), Poland.

References


TARGET DEPENDENCE OF LIGHT FRAGMENT PRODUCTION
IN NEUTRON- AND ALPHA-INDUCED NUCLEAR REACTIONS
AT INTERMEDIATE ENERGIES

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The formation of light nuclei, such as \(^7\)Be, \(^10\)Be and \(^22,24\)Na, in high-energy nuclear reactions on
medium- to heavy-mass targets, called “nuclear fragmentation [1, 2]”, is not yet clear
concerning the reaction mechanisms. The term “fragmentation” has been coined for the
formation process for these light nuclei, in which the split off of a relatively large piece of
nuclear fragment, compared with \(\alpha\) particle, from an excited nucleus during a nucleonic
cascade is somehow supposed. Therefore, no theoretical calculation code for nuclear reactions
is able to satisfactorily reproduce the fragmentation. In order to provide experimental
information about the fragmentation peculiarity, we measured radiochemically in previous
works [3-5] yields of several light products (\(^7\)Be, \(^10\)Be, \(^22\)Na and \(^24\)Mg) of
bremsstrahlung-induced reactions from 23 targets at the maximum end-point energies (\(E_0\)) of
200 to 1200 MeV. We found that the neutron-to-proton ratios of the targets strongly affect the
formation of nuclei by fragmentation, as revealed by the yields of the isotopic pairs.

In the present work, we tried to investigate other projectiles, which were neutron and \(\alpha\)
particle having the same energy as the effective energies in photonuclear reaction at \(E_0 = 1000\)
MeV. The initial interactions of photons with nuclei are purely electromagnetic and are quite
different from that of hadron induced reaction initiated by the strong nucleon-nucleon
interaction. It is interesting to investigate whether there are similarities or not in the
fragmentation process. For the \(^7\)Be and \(^10\)Be productions, therefore, the neutron-induced
reaction rates at the maximum energies (\(E_{\text{max}}\)) of 500 MeV and the \(\alpha\)-induced cross sections at
$E_{\text{irr}} = 400 \text{ MeV}$ were measured by $\gamma$-ray spectrometry or accelerator mass spectrometry. For neutron irradiation, the irradiation space, called “slot 2”, of the high-energy neutron-irradiation course of KENS [6] was used. Secondary neutrons were generated by bombarding 500 MeV protons on W targets, and the zero-degree direction was used for the irradiation of the targets by collimating with a beam guide. The primary protons were completely stopped in W targets. The neutron spectrum was calculated using the MARS14 code. The alpha irradiations were carried out with 400 MeV $\alpha$ from Heavy Ion Medical Accelerator in Chiba (HIMAC) of National Institute of Radiological Sciences. The PH2 course of HIMAC was used for the irradiations. Target elements over the periodic table, C, Al, Cu, Ag and Au, were selected.

Fig. 1. Reaction rates of $^7\text{Be}$ production in the neutron reactions at $E_{\text{max}} = 500 \text{ MeV}$ (reverse triangles), cross sections of $^7\text{Be}$ production in $\alpha$ reactions at $E_{\alpha} = 400 \text{ MeV}$ (squares) and yields of $^7\text{Be}$ in photoreactions at $E_\gamma = 1000 \text{ MeV}$ (circles) as a function of $A_t$. The values in neutron and $\alpha$ reactions were obtained in this work, and those in photoreaction were obtained in our previous works [3-5] and taken from [7, 8]. The unit of the reaction rate in neutron reaction is atom$^{-1}\mu\text{C}^{-1}$, which means the probability per target atom and per $\mu\text{C}$ of primary protons.
The results of neutron- and \( \alpha \)-induced nuclear reactions were compared with those of photoinuclear reactions. In Fig. 1, for example, the target-mass \((A_t)\) dependence of the reaction rates of \(^{7}\text{Be}\) production in the neutron reactions and the cross sections of \(^{7}\text{Be}\) production in \( \alpha \) reactions were compared with the yields of \(^{7}\text{Be}\) in photoreactions at \( E_0 = 1000 \) MeV. Although the results cannot directly be compared with each other because of the units of \( \text{mb} \)/eq.q. of photoreaction and atom/\( \mu \text{C}^{-1} \) of neutron reaction in irradiation by bremsstrahlung and neutrons with the continuous energy spectra, the \( A_t \) dependence in the neutron and \( \alpha \) reactions appears to be very similar in shape to that in the photoreaction. No clear effect due to the difference of the initial interactions of photons, neutrons and \( \alpha \) particles was found in the \(^{7}\text{Be}\) production. In the conference presentation, we are going to discuss the production ratios of isotopic pair also.

References
INFLUENCE OF REACTION CHANNEL ON THE ISOMERIC CROSS-SECTION RATIO

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Studies of isomeric cross sections are of considerable fundamental interest. It has been shown [1] that the isomeric cross-section ratio is primarily governed by the spins of the two levels involved, rather than their separation and excitation energies. Furthermore, through detailed studies on the formation of $^{73m,2}\text{Se}$ in six nuclear reactions [2], $^{58m,2}\text{Co}$ in seven nuclear reactions [3] and $^{94m,2}\text{Tc}$ in three nuclear processes [4], involving different combinations of target, projectile and ejectile, the effects of the angular momentum distribution in pre-equilibrium decay, branching ratios of γ-rays from discrete levels, etc. have been studied. The influence of the reaction channel on the isomeric cross-section ratio in neutron induced reactions was also investigated but the result was rather inconclusive [5]. The aim of the present work was to investigate the formation of an isomeric pair in a few neutron threshold reactions, and to study the formation of another isomeric pair in charged particle induced reactions. Two types of studies should shed some useful light on the possible influence of reaction channel on the isomeric cross-section ratio.

Neutron threshold reactions

We chose to study the isomeric pair $^{71m,2}\text{Zn}$ formed in $^{74}\text{Ge}(\alpha,\gamma)$- and $^{71}\text{Ga}(\gamma,n)$- reactions. The metastable state has a spin $9/2^+$ and the ground state $1/2^-$. Both decay independently by $\beta^-$ emission.

Samples for irradiations consisted of $^{74}\text{GeO}_2$ (98.44 % enriched) or $^{68}\text{Ga}_2\text{O}_3$. Irradiations with quasi-monoenergetic neutrons in the energy range of 6 to 12.5 MeV were carried out using a d-d gas target at the compact cyclotron CV28. The neutron fluxes were determined using monitor reactions. The product activities were determined using two different techniques: in the case of $3.9$ h $^{71m}\text{Zn}$, HPGe detector γ-ray spectrometry was used, but for the 2.4 min $^{71}\text{Zn}$, antioincidence $\beta^-$ counting was applied. For an unambiguous identification of the products, in a few cases radiochemical separations were performed. Full experimental details are given elsewhere [6,7].

In addition to experimental studies, nuclear model calculations based on the statistical model in combination with preequilibrium effects, were carried out. For this purpose the commonly used code STAPRE was applied. The experimental results on the isomeric cross-section ratios were reproduced by the theory within the limits of uncertainties. The experimental isomeric cross-section ratios for the formation of $^{71m,2}\text{Zn}$ in the two investigated neutron threshold reactions are given in Fig. 1. As expected, the ratio increases with the increasing projectile energy, i.e. the yield of the high spin isomer increases with energy. However, the magnitudes of the ratios are different for the two reactions concerned and the increase in the ratio is more
pronounced in the (n,p) reaction than in the (n,α) reaction. Thus a reaction channel has an influence on the isomorphic cross-section ratio.

**Charged particle induced reactions**

We chose to study the isomorphic pair $^{52m\text{B}}\text{Mn}$ in $^{52}\text{Cr(p,n)}$, $^{52}\text{Cr(}{}^{3}\text{He,}\text{t)}}$, $^{54}\text{Fe(d,α)}$, and $^{54}\text{Fe(}{}^{3}\text{He,αp)}$-reactions. The metastable state has a spin 2$^+$ and the ground state 6$. Both of them decay by EC + β$^-$ emission, the metastable state almost independently to $^{52}\text{Cr}$. For each reaction the standard stacked-foil technique was used. Thin samples were prepared by electrolytic deposition. Irradiations were done at the compact cyclotron CV28 at Jülich and the beam currents were measured via monitor reactions. The radioactivities of the two isomorphic states were determined using HPGe detector γ-ray spectrometry. Due to relatively low cross section for the formation of $^{52m}\text{B}^{52\text{Mn}}$ at low incident particle energies, the product was radiochemically separated. More details are given elsewhere [8 - 10]. From the individual cross sections the isomorphic cross-section ratios were deduced. In the case of simple reactions like (p,n) and (d,α), statistical model calculations using the code STAPRE (see above) were carried out. The agreement between the experimental and theoretical isomorphic cross-section ratio was fairly good. All the experimental isomorphic cross-section ratios were plotted against the incident projectile energy and the results are shown in Fig. 2. For each reaction, initially the ratio decreases, but becomes almost constant at high excitation energies. It is interesting to note that the (p,n) and (He,t) reactions (curves A and B) occur on the same target nucleus and the product studied is also the same. The same is true for the(He,αp) and (d,α) reactions (curves C and D). The magnitudes of the isomorphic cross-section ratios, however, differ considerably.
Fig. 2 Experimental isomeric cross-section ratios for the formation of $^{52}$Mn in several charged particle induced reactions, plotted as a function of incident particle energy.

It is concluded that the reaction channel does affect the isomeric cross-section ratios; the roles of the spins of isomers and the kinetic energy of the projectile, however, are much more important.

References


EXCITATION FUNCTION OF $^{63}\text{Cu}(n,p)^{64}\text{Ni}$ REACTION IN THE NEUTRON ENERGY RANGE BELOW 15 MeV

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Introduction

The excitation function of $^{63}\text{Cu}(n,p)^{64}\text{Ni}$ reaction was first measured radiochemically by [Ref. 1]. This excitation function is available for an estimation of neutron activation of copper materials at accelerators and reactors, and is important parameter for evaluation of neutron fluence emitted by Hiroshima/Nagasaki Atomic bomb [2, 3]. However, there is no extensive experimental data for the reaction because of difficulty in measuring $^{64}\text{Ni}$ which decays with no gamma-ray emission. And there exists a large discrepancy in the excitation function calculations by the statistical model, e.g. JENDL-3.3 [4], ENDF/B-VI [5], and FENDL/A-2.0 [6] especially in the energy region higher than 3 MeV. In this work, seven irradiation experiments were carried out in the neutron energy range below 15 MeV and the detailed excitation function of the reaction was obtained.

Experiment

Seven neutron irradiation experiments were carried out. For each irradiation experiment, multiple copper samples were placed around the neutron emission center (neutron source) to irradiate these samples at a time. Plate and sphere shaped samples were used in this work. Samples of plate shape were placed as the center of each sample, the emission center being on the same horizontal surface [7]. On the other hand, samples of sphere shape were placed as the center of sphere and the emission center being the same. The samples of sphere shape were constructed by multiple rings of separated hollow copper sphere. The amount of Ni as an impurity in copper sample was determined before irradiation to correct the amount of $^{64}\text{Ni}$ produced in copper
samples by neutron capture reaction of $^{63}$Ni and was found to be negligibly small.

All irradiations were carried out using 4.5 MV Dynamitron accelerator at the Fast Neutron Laboratory in Tohoku University. Deuteron or proton beam fell on $D_2$ or $T_2$ occluded titanium target to produce energetic neutrons. The mean energy of the emitted neutron for each copper sample can be estimated by time-of-flight measurement of neutrons at 0 degree and geometric alignment of copper samples. For the measurement of the neutron fluence, eight nickel foils were placed on each copper sample. Four foils were on the direction of the neutron emission center, and others on the counter side. After neutron irradiations, gamma-ray spectrometry for Ni monitors was carried out by using Ge-detector. Activities of $^{58}$Co produced by $^{58}$Ni(p,$\alpha$)$^{58}$Co were determined, and the neutron fluence was estimated for each copper sample.

$^{63}$Ni produced in each irradiated sample was chemically separated from copper target and other reaction products. In the first step, copper samples with Ni and Co carriers (1 mg Ni and 5 mg Co for each sample) were dissolved in mixed acid, and almost the whole Cu was removed by electrolysis. Then 6 N NaOH was added to precipitate Ni and other components as complex. The precipitate was filtered and washed by hot water. The washed precipitate was dissolved with 6 N HCl and evaporated. The evaporation residue was dissolved in 9 N HCl and injected into anion exchange column (DOWEX 1X8). After injection, 9 N, 4 N and 0.1 N HCl were poured into the column to elute Ni, Co, and Cu component, respectively. Ni components were dissolved in dimethylglyoxime/EtOH solution and extracted into chloroform by solvent extraction. The back-extraction to 1N HCl was carried out to refine Ni components. Finally Ni components were dissolved in HNO$_3$ and evaporated three times to remove organic materials (e.g. ion exchange resin). The chemical yield of Ni after these separations was determined by means of ICP-AES measurement for each aliquot of Ni component. We extracted Ni components from copper samples with chemical yields of over 80 percent on the average in this work.

Beta-rays of separated Ni components were measured by low-background liquid scintillation counter to determine the activities of $^{63}$Ni at R1 centre in University of Tokyo. Used scintillator was Clearsol-I. Standard $^{63}$Ni solutions of various concentrations were measured to obtain the detection efficiency including quenching effect. The activities of $^{63}$Ni samples were determined by the obtained counting rates of beta-ray for each sample. The production yields of $^{63}$Ni were estimated by activities of $^{63}$Ni and chemical yields of Ni for each copper sample.

Results and discussion

The cross section data of the reaction $^{63}$Cu(p,$\alpha$)$^{63}$Ni were obtained by the production yields of $^{63}$Ni for each experiment. The excitation function obtained in these experiments is shown in Fig. 1. In this figure, squares and circles show results by irradiation experiments using copper samples of plate shape and sphere shape, respectively. The vertical error bars involve statistical errors of each radiation measurement and systematic errors of each chemical yield measurement. The horizontal error bars mean the energy range of neutron irradiated to copper samples. The broken, dashed-dotted, and solid lines show statistical model calculations of JENDL-3.3, ENDF/B-VI, and FENDL/A-2.0, respectively. In overall energy range, statistical calculation by FENDL/A-2.0 shows good agreement with our experimental results. Open and closed triangles in Fig. 1 show the experimental results by Qaim et al. [1] measured radiochemically and Tsabaris et al. [8] determined by spectral measurement, respectively. There exist a discrepancy between these two reference data. However, any results seem to be nearer to the data of Qaim et al both at 15 MeV
and around 7 MeV. The cross section data in the energy region around 10 MeV should be measured by the same method in the future.

![Graph showing excitation function of $^{63}$Cu(n,p)$^{63}$Ni reaction](image_url)

Fig. 1 The excitation function of $^{63}$Cu(n,p)$^{63}$Ni reaction. Squares and circles show our results. Triangles show the reference results. Lines show the estimations by statistical calculations.

References

PREPARATION AND HALF-LIFE MEASUREMENT OF SAMARIUM-146

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1. Introduction
Samarium-146 (an alpha emitter with a particle energy of 2.455 MeV, and currently adopted half-life of $1.03 \times 10^8$ y [1]) is known as an extinct nuclide in the present solar system. It is expected that if $^{146}$Sm were produced in supernovae occurred in the vicinity of the solar system within the last few hundred million years, it might be present in the deep-sea sediment or ferromanganese crust as a result of cosmic fall-out from supernovae. It is, however, identified that the half-life values of $^{146}$Sm reported between 1953 and 1966 were largely scattered from $5 \times 10^7$ y to $1.03 \times 10^8$ y [1–3]. Additionally, some problems are also found in the previous works. For example, poor energy resolution of a detector in alpha spectrometry and uncertainty in mass spectrometry are considered as the problems. For detailed discussion for cosmochemistry of $^{146}$Sm, the half-life of $^{146}$Sm needs to be reevaluated as well as its search on the Earth. In this work, $^{146}$Sm was produced by methods different from the previous ones to determine its half-life using modern techniques.

2. Method for the determination of $^{146}$Sm half-life
The half-life of $^{146}$Sm can be determined by reference to the half-life of $^{147}$Sm [4]; when the data of $^{146}$Sm/$^{147}$Sm atomic ratio and the alpha activity ratio for a given $^{146}$Sm sample are substituted in the following equation, we obtain the half-life value of $^{145}$Sm.

$$T_{146} = \frac{A_{147}}{A_{146}} \times \frac{N_{146}}{N_{147}} \times T_{147},$$

where $T_{146}$ and $T_{147}$ are the half-lives of $^{146}$Sm and $^{147}$Sm, respectively, $A_{146}/A_{147}$ is the alpha activity ratio of $^{146}$Sm and $^{147}$Sm by alpha spectrometry, and $N_{146}/N_{147}$ is the atomic ratio of $^{146}$Sm and $^{147}$Sm by mass spectrometry.
3. Experimental

Samarium-146 atoms were produced in the $^{147}\text{Sm}(\gamma,\alpha)^{146}\text{Sm}$ reaction and $^{147}\text{Sm}(\alpha,p)^{146}\text{Eu}$ reaction. For the former, we irradiated enriched $^{147}\text{Sm}$ target with bremsstrahlung for many hours at Laboratory of Nuclear Science, Tohoku University. Since the high alpha activity of

$^{147}\text{Sm}$ would interfere with the measurement of $^{146}\text{Sm}$ alpha activity, we produced $^{146}\text{Sm}$ in the $^{147}\text{Sm}(\alpha,p)^{146}\text{Sm}$ reaction, for which we can obtain relatively high $^{146}\text{Sm}/^{147}\text{Sm}$ activity ratio in comparison to the $^{147}\text{Sm}(\gamma,\alpha)$ reaction. The detailed $^{147}\text{Sm}(\alpha,p)^{146}\text{Sm}$ method is described as follows: EC or $\beta^-$ emitting nuclide of $^{146}\text{Eu}$ with the half-life of 4.59 d was produced in the $^{147}\text{Sm}(\alpha,p)^{146}\text{Eu}$ reaction by irradiating with 20 MeV proton beam for ~12 h at Research Center for Nuclear Physics, Osaka University. After irradiation, most of the $^{147}\text{Sm}$ atoms were removed from the target by means of an HPLC technique using $\alpha$-hydroxyisobutyric acid as an eluant to concentrate $^{146}\text{Eu}$. The separated $^{146}\text{Eu}$ sample was left for about 3 months to allow growth of $^{146}\text{Sm}$.

The $^{146}\text{Sm}$ sample produced by the methods described above was precipitated with ammonia water and collected on a membrane filter to prepare a thin counting source for alpha spectrometry. The source was subjected to alpha spectrometry to determine the alpha activity ratio of $^{146}\text{Sm}$ and $^{147}\text{Sm}$. The measurement of the atomic ratio of $^{146}\text{Sm}$ and $^{147}\text{Sm}$ with thermal ionization mass spectrometer is currently under way.

4. Results and discussion

An alpha spectrum of $^{146}\text{Sm}$ produced through the $^{147}\text{Sm}(\alpha,p)^{146}\text{Sm}$ reaction and measured for 39 days is shown in Fig. 1. $^{147}\text{Eu}(T_{1/2} = 4.59 \text{ d})$ produced in $^{147}\text{Sm}(\alpha,n)$ reaction etc. is also observed in the spectrum. The $^{146}\text{Sm}^{147}\text{Sm}$ alpha activity ratio of $(4.96 \pm 0.51) \times 10^{-4}$ is obtained, although the amount of $^{147}\text{Sm}$ is too abundant in the $^{146}\text{Sm}$ sample. Alpha spectrometry is needed to

Fig. 1 Alpha spectrum of $^{146}\text{Sm}$ produced from the $^{147}\text{Sm}(\alpha,p)^{146}\text{Eu}$ reaction.
continue to reduce statistical error. Hereafter, mass spectrometry will be carried out to
determine the $^{144}\text{Sm}/^{147}\text{Sm}$ atomic ratio. We expect that more reliable data will be obtained
using both modern mass spectrometer and alpha spectrometer with high performance.

References

(1964).
INVESTIGATION OF THE DECAY PROPERTY OF $^{229m}$Th BY PHOTON DETECTION AND ALPHA-SPECTROMETRY

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Introduction

The chemical and physical properties of the isomeric state of $^{229m}$Th, having the lowest excitation energy, are an interesting subject in both experiment and theory. Helmer and Reich reported that the excitation energy of $^{229m}$Th is about 3.5 eV from the result of precise $\gamma$-ray spectroscopy for the $\alpha$-decay of $^{233}$U [1]. This level corresponds to a 3/2$^+$ [631] Nilsson state while the ground state to a 5/2$^+$ [633] one [2]. The emission of internal conversion electrons is forbidden because the nuclear excitation energy is lower than the first ionization energy of thorium atoms. Thus the deexcitation from $^{229m}$Th to the ground state is expected to occur through a direct $\gamma$-ray transition. Furthermore, if the outer-shell electron of $^{229m}$Th can be involved in the decay of $^{229m}$Th nucleus, $^{229m}$Th may decay via an electron bridge (EB) mechanism [3]. The diagram of EB mechanism is shown in Fig.1. This implies that the half-life of $^{229m}$Th changes depending on its chemical state. The photons emitted in a direct isomeric transition from this level should have about 350 nm wavelength, and the photons involved in the transition via EB process are deduced to correspond to visible rays. However, there has been no direct observation for the transition of $^{229m}$Th yet. The successful observation will allow us to research the details of EB mechanism. The $^{233}$U sample contains a given amount of $^{229m}$Th produced through an $\alpha$-decay from $^{233}$U with a branching ratio of about 1-2 percent. Several kinds of experiments were performed by other groups for the observation of photons emitted from the $^{233}$U sample [4,5]. These observations were not successful, however, owing to the $\alpha$-particle-induced fluorescence of the materials (nitrogen and quartz, etc.) around the radioactive sample $^{233}$U [6]. A review of the recent work is presented in reference [7]. Although a photon measurement has many difficulties, it is essential to investigate the EB mechanism for $^{229m}$Th. Our group has pursued photon measurements as well as
α-particle detections for $^{229m}$Th using samples purified by a chemical separation. The α-particles emitted from $^{229m}$Th are expected to be observed, since the partial half-life of α-decay in $^{229m}$Th is considered to be shorter than that in $^{229}$Th. The $^{229m}$Th samples were prepared by two different methods, chemical separation of the decay product from $^{231}$U or $^{229}$Ac, and direct production via several nuclear reactions. An α-particle spectroscopic technique and the results of the α-particle measurement for the decay product from $^{231}$Ac produced by a photon-induced nuclear reaction are reported elsewhere [9]. Here the results of the α-particle measurement for $^{229m}$Th directly produced in the $^{230}$Th(p,d)$^{229}$Th reaction are described. In this method, background events were relatively high, because a measured sample could not be separated from the target material and other by-produced thorium isotopes in the reaction. A comparison of the respective results of the two independent experiments is important to determine the α-particle energy and half-life of $^{229m}$Th. In the photon measurement, we have developed a new photon detection system using a spectroscope. It should be ascertained that the results obtained in the photon measurement are attributed to the nuclear phenomenon by examining the consistency with the results for the α-particle measurement.

Experiment

α-decay from $^{231}$U

The half-life of $^{229m}$Th has not been determined experimentally yet, estimated in wide range from about $10^3$'s to tens of hours [1, 8]. So we developed a rapid ion exchange apparatus so as to make successfully the measurement even when the lifetime was rather short. $^{231}$U was adsorbed on an anion exchange resin layer in 8M hydrochloric acid solution. $^{229}$Th grown up during a certain time (Growth Time) was eluted and separated from $^{231}$U. It takes only a few minutes for this separation. The growth time was set for various times; mainly tens of hours or tens of days, taking the unknown half-life of $^{229m}$Th into account. The sample measured was usually solution put in a quartz tube (48mm, 1cm). Several droplets of eluent at elution peak of thorium were collected in it.

In photon measurement, a low noise photomultiplier (PM) was used for the photon detection. PM was installed in a PM cooler to lower the thermal noise. Further, the oval reflector was employed to focus as many photons emitted from the sample as possible on the photocathode of PM. The output signals from PM was transformed, through only Pre-Amplifier and Discriminator, to MCS-mode data collecting system.

$^{230}$Th(p,d)$^{229}$Th

Proton irradiation was carried out with AVF Cyclotron at Research Center for Nuclear Physics in Osaka University. 10 μg of $^{230}$Th molecular-plated on a 5N aluminum plate was prepared as a target. Proton beam energy was 18-24 MeV, the beam current about 1 μA and the duration of irradiation 10 hours. Protactinium and fission products produced simultaneously were first removed by an anion exchange separation. After removal of aluminum by precipitation adding NaOH, the Th fraction was separated from Ac and the other elements by a cation exchange method. The sample for α-spectrometry was prepared by coprecipitating thorium isotope with sarrarium as hydroxide on 0.02 μm pore size filter. The precipitate was subjected to α-spectroscopy using a 420 mm² silicon detector.
Results and discussion
Photon emissions were observed for the solution samples separated from $^{233}$U. There was no decay component in the time dependence of the photon counting. It is difficult to attribute the origin of the photon emission to $^{229m}$Th nucleus.

We are now developing a spectroscope for one-photon counting to distinguish the decaying component of each specific wavelength. A new photomultiplier was used, which is attached to 16 rectangular photocathodes arranged in parallel side by side.

In the $^{230}$Th($p$,d)$^{229}$Th experiment, $\alpha$-particles from $^{229}$Th were observed as shown in Fig. 2. However, those from $^{229m}$Th were not measured clearly by sum effect of $\alpha$-particles from $^{230}$Th and $\beta$, $\gamma$-rays emitted from various elements.

In the $^{228}$Th($\gamma$,p2n)$^{229}$Ac experiment, $\alpha$ peaks seemingly assigned to the decay of $^{228m}$Th were detected as described elsewhere [9]. We are planning to detect photons from $^{229m}$Th with a new detection apparatus taking the results into account.

![Alpha-particle spectrum for $^{229}$Th sample produced in the $^{230}$Th($p$,d)$^{229}$Th reaction.](image)

Fig. 2. Alpha-particle spectrum for $^{229}$Th sample produced in the $^{230}$Th($p$,d)$^{229}$Th reaction.

References
PRODUCTION OF Th-229m IN NUCLEAR REACTION AND ITS IDENTIFICATION BY ALPHA-SPECTROMETRY

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Introduction
Recent investigations of Th-229 have determined that the energy difference between the
ground state and the first excited state is (3.5 ± 1.0) eV [1,2]. The internal conversion process
is prohibited in this energy range so that the isomer of Th-229 is expected to provide a good
verification of the Electron Bridge Mechanism (EBM) [3], which is a de-excitation process
competing with UV emission and alpha-decay. Since the probability of decay by EBM is
dependent on the state of the outer-shell electrons, the half-life of Th-229m could vary with its
chemical state; therefore, the isomer is interesting from a chemical viewpoint.
In most of the previous investigations on the decay properties of Th-229m, the nuclide was
produced from alpha-decay of U-233, which has a small branch producing Th-229m (2 %);
however, the presence of Th-229 interfered with the measurement of Th-229m. Our research
group has undertaken the production of Th-229m in the reaction, Th-232(γ, p2n)Ac-229,
followed by disintegration to Th-229m,g [4]. The sample of Th-229m,g was prepared making
good use of several chemical separation methods, and was measured with an
alpha-spectrometer. Alpha-particles from Th-229m are distinguishable from those from
Th-229g because of a difference in the decay channel [4,5].

Experimental
About 1.5g of purified $^{232}$ThO$_2$ was enclosed in a quartz tube for irradiation with
bremsstrahlung. The irradiation was carried out using an Electron Linear Accelerator at
Tohoku University. The Linac was operated at an electron energy of 30 MeV with a peak current around 0.1 mA. The $^{232}$ThO$_2$ target was placed in close contact with the back of a platinum converter and cooled with running tap water during the 1-hour irradiation. After the irradiation, the target was chemically treated according to the procedure outlined in Fig.1.

**Fig.1.** Chemical procedure for the preparation of Th-229m,g sample.

**Results and discussion**

Collection of alpha events was started 10 minutes after the completion of the counting source preparation, and 10000 sec counting was repeated. The obtained alpha-spectra are shown in Fig. 2. Although the decontamination factor of thorium isotopes from the Th-229m,g sample was about 10$^5$, it was confirmed that Pa-231, which is a decay product of Th-231 produced in the Th-232($\gamma$, n) reaction, interfered with the identification of Th-229m. The individual count rates for thorium isotopes were plotted against the elapsed time after the chemical separation of Th-229m,g (Fig. 3). In Fig.3, a solid curve represents the calculated appearance of Pa-231 on the assumption that Pa-231 is completely eliminated at the end of the chemical procedure ($T = 0$). For the alpha-spectrum obtained from 10 minutes to ca. 3.5 days after chemical separation, Pa-231 did not represent a significant fraction of the activity, and the alpha-activity between 4.85 MeV and 5.05 MeV was ascribed to Th-229m. The decrease of alpha-activity between 4.85 MeV and 5.05 MeV was corresponds to a half-life of about 10 hours.

**References**


Fig. 2. Expanded alpha-spectra (a) acquired at 10 minutes after the chemical separation, and (b) acquired at 1 week after the chemical separation (counting time : 300000 s).

Fig. 3. Plots of counting rates of ROIs for thorium isotopes vs. elapsed time. Solid curve: calculated increase of Pa-231, dashed line: decay component of Th-229m region.
ENERGY SHIFT OF ELECTRONIC X RAYS
EMITTED FROM PIONIC ATOMS

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1. Introduction

Negative pions captured in matter result in the formation of pionic atoms. In previous studies, the LMM model describing the capture process was confirmed by the experimental results based on the measurements of pionic X rays and neutral pion decays\cite{1,2}. We have studied the pion capture process in molecules, especially focused on hydrogen compounds, in liquid and gas phases\cite{3-6}. Negative pions exist in highly excited states at the beginning of the capture process, and then they cascade down to lower excited states by emitting pionic X rays or Auger electrons. Moreover Auger electron emission is followed by electronic X-ray emission from pionic atoms. Since the pion mass is about 270 times as large as the electron mass, pionic orbital have small radii; the pion strongly shields the orbital electrons from the nuclear charge. Therefore characteristic X-ray energies of pionic atoms are not those of the target atom (atomic number \textit{Z}) but close to those of \textit{Z}-1 atom. We attempted to examine electronic X-ray emission correlated with each pionic X ray to understand electron rearrangement in the pionic atom during the pionic cascade.

2. Experiment

The measurements were performed at \pi\mu-channel of KEK-PS. As illustrated in Fig 1, the measuring system consists of four plastic scintillation counters and three Ge detectors. The target chamber was filled with He gas to reduce background. The signals from Ge detectors were taken in coincidence with the stop events by PS1, PS2, PS3 and veto PS4. To examine
the correlation between pionic X rays and electronic X rays, the photon events are recorded in a list mode. We used Zn, Mo, Ag, Sn, Ta, and Pb metal foils as the targets. In addition, we measured electronic X-ray energies of these atoms and their Z-1 atoms induced by photoionization with a Co-57 source in the same apparatus.

3. Result and discussion

Obtained X-ray spectrum for a Mo target is shown in Fig 2. Al pionic X rays were observed due to aluminum chamber, and electronic X rays of Mo were caused by ionization with fast pions. We tried to measure the electronic X rays emitted from each excited state of a pionic atom. However, the number of correlated events is too small to discuss the difference in the electronic X-ray energies between pionic states quantitatively. Here, we used the gross spectrum for the analysis below. As shown in Fig 3, we can find clear energy difference between characteristic X rays of pionic Mo atoms (measured in the beam experiment) and those of Nb atoms (measured in the photoionization experiment). The energy shifts were found in both Kα and Kβ lines of other targets. We show atomic number dependence of the energy shift of the Kα rays in Fig 4, together with that for muonic atoms [7-9]. We should notice that there are some differences between pionic atoms and muonic atoms. Because pions are absorbed by the nucleus through strong interaction in the inner shell, in most elements they do not reach the 1s state. On the other hand, muons in a muonic atom stay in the 1s state for a relatively long time. In the experiments [7-9] of muonic atoms, the authors measured electronic X ray only within 10 - 20 ns after the muon was stopped in the target to examine the electronic configuration during the muonic cascade. Since pions have short lives (26ns) and are absorbed by nucleus before their decay, the electronic X rays that we measured were emitted from the pionic atoms in an excited state.

![Figure 1. Schematic drawing of experimental arrangement. “PS” means plastic scintillation counter.](image1)

![Figure 2. Observed X-ray spectrum for Mo target. The numbers in parentheses indicate the main quantum numbers relevant to the pion transition.](image2)

![Figure 3. X-ray spectrum for the pion capture in Mo target. The open squares and triangles show Nb and Mo electronic X-ray spectra, respectively.](image3)
Figure 4. Energy shifts of the electronic X rays. This work is shown in filled square. The shifts in muonic atoms are illustrated with empty circles[7], triangles[8] and diamonds[9].

Figure 5. Atomic number dependence of the effective nuclear charge in pionic atoms.

The effective nuclear charge of pionic atom against atomic number is shown in Fig 5. We estimate them by calculations based on hydrogen atom approximation. It turns out that the shift becomes smaller with increasing atomic number. We suppose the dependence is caused by the following fact. According to the relations between the pionic transition energy and the electron binding energy, for Zn, Mo, Ag and Sn targets, the pionic atom emits electronic KX ray when the pion reached the $n = 8$ (n means main quantum numbers) or father inner state. On the other hand, for Ta and Pb targets, the pionic atom emits electronic KX ray when pions are in $n = 7$ or deeper state. This difference causes the discontinuity of effective nuclear charge between them, because the screening effect becomes stronger as the main quantum number becomes smaller. We are now aiming to measure electronic X rays of the various elements to confirm the conjecture.

References
TIME-DIFFERENTIAL PERTURBED ANGULAR CORRELATIONS OF
\(^{140}\text{Ce}\) AND \(^{19}\text{F}\)

IMPLANTED IN HIGHLY ORIENTED PYROLYTIC GRAPHITE


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Graphite-intercalated compounds have been investigated from various aspects, and it has been found that they show unique properties depending on the doped elements. Zabel et al. succeeded, for instance, in observing dynamic motion of intercalate alkali-metal atoms (Li, K, Rb, and Cs) in graphite, estimating the diffusion constants and activation energies for each of the atoms[1], whereas doped borons are reported substituting for the carbon atoms rather than being intercalated in the layers[2]. Because doped graphite is expected to exhibit unique properties on account of its two dimensional structure, we have further investigated the behavior of other elements, Ce and F, implanted in highly oriented pyrolytic graphite (HOPG) by means of the time-differential perturbed angular correlation (TDPAC) method.

Implantation of a fission product, \(^{140}\text{Cs}\), into an HOPG sheet was performed at the isotope separator on-line at Kyoto University Reactor[3]. The dopant disintegrates into a TDPAC probe \(^{140}\text{Ce}\) in the decay process as shown in Fig. 1. TDPAC measurements were performed on the 329-487 keV cascade \(\gamma\) rays with the intermediate state of 4 having a half life of 3.5 ns. In the present work, the directional anisotropy of the angular correlations of the cascade \(\gamma\) rays was observed at \(\pi/2\)- and \(\pi\)-radian directions with a conventional four-detector system. For the coincidence detection, \(\text{BaF}_2\) scintillation counters were adopted.

![Fig. 1. Simplified level scheme of \(^{140}\text{Ce}\) formed in the disintegration of \(^{140}\text{Cs}\).](image)

The other TDPAC experiment of the \(^{19}\text{F}\) probe was performed at the RIKEN Accelerator Research Facility[4]. The primary \(^{22}\text{Ne}\) ions were accelerated up to 110 MeV/u at a beam intensity of 280 pA. A variety of radioactive nuclides were formed at the Be production
target by a projectile-fragmentation reaction, and the secondary beam of interest, $^{16}$O, was separated by the RIKEN projectile-fragment separator[5]. The well-focused pulsed beam of 65 MeV/u was implanted in an HOPG sheet, and on-line TDPAC measurements were performed on the (1357-197)-keV cascade $\gamma$ rays (Fig. 2). In order to obtain better statistics of coincident events, we used sixteen BaF$_2$ scintillators and arranged them in four independent detector planes.

TDPAC spectra of $^{16}$Ce and $^{19}$F implanted in the HOPG are shown in Fig. 3. The time-variant directional anisotropy $R(t)$, which is given by a simple arithmetic operation as

$$R(t) = \frac{2[N(\pi, t) - N(\pi/2, t)]}{N(\pi, t) + 2N(\pi/2, t)},$$

is plotted as a function of the time interval, $t$, between the cascade $\gamma$ rays. Here $N(\theta, t)$ denotes the number of the coincident events observed at an angle, $\theta$. The directional anisotropy shows gradual relaxation for $^{16}$Ce, while for $^{19}$F is seen an explicit oscillatory structure reflecting an electric quadrupole interaction with the extranuclear charge distribution. It is obvious that the $^{19}$F probe has an electrostatic interaction with the outer surrounding carbon atoms, evidently showing the occupation of a fixed site. On the other hand, the exponential-type relaxation for the $^{16}$Ce probe can be attributed to a dynamic perturbation from the extranuclear field[6], possibly suggesting a thermally activated hopping of the probes.
just as observed for alkali-metal atoms. In the presentation, the $c$-axis orientation dependence of the TDPAC spectra is also discussed.

References

CHEMICAL STABILIZATION OF RECOIL $^{56}$Mn IN MnSO$_4$–KClO$_4$
MIXED CRYSTALS FOLLOWING (n,$\gamma$) PROCESS

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Stabilization of recoil $^{56}$Mn in mixed crystal of MnSO$_4$–KClO$_4$ was studied with especial emphasis on isothermal annealing of neutron irradiated target. It has been inferred that coping by foreign materials or atoms of different valence states possibly changes the distribution of different recoil species as the transient reaction of metastable precursors are modified by the presence of defects in the irradiated matrix [1]. The doped components are able to introduce controlled concentrations of different types of defects, which participate in annealing reactions [2]. The recombination reaction between the recoil species and the defects present in crystal accounts for the formation of the parent form of permanganate. If $^{56}$Mn recoil in permanganate systems originates to lower valence states (Mn$^{2+}$) and get stabilized in parent form or non parent form (Mn$^{4+}$ as MnO$_2$) then it is also to be expected that as a result of recoil Mn$^{2+}$ may get transformed into Mn(VII) and Mn$^{4+}$ states and in case of matrix containing anions having permanganate like structure (e.g., MnO$_4^{2-}$) then formation of MnO$_4^{-}$ is also to be expected through atom exchange (Mn or Cl). Thus, Mn$^{2+}$ recoil yields MnO$_4^{-}$ either via multistep oxidation through recoil or / and via atom exchange of recoil $^{56}$Mn in MnSO$_4$–KClO$_4$

system. The results showed that $\text{MnO}_4^{-}$ yield (%) in MnSO$_4$–KClO$_4$ mixed crystals varies linearly with the increase in perchlorate concentration from 0.100-0.500 mol fraction. The increase in yield ($\text{MnO}_4^{-}$) with the increasing amount of ClO$_4^{-}$ additive was found to be 89.0% $\pm$ 1.1 (max). However, the value of intercept ($P_0$) is obtained to be 63.0% $\pm$ 1.2 evaluated through least squares fit of data obtained.
Isothermal annealing of $^{54}$Mn in present mixed crystals (MnSO$_4$-KClO$_3$) for different molar concentration (i.e., from 0.100 m.f. to 0.500 m.f.) of perchlorate at different temperatures for desired length of time have been studied which showed that retention values increase with increasing temperature and time of annealing for both the samples. However, a low value of retention is obtained in a lower molar ratio (0.1) of the target in comparison to higher molar ratio (0.5) at different temperatures. Initial retention (i.e., $^{54}$MnO$_4^-$ yield) was found to be 67.0% ±1.0 and 89.0% ±1.1, respectively, for 0.100 and 0.500 molar ratio at room temperature. Retention value increased gradually in the beginning that slows down with a lapse of time and finally attained saturation within ca 20 min of heating at 373 K in both cases. Limiting saturations were found to be 86.0% ±1.0 (max) for 0.100 molar concentration and 96.0% ±0.8 (max) for 0.500 molar concentration.

The rate of annealing was found to increase while the extent of annealing decreased. Recoil re-entry process obeys first order rate law. Energies of activation for the system (MnSO$_4$ - KClO$_3$) were found to be 0.15 ±0.05 eV for 0.1 molar ratio and 2.5 ± 0.06 x $10^{-7}$ eV for 0.5 molar ratio and computed by the classical Arrhenius plots. The low value of activation energy indicates that there is recombination in recoil fragments and participation of defect controlled reactions in thermal annealing leading to higher saturation retention in 0.500 molar ratio. The results obtained are discussed in the light of vacancies created by the dopant and proposed recoils stabilization mechanism.

References

THE INFLUENCE OF A NUCLEAR PREHISTORY ON TRANSPORT RATE
OF IMPURITY "HOT" ATOMS $^{111}\text{In}$, $^{114m}\text{In}$ and $^{115m}\text{In}$
IN THE IRRADIATED METAL CADMIUM

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In our previous publications (see for example [1]) it was shown, that the velocity of migration of radioactive microimpurities (formed as a result of a nuclear change) in irradiated metals is instituted by a nuclear prehistory. In the present work this problem was explored in detail. The selected system « cadmium - impurity atoms of indium » is unique for such experiments: it is possible to gain the same impurity "hot" atoms ($^{111}\text{In}$, $^{114m}\text{In}$ and $^{115m}\text{In}$) via different "nuclear channels" (see Table 1) and to explore their behavior depending on a nuclear prehistory.

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<th>Nuclear transformations</th>
<th>Beam current, μA</th>
<th>Flux of neutrons, n/cm²s</th>
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<td>8.3·10³⁰ 8.3·10³⁰</td>
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<tr>
<td>$^\prime\text{He}$</td>
<td>11.5/1.8</td>
<td>$^{108}\text{Cd}(\alpha, n)^{111}\text{Sn} \rightarrow^{111}\text{In}$</td>
<td>1.2 2.3</td>
<td>-</td>
<td>3.7·10³⁰ 2.5·10³⁰</td>
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<td>$^{108}\text{Cd}(\alpha, n)^{111}\text{In}$</td>
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<td>-</td>
<td>5.0·10³³</td>
<td>4.5·10³³ 9.0·10³³</td>
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The carried out experiments have shown, that two basic tendencies in diffusion behaviour of impurity "hot" atoms are clearly traced.
Fig. 1. The yield of impurity atoms of $^{117}$In and $^{116}$In (from volume) on a surface of the irradiated metal cadmium as a result of annealing (at RT) of radiation damages after bombardment: $^4$He: fluence – 2.5 $\times$ 10$^{20}$ particles/m$^2$, beam current – 2.3 $\mu$A; d: fluence: 8.3 $\times$ 10$^{20}$ particles/m$^2$, beam current – 2.9 $\mu$A.

Fig. 2. The yield of impurity atoms of $^{117}$In and $^{116}$In (from volume) on a surface of the irradiated metal cadmium as a result of annealing (at RT) of radiation damages after bombardment: $^4$He: fluence – 3.7 $\times$ 10$^{20}$ particles/m$^2$, beam current – 1.2 $\mu$A; d: fluence: 8.3 $\times$ 10$^{20}$ particles/m$^2$, beam current – 1.4 $\mu$A.

Fig. 3. The yield of impurity atoms of $^{117}$In and $^{114}$In (from volume) on a surface of the irradiated metal cadmium as a result of annealing (at RT) of radiation damages after bombardment of deuterons (fluence – 8.3 $\times$ 10$^{20}$ particles/m$^2$) with different beam currents.

Fig. 4. The yield of impurity atoms of $^{117}$In and $^{116}$In (from volume) on a surface of the irradiated metal cadmium as a result of annealing (at RT) of radiation damages after bombardment of $^4$He with different beam currents: 2.3 $\mu$A (2.5 $\times$ 10$^{20}$ particles/m$^2$) and 1.2 $\mu$A (3.7 $\times$ 10$^{20}$ particles/m$^2$).
One of them - direct dependence of transport rates of $^{111}\text{In}$, $^{114m}\text{In}$ or $^{115m}\text{In}$ from a degree of radiation damage of cadmium targets at bombardment (see Figures 1-6). The velocity of migration of impurity atoms is inhibited by "unsoundness" of structure after bombardment and depends on the type, energy and intensity of beams of bombarding particles, total fluence (and thereof - from the total and specific radioactivity). The value is the mass of bombarding particles (or, more precisely, relative change of their mass). That such general tendency is traced and under study of manifold properties (microhardness, plasticity, impact elasticity, etc.) of irradiated metals and alloys.

Other feature in behaviour of radioactive microimpurities - diminution of transport rate of $^{111}\text{In}$, $^{114m}\text{In}$ or $^{115m}\text{In}$ during thermal annealing of the irradiated metals (see Figures 5, 6).

![Graph 5](image1.png)  
**Fig. 5.** Change of transport rate of impurity "hot" atoms $^{115m}\text{In}$ with a different nuclear prehistory at sequential isothermal isochronal annealings of the irradiated targets:
- $^{114}\text{Cd}(n,\gamma)^{115}\text{Cd} \rightarrow \beta^{-} \rightarrow ^{115m}\text{In}$ (fluence - $4.5 \times 10^{19}$ particles/m$^2$);
- $^{114}\text{Cd}(d, p)^{115}\text{Cd} \rightarrow \beta^{-} \rightarrow ^{115m}\text{In}$ (fluence - $8.3 \times 10^{19}$ particles/m$^2$).

![Graph 6](image2.png)  
**Fig. 6.** Change of transport rate of impurity "hot" atoms $^{115m}\text{In}$ at sequential isothermal isochronal annealings of the irradiated targets after bombardments by neutrons with different fluences.

The investigations are supported by ISTC (project No. 1795) and RFBR (project No. 03-02-17391).

2. Actinides
ACTINIDE CHEMISTRY, METHODS, DATA AND MODELS

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The actinide group still provides a number of scientific challenges, despite more than sixty years of experimental and theoretical efforts. There are several reasons for this:

- The difficulty to perform even “standard” chemical experiments using the rare and strongly radioactive actinides, a difficulty that is aggravated when implementing many of the “state-of-the art” methods used in other areas of chemistry, e.g. NMR and EXAFS spectroscopy and X-ray diffraction.

- The theoretical challenges posed by the need to include relativistic effects, a large number of electrons in the valence orbitals and spin-orbit effects when applying quantum chemical methods in actinide chemistry.

- The very large decrease in the number of actinide chemists worldwide, particularly at the universities.

Actinide chemistry, like most experimental sciences, rests on a fundamnet of methods, data and models; it is the successful combination of these on relevant problems that leads forward. This presentation will focus on the structure of actinide compounds, the thermodynamics and reaction mechanisms of their reactions by using a combination of experimental data and quantum chemical methods. The focus will be on actinide chemistry in water solution but reactions in gas-phase will also be discussed, as this is a necessary starting point to develop models for solutions.

Quantum chemistry is based on “first principles” and the solution of the (time-independent) Schrödinger equation. In principle it provides information on all chemical and physical properties of a particular compound. However, the practical solution of the equation requires approximations that will affect the accuracy. It is necessary to strike a balance between the level of detail in the quantum chemical methods used and the accuracy required; the more details the longer the computation time and the larger the cost.

The solution of the Schrödinger equation provides the energy of a compound in gas phase at 0 K; the zero point for the energy is the separate atomic nuclei and electrons of the atoms in the compound at an infinite distance. Hence the total electronic energy of a chemical compound is a very large number, a factor of $10^3$ or $10^4$ larger than the energy changes for chemical reactions. This requires a high accuracy in the calculations, but more important is that systematic errors remain essentially constant so that they cancel between reactants and
products in a chemical reaction. The latter aspect is very important when designing the chemical models on which the quantum chemical methods are applied. Another point to consider is the possibility of “false” geometries, a result of geometry optimization at 0 K in systems where the energy surface, a function of the geometry parameters, is not a simple generalized second-degree surface. This type of error is less likely to appear when making geometry optimization using molecular mechanics or molecular dynamics methods.

Quantum chemistry in gas phase and solution.
It is straightforward to obtain information on the geometry and the total energy both for gas phase and solutions. The thermodynamic functions at higher temperature are obtained from the molecular partition functions using the gas phase vibration and rotation energy levels from quantum chemical calculations; this is straightforward for systems in gas-phase as exemplified by the following reactions, where M is U, Np or Pu

\[ 2\text{MO}_2(g) + \text{MF}_6(g) \rightarrow 3\text{MO}_2\text{F}_2(g) \]  
\[ \text{MO}_2\text{F}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{MO}_2(\text{OH})_2(g) + 2\text{HF}(g) \]  
\[ \text{MF}_6(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{MO}_2\text{F}_2(g) + 4\text{HF}(g) \]  
\[ \text{MO}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{MO}_2(\text{OH})_2(g) \]  
\[ \text{MF}_6(g) + 3\text{H}_2\text{O} \rightarrow \text{MO}_3(g) + 6\text{HF}(g) \]

The \textit{ab initio} and experimental data for uranium agrees within the experimental error. Thermodynamic data for solutions requires a proper model for the solvent, and different solvent models will be discussed and compared to experimental structure and thermodynamic data.

The modelling and calculation of thermodynamic data for equilibria in solution.
The complex formation between a metal ion, M\textsuperscript{**} and a ligand, L\textsuperscript{-}, in aqueous solution is often described as follows

\[ \text{M}^{n+}(\text{aq}) + \text{L}^{m-}(\text{aq}) \rightarrow \text{ML}^{(m-n)+}(\text{aq}) \]  
\[ \text{M}^{n+}(\text{H}_2\text{O})_x^{m+} + \text{L}(\text{H}_2\text{O})_y^{m-} \rightarrow \text{ML}(\text{H}_2\text{O})_z^{(m-n)+} + (x + y - z)\text{H}_2\text{O} \]

In equation (6) the notation (aq) is used because it is not necessary to include the hydration of reactants and products in solution thermodynamics; in fact these quantities are rarely known. Quantum chemistry is a molecular method and requires a more specific system definition than that in Eqn. (6); here it is necessary to know at least the coordination number in the first coordination sphere. We can also describe the reaction using the thermodynamic counterpart of the well-known Eigen-Wilkins mechanism for ligand substitution reactions,
(for simplicity, the ligand has only one donor atom that binds to the metal ion and its solvation is not shown):

\[
\begin{align*}
M^{m^+}(H_2O)_{n \cdot m^+} + L^- & \rightarrow [M(H_2O)_{n \cdot m^+}]_\mathcal{L}(L^-); \\
[M(H_2O)_{n \cdot m^+}]_\mathcal{L}(L^-) & \rightarrow [ML(H_2O)_{n \cdot 1 \cdot m^+}](H_2O); \\
[ML(H_2O)_{n \cdot 1 \cdot m^+}](H_2O) & \rightarrow ML(H_2O)_{n \cdot 1 \cdot (m^+)^+} + H_2O;
\end{align*}
\]

The square and ordinary parentheses denote the first coordination and second coordination spheres, respectively. The equilibrium constant for the formation and dissociation of the outer-sphere complex in reactions (8) and (10) can be estimated using the Fuoss equation, while the quantum chemical calculation is made on the reactant and product of the intramolecular reaction (9). The magnitude of the solvent effect depends on the charge and size of the reactants and products and when they have the same charge and about the same size, one can expect that systematic errors in the solvent model will compensate one another as in reaction (9). In reaction (7), on the other hand, the reactants and products have different size and charge; hence the compensation of errors in the solvent model will be much smaller, resulting in larger discrepancy between model and experiment. The principle is demonstrated by thermodynamic data for Zn(II) and UO$_2^{2+}$ complexes.

**Rates and mechanism of ligand exchange reactions in actinide complexes.**

The analysis of the rate and mechanism of chemical reactions requires information on the thermodynamics of the reaction studied; in addition the structure and coordination geometry of reactants, intermediates and products provide important clues on the mechanistic course of the reaction. The mechanisms for ligand exchange reactions for uranium(III - VI) complexes will be discussed using both experimental and quantum chemical information.

**Why theory?** There are a number of important chemical problems that cannot be solved using only experimental data; the assignment of reaction mechanisms is a typical example. Another is the selection of a proper structure model from EXAFS data, where the “radial distribution” function gives only limited information. A third example is the determination of the relative energy of isomers both in gas-phase and solution. Finally, and perhaps most important, one can use the chemical similarity between actinides in the same oxidation state and calibration with experimental data for uranium, to make predictions using theory that can be used for planning of experiments with transuranium elements.
SOLUBILITY AND TERNARY HYDROXO-CARBONATE COMPLEXES OF THORIUM

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Geochemical modeling of actinide solubilities in performance assessment calculations on the safety of nuclear waste disposal requires a reliable and accurate database. Under carbonate free conditions and alkaline pH, the solubility of Thorium(IV) is controlled by amorphous Th(OH)₄(aml) hydroxide or ThO₂xH₂O(aml) hydrous oxide. The solubility product of this solid (log K°sp = - 47.8 ± 0.3) is well known from our previous work [1]. For natural systems, carbonate complexation has also to be taken into account. Because of the strong tendency of tetravalent actinides towards hydrolysis, ternary hydroxo-carbonate complexes are formed:

\[ \text{Th}^{4+} + y \text{OH}^- + z \text{CO}_3^{2-} \rightleftharpoons \text{Th(OH)}_a(\text{CO}_3)_b^{4+y-2z} \]

In the present study, the solubility of x-ray amorphous Th(IV) hydroxide was determined in the system NaHCO₃-Na₂CO₃-NaOH- NaCl at 1 = 0.5 M and 22°C. In two series of open system experiments at \(-\log [\text{H}^+] = 4.5 - 7.5\), a dispersed gas stream (either pure CO₂ or 10% CO₂ / 90% Ar) was bubbled through 0.5 M NaHCO₃-NaCl until equilibrium was reached. In three series of closed system experiments at constant total carbonate concentrations of C₂tot = [HCO₃⁻] + [CO₃²⁻] = 0.1, 0.04 and 0.015 M, the \(H^+\) concentration was varied in the range \(-\log [\text{H}^+] = 8.5 - 13.5\). The constant solubility data measured after equilibration times of 15-130 days in the closed system experiments or after 5-20 days in the open system experiments under pCO₂ = 1 and 0.1 bar indicate that solid-liquid equilibrium was reached. Phase separation, e.g. the removal of colloidal Th(IV) fractions, was achieved by ultracentrifugation (centrifugal force \(-5 \times 10^5\) g) and ultrafiltration (2 nm). Under the conditions of the present studies, there was no indication of a solid transformation leading to the formation of a thorium carbonate solid. In Fig.1 our experimental results are shown together with comparable data of Östhols et al. [2] at C₂tot = 0.1 M in NaClO₄.

The evaluation of the 5 different sets of experimental data shows that only few of the possible complexes Th(OH)₄(\text{CO}_3)₉^{4+y-2z} = (1yz) are predominant under the present conditions. The high solubilities at pH < 11 in the closed system experiments are caused by the complex Th(OH)(\text{CO}_3)₉². No other complex or combination of other complexes describe these data. The slight solubility increase at pH > 12 and C₂tot = 0.1 M (compared to log [Th(OH)₄(aq)] = -8.8 in carbonate free solution) is caused by the formation of Th(OH)₄(\text{CO}_3)²⁻.
Fig. 1. Solubility of ThO$_2$·H$_2$O(am) in carbonate solution (I = 0.5 M, 22°C); above: open system experiments at pH 3 - 8 under pCO$_2$ = 1 and 0.1 bar, below: closed system experiments at pH 8 - 13.5 and total carbonate concentrations (C$_{tot} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) = 0.1, 0.04 and 0.015 M). The solid curves are calculated with the formation constants derived in this work.
The solubility in the open system experiments at pH > 5 under pCO₂ = 1 and 0.1 bar, is
dominated by the complexes Th(OH)₂(CO₃)₂²⁻ and Th(OH)(CO₃)₃³⁻. Minor but significant
contributions come from the complexes Th(OH)₂(CO₃)₃(aq) and Th(OH)₃(CO₃)⁴⁻. The
evaluation of our experimental data gives no significant values for the pure carbonate
complexes and other ternary complexes. Only upper limits can be derived for their formation
constants. The formation of the limiting complex Th(CO₃)₅⁶⁻ requires carbonate
colorations considerably above 0.1 M. This is confirmed by additional experiments in
0.5 – 2 M Na₂CO₃ solutions containing 0.1 M NaOH. The solubility measured in these
solutions is in agreement with data from Felmy et al. [3] (log K°sp + B'₁₂₁ = -18.4). The
formation constants of the Th(IV) hydroxocarbonate complexes at l = 0.5 are extrapolated to
l = 0 with the SIT. They refer to the solubility product of ThO₂·xH₂O(am) from [1]:

\[
\begin{align*}
l = 0.5 \text{ M:} & \quad \log K'_{\text{sp}} = -44.5 \pm 0.3 \\
& \quad \log B_{114} = 34.5 \pm 0.3 \\
& \quad \log B_{122} = 33.3 \pm 0.4 \\
& \quad \log B_{121} = 27.0 \pm 0.4 \\
& \quad \log B_{131} = 34.8 \pm 0.6 \\
& \quad \log B_{141} = 37.4 \pm 0.5 \\
\end{align*}
\]

\[
\begin{align*}
l = 0: & \quad \log K''_{\text{sp}} = -47.8 \pm 0.3 \\
& \quad \log B''_{114} = 35.8 \pm 0.3 \\
& \quad \log B''_{122} = 37.0 \pm 0.4 \\
& \quad \log B''_{121} = 30.7 \pm 0.4 \\
& \quad \log B''_{131} = 38.5 \pm 0.6 \\
& \quad \log B''_{141} = 40.7 \pm 0.5 \\
\end{align*}
\]

The present work establishes a comprehensive set of equilibrium constants for the ternary
system Th(IV)-OH-CO₃.

[1] Neck, V., Müller, R., Bouby, M., Altmaier, M., Rothe J., Denecke, M.A., Kim, J.I.,
COMPLEX FORMATION OF U(VI) WITH AMINO ACIDS STUDIED
BY UV-VIS SPECTROSCOPY, TRLFS AND EXAFS

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Introduction
The understanding of the interaction of radioactive metals with biological systems on the molecular levels is very important in view of the distribution of radioactive elements via the food chain soil–water–plant–animal–human. We carried out experiments for the determination of the chemical speciation of uranium in plants and in bacteria. The spectroscopic results showed that uranium(VI) is predominantly bound to inorganic and/or organic phosphorous groups and/or ligands with carboxylic function [1-3]. The amino acids, peptides and proteins play an important role in the metabolism of the several biological processes. Therefore we have studied the systems U(VI)/threonine and U(VI)/p-threonine for better interpretation of the obtained spectra of original biological system.

Experimental
Solutions and reagents
The stock solutions of uranium(VI) were made from uranium oxide dissolution in HClO₄. The ionic strength was kept constant by adding NaClO₄. The pH value was adjusted with HClO₄ or NaOH and was 4. The stock solutions of the amino acids threonine (thr) and p-threonine (p-thr) (see Fig.1) were prepared freshly for each experiment. All stock solutions were prepared with deionized water.

![Fig. 1](attachment:image)

UV-Vis measurements
The absorption spectroscopy measurements were performed using a CARY5G UV-Vis-NIR spectrometer (Varian Co.). The experiments were carried out at a fixed uranyl concentration of 10⁻⁵ M as a function of the organic ligand concentration in the range of 10⁻⁵ to 2.5·10⁻¹ M. The ionic strength was constant 0.5 M.

TRLFS measurements
The TRLFS spectra were recorded with a pulsed Nd:YAG laser system. The excitation wavelength of the uranyl fluorescence was 266 nm by a laser energy of 200 – 350 μJ. The setup of the time-resolved laser-induced fluorescence spectroscopy (TRLFS) was described in [4]. The experiments were performed at a fixed uranyl concentration of 5·10⁻⁵ M. The ligand concentration of the organic ligands varied between 1·10⁻⁵ and 1·10⁻² M. Using NaClO₄, the ionic strength of the complex solutions was adjusted to 0.1 M.
**XAS-measurements**

The EXAFS spectra of the complex solutions were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. The U L\textsubscript{III} edge spectra were measured in fluorescence mode. The EXAFS spectra were analyzed according to standard procedures using the suite of program EXAFSPAK [5]. The theoretical scattering phases and amplitudes were calculated with the scattering code FEFF8 using the model compound sodium tris(acetato)dioxouranate [6]. The minor component in the spectra was analyzed by the difference technique described in [7].

**Results and discussion**

The absorption spectra from U(VI)/thr and U(VI)/p-thr systems are shown in Fig. 2. The observed red shift of the absorption maxima in case of both amino acids and a clear increase in the absorbance by addition of p-threonine indicate the formation of uranyl complexes with these ligands.

![Fig 2: UV-Vis spectra of the 1×10^{-3} M uranium (VI) without and with threonine and p-threonine at pH 4](image)

![Fig 3: Fluorescence spectra of uranium (VI) as function of the threonine concentration at pH 4](image)

Fig. 3 shows the fluorescence spectra of uranium(VI) as a function of the total threonine concentration as one example. We observed an increase in the fluorescence intensity and a red shift of the emission bands with the increasing threonine concentration compared to the measurement of the uranyl test solution of 5×10^{-5} M. The time-resolved fluorescence spectra showed a bi-exponential fluorescence decay indicating a mixture of two species. The longer lifetime (1700 ns) is typical of the free uranyl ion. The shorter lifetime (880 ns) can be assigned to the uranyl-thr complex.

The single spectra of the different species, which fluorescence, were determined from the composite spectrum using conventional peak deconvolution. The main fluorescence emission bands of the uranyl-thr complex are located at 476, 492, 514, 537 and 565 nm. The reaction of the UO_2^{2+} and threonine at pH 4 can be written as:

\[
\text{UO}_2^{2+} + x \text{NH}_2\text{CHCOO}^- + (\text{CH(OH)}\text{CH}_3) \rightleftharpoons (\text{UO}_2\text{(thr)}_x)^{2+}
\]

After rearranging and transforming the mass action law into logarithmic form it becomes:

\[
\log \frac{[\text{UO}_2\text{(thr)}_x)^{2+}]}{\text{UO}_2^{2+}} = \log K + x \log [\text{thr}]
\]
By plotting the log ([UO2\textsuperscript{2+}] / [UO2\textsuperscript{2+}]) vs. the log [thr]\textsubscript{free}, we obtain the stoichiometry of the complex reaction from the slope. The value x is found to be 1.12 ± 0.06, which clearly shows a 1:1 complex formation. From the intersection we obtain the formation constant for the (UO2\textsuperscript{2+} thr)\textsuperscript{2+} to be log K = 2.71 ± 0.12.

In contrast to the U(VI)/thr system we determined two uranyl complex species by analysis of the fluorescence decay of the U(VI)/p-thr system. These species have a clearly higher fluorescence yield than the uranyl-thr complex and show a red shift of the emission bands compared to the free uranyl ion. The lifetimes are 1600 ns for the free UO2\textsuperscript{2+} (aq) and 700 ns for the 1:1 complex, respectively. The lifetime of 4400 ns corresponds to the 1:2 complex. To describe the complex formation reactions in the U(VI)/p-thr system according to the total equation:

\[ \text{UO}_2^{2+} + x \text{(p-thr)} \rightleftharpoons (\text{UO}_2\text{(p-thr)})^{2+x+} + y \text{H}^+ \]

we used the factor analysis calculation program code SPECFIT [8]. The formation constants were calculated to be log\( \beta_x = 4.40 \pm 0.09 \) for the 1:1 complex and log\( \beta_2 = 6.84 \pm 0.17 \) for the 1:2 complex at pH 4 for \( y = 0 \). The main emission bands of the first uranyl-p-thr complex are 481.4, 496.5, 517.7, 541.0 and 567.0 nm. 483.7, 500.1, 521.5, 544.6 and 569.3 nm are the emission bands for the second complex species and differ only slightly from the bands of the 1:1 complex. In further experiments we shall investigate the pH dependence of the complex constants.

From the EXAFS study we can conclude that the coordination of U(VI) is similar for all investigated unphosphorylated amino acids. The calculated equatorial distance of 2.38 to 2.39 indicates that uranyl is predominantly bound by the carboxylic group [9]. Structural parameters of the various complex species of both systems will be discussed.

Acknowledgements

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References

COORDINATION CHEMISTRY OF TRIVALENT f-ELEMENTS IN SOLUTION WITH CALIXARENE-TYPE LIGANDS

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Owing to coordination numbers exceeding 8 or 9, the complexion of trivalent lanthanide and actinide ions usually requires a stoichiometry involving several mono- or bidentate ligands per metal ion. In case of solvent extraction of these ions, their hydration sphere should be completely substituted by the extractant molecules. In order to gain better control over the complex stability and selectivity, we apply cage-type compounds with multiple coordination sites as ligands [1]. For this purpose, calix[n]arenes (n=4, 6) turned out to be a suitable molecular platform for covalently anchoring ligating groups [2]. These groups can be monodentate, because the macrocyclic effect of a pre-organized molecular structure causes an enhanced complex stability as compared with non-cyclic monodentate ligands.

Previously we have shown that carboxylic acid derivatives of calix[6]arenes are useful for the extraction and backextraction of trivalent lanthanides and actinides from weakly acidic media [3] and from more strongly acidic solutions [4]. f-Element group separation could be achieved with the concept of mixed functionalities, which we interpreted in terms of stabilizing actinide(III)-π-interactions, promoted by relativistic f-orbital expansion. The electrostatic interactions in these complexes were restricted by partly functionalizing the calixarene with only 3 acidic groups.

In this contribution, we present the first results on fully substituted calix[6]arenes bearing six alpha-halogenated carboxylic acid groups. We discovered a smooth synthetic route with high chemical yields and subsequently characterized the extraction equilibria of Am(III). The fluorne-atoms in L1 increase the acidity and the difference in pKₐ directly translates into improved extractability, expressed as the distribution ratio D, by nearly 2 orders of magnitude at a given pH compared with L2. As expected, one ligand molecule matches the Am(III) coordination sphere, forming a 1:1 complex, accompanied by the release of 3 protons. At the same time, we prove our concept about the influence of electrostatic interactions and of size compatibility on group separations by macrocyclic ligands.

Scheme 1: Structures of the investigated ligands for extracting Am(III)

L1: R = tert-Butyl
    X = F

L2: R = tert-Octyl
    X = H
Figure 1: Influence of electronegative substituents on the extraction of $^{241}$Am(III) by ligands bearing carboxylic acid groups.

Aq. Phase: HNO$_3$, $^{241}$Am (80 MBq/L), if indicated 5 mM NaNO$_3$ was contained, Org. Phase: CHCl$_3$ containing L1 (2.5 mM) or L2; volume ratio 1, T 296 K, t 1 h of magnetic stirring, analysis: LSC of aq. phase.

For example, a 2000-fold excess of Na$^+$ over Am$^{3+}$ doesn’t interfere the extraction of Am(III) as seen in Figure 1, because the ligand is not selective for Na$^+$ due to the difference in diameters between cation and ligand cavity.

The slope of 3 represents the cation exchange mechanism according to eqn. (1).

\[
H_4L + Am^{3+} \rightleftharpoons AmLH_3 + 3 H^+ \tag{1}
\]

The next works are concerned with determining the extraction constants for actinides and lanthanides as well as with determining $pK_a$-values of the ligands.

References

pH DEPENDENCE OF URANYL UPTAKE ON QUARTZ :
AN XPS STUDY

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Introduction

Uranium release in ground- and drinking water is of concern at several U-contaminated areas in the world. U mining and reprocessing has led to large amounts of U-rich soils, sediments or mill tailings, which are a local source for water contamination in specific environments. Predicting the transport of uranium in the near-field of highly U-contaminated sites is thus critically needed. It requires detailed knowledge on both sorption and precipitation processes of uranyl occurring at high concentrations of U(VI) in the aqueous phase.

In this work, we aimed at gaining insights into a pH-dependence of the « uranyl components » – such as uranyl surface species, (surface-) precipitates – formed on a quartz fraction equilibrated with concentrated uranyl solutions, i.e. under conditions favouring aqueous polynuclear species and / or formation of U(VI)-colloids or UO\textsubscript{2}(OH)\textsubscript{2} precipitates. X-ray Photoelectron Spectroscopy (XPS) was used to distinguish between different types of uranyl ions on the quartz fractions and thus to assess whether distinct uranyl « components » contribute to a pH-dependent U(VI) uptake. The U 4f spectra were interpreted in terms of coordination environments of the uranyl ions in the components, on the basis of EXAFS data published in the literature on sorbing uranyl species. Our study provides thus valuable insights into the uranyl sorption complexes / (surface-) precipitates governing a pH-dependence of U(VI) uptake in a poorly sorbing medium. XPS is a surface technique which provides direct chemical and structural information on ions in / on minerals. The energy of the emitted photoelectron for a given atom in an XPS spectrum is indeed related to its coordination environment. Different bonding environments can induce binding energy shifts. Many studies have already shown that XPS is a valuable tool for studying chemical speciation of several sorbing ions, including U(VI) [1, 2].

Experimental and analytical procedure

Batch experiments were carried out to prepare the U(VI)-containing quartz fractions to be analysed by XPS. We measured the partitioning of U(VI) between a quartz fraction, a colloidal phase and an aqueous phase at 298 K under a CO\textsubscript{2}-free atmosphere. The initial aqueous uranyl concentrations are 10 μM, 50 μM and 100 μM. The quartz / solution ratio of the samples is equal to 25 g / L. The ionic strength (I.S.) of the solution is kept at a value of 0.1 M using a NaNO\textsubscript{3} electrolyte solution. The parameter under investigation is the final solution pH (5 <pH< 8).

The specific surface area of the quartz used is low and may be taken as representative of the surface area of primary minerals which may immobilize U(VI) in rocks. Due to the low
sorbing properties of quartz and to high aqueous U(VI) concentrations, in this work, particular attention was paid to detect a possible formation of colloids or a precipitation of schoepite-type minerals in our experiments. So, (meta-) schoepite was synthesized and its XPS spectrum was recorded and taken as a uranium(VI) oxide hydrate reference.

In order to gain insights into the coordination environments of sorbed / precipitated uranyl ions in the quartz fraction, we recorded the U 4f XPS spectra of the U(VI)-containing quartz samples (Figure 1). All the spectra, including the metaschoepite ones, were shifted to reposition the Si 2p peak at a binding energy value of 103.5 eV.

![Figure 1: U 4f XPS spectrum of a U(VI)-containing quartz sample recorded at pH 7.1 and its fitting curve showing a contribution of two components for uranyl ions (dashed line: “component I” or metaschoepite-like component; solid line: “component II”) from Froideval et al., 2003 [3]. Experimental sample conditions: [U]_0 = 100 μM, I.S. = 0.1 M NaNO₃, electrolyte solution, N₂-free atmosphere, 298 K.](image)

**Interpretation of the U 4f XPS binding energies in terms of U(VI) coordination environment**

- Because all uranyl ions in metaschoepite display a single coordination environment [4], a single component was used to fit the U 4f peaks of our synthetic metaschoepite. The U 4f lines were found to be positioned at 382.0 eV for U 4f₁/₂ and at 392.85 eV for U 4f₃/₂.

- The U 4f XPS spectra of the U(VI)-containing quartz samples could not be fitted by assuming the same and single component for uranyl ions, which suggested convoluted signals. The U4f XPS spectra allowed to identify unambiguously the presence of two uranyl components. A high binding energy component, whose relative proportion increases with pH, exhibits the U 4f lines characteristics of our synthetic metaschoepite. A second uranyl component exhibits binding energies for the U4f core levels at values significantly lower (ΔE₀ = 1.2 eV; U 4f line at 380.8 eV for U 4f₁/₂ and at 391.65 eV for U 4f₃/₂) than for metaschoepite. This is an evidence for the presence of uranyl ions having a coordination environment significantly different from that of uranyl ions in U(VI) oxide hydrates. The high binding energy component is interpreted as a component having a U(VI) oxide hydrate character, either as polynuclear surface oligomers and / or as amorphous schoepite-like (surface) precipitates. Its pH-dependence suggests that a binding of polynuclear species at
quartz surfaces and/or a formation of amorphous schoepite-like (surface) precipitates is favoured when increasing the proportion of aqueous polynuclear species (pH increase). The second component may be attributed to monomeric uranyl surface complexes on the basis of EXAFS data on uranyl surface complexes [5-7]. A finding of two uranyl components on our quartz fractions suggests anyway that the uranyl surface speciation on silica minerals is not uniquely controlled by the aqueous uranyl speciation.

Conclusions

Our XPS analyses allowed to identify unambiguously the presence of two pH-dependent uranyl components on a quartz fraction equilibrated with concentrated uranyl solutions over a pH range 5-8. An important contribution of our XPS study is to identify unambiguously the presence of a component in which the U(VI) coordination environment differs significantly from that of uranyl ions in U(VI) oxide hydrates, at pH values where aqueous polynuclear species/uranyl colloids predominate in solution. A valuable information is that the $U\,4f$ binding energies of such species are positioned at values significantly lower than those obtained for metaschoepite. Such a position may be consistent with EXAFS data published on the coordination environment of uranyl ions in monomeric uranyl surface complexes. Such species were reported to be formed on various minerals brought in contact with acidic solutions [5-7] or at the surface of Fe- or Al-oxihydroxides in contact with near-neutral solutions [7]. Our XPS results suggest that pH-dependent monomeric surface complexes may also be formed at a high surface coverage on silica minerals, together with polynuclear surface oligomers and/or schoepite-like (surface) precipitates.

Our study shows that XPS is a powerful tool for evidencing a coexistence of uranyl ions having very distinct coordination environments and for providing valuable qualitative and quantitative information on the uranyl « surface speciation ». XPS analyses can thus complement EXAFS studies by offering a possibility to discriminate unambiguously between several kinds of surface species/precipitates on a mineral.

References

X-RAY ABSORPTION SPECTROSCOPY (XAS) STUDY OF U(VI) IMMOBILIZATION BY HARDENED CEMENT PASTE (HCP)

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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of low and intermediate level radioactive waste. Cement is used to condition the waste materials, for the engineered barrier and for the construction of the repository. The near field of a cementitious repository acts as a chemical barrier for radionuclides, thus retarding migration of waste ions into the surrounding geosphere. In cement-stabilized waste forms the uranium inventory mainly originates from the reprocessing of spent fuel. The objective of the present study is to elucidate immobilization processes in hardened cement paste (HCP) at pH = 13.3 and to provide information that can be used to assess the release of the U(VI) into the geosphere.

Under the highly alkaline conditions prevailing in a cementitious environment (pH > 12) U(VI) solubility is expected to be low due to the formation of Ca or K uranates. Under these conditions U(VI) speciation is dominated by the monomeric species [UO₂(OH)₆]²⁻ and [UO₂(OH)₅]³⁻ [1-4]. Depending on the uranium inventory in cement systems the following immobilization processes are possible: 1) precipitation of a uranate compound at high U(VI) inventories, or 2) sorption onto cement minerals at low U(VI) inventories. Figure 1 shows that, in cement systems at pH = 13.3, each process is associated with a specific region of the U(VI) sorption isotherm on HCP.

Figure 1: U sorption isotherm: U(VI) sorbed on fresh HCP (pH = 13.3) is shown as a function of the U(VI) solution concentration after equilibration.
U(VI) containing HCP samples, representative of each region of the isotherm, were prepared together with reference samples consisting of U(VI) precipitated in the presence of KOH, NaOH or Ca(OH)$_2$. All samples were characterized by X-ray absorption spectroscopy (XAS) and, in addition, the precipitates by X-ray diffraction (XRD). In the past XAS was successfully employed to investigate the speciation and binding mechanisms of various elements in cementitious materials [5-9].

X-ray absorption near edge spectroscopy (XANES) results proved that the U(VI) formal oxidation state remained unchanged in all the samples. The pseudo radial distribution function (PRDF) of U(VI) containing samples representative of the two regions of the isotherm are shown in Figure 2.

![Figure 2](image)

**Figure 2**: Comparison of the U L$_3$-edge raw (—) and simulated (---) modulus and imaginary part of the PRDF for HCP samples with a) a high U inventory (U(VI) solubility limiting phase) and b) a low U inventory (U(VI) sorption).
Fitting of the extended X-ray absorption fine structure (EXAFS) spectra allowed us to determine the local structure of U(VI) immobilized in HCP. For both the sorption and precipitated samples U-O_{total} distances above 1.84 Å are found (dU-O_{total} = 1.88 Å; 1) = 1.84 Å), indicating that U(VI) is present in the form of uranate compounds. Note that changes in the typical O=U=O multiple scattering XANES features further corroborate this finding.

Under conditions where the solution was over-saturated with respect to the U(VI) solubility-limiting phase, U-U distances could be deduced from the EXAFS spectra (dU-U = 3.8 Å). Moreover, the local U(VI) environment was found to be similar to that of the U(VI)-Ca(OH)_2 reference. Based on the available EXAFS and XRD results, crystallographic identification of the U(VI) solubility limiting phase will be discussed. A comparison of the Sn(IV) and U(VI) immobilization in HCP further shows that Ca^{2+} containing solid phases are responsible for solubility limitation of these radionuclides in cement matrices [7].

Under conditions where the solution was under-saturated with respect to the formation of the U(VI) solubility limiting phase, no U-U backscattering appears in the EXAFS spectra. The splitting of the U-O_{equatorial} distances (dU-O_{eq}; 2.27 Å, 2.43 Å) as observed in the present study is a common feature previously reported for U(VI) sorbed on mineral phases (e.g. [10]), indicating the formation of inner-sphere complexes with the uptake-controlling cement mineral. At the present time, however, a more detailed interpretation of the data in view of identifying the cementitious phase that controls U(VI) immobilization in HCP is difficult because no further U-metal backscattering contribution could be deduced from the EXAFS spectra. The present study reveals the potential and limitations of XAS for investigating immobilization processes in cementitious systems.

References

THE INFLUENCE OF ITINERANT VS. LOCALIZED F-ELECTRONS IN ACTINIDE ALLOYS AS NUCLEAR TRANSMUTATION FUELS

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Part of the mission of the United States Department of Energy (US-DOE) Advanced Fuel Cycle Initiative (AFCI) is to develop nuclear fuels for the transmutation of long lived radioisotopes. Certain actinides are of particular concern and include Np, Pu, Am and Cm. For this reason, Argonne National Laboratory - West is producing metal alloy test nuclear fuels for the transmutation of actinide isotopes in either fast spectrum reactors or accelerator driven systems. Specifically, the binary (in wt.%) Pu-40Zr and Pu-60Zr alloys, the ternary Pu-10Np-40Zr and Pu-12Am-40Zr alloys, the quaternary Pu-10Np-10Am-40Zr and U-28Pu-7Am-30Zr alloys and the quintary U-34Pu-4Am-2Np-20Zr, U-29Pu-4Am-2Np-30Zr and U-25Pu-3Am-2Np-40Zr alloys have been prepared via an arc-casting method. The non-fertile uranium free alloys are currently under irradiation testing in the Advanced Test Reactor in the United States and two of the fuel compositions (Pu-12Am-40Zr and U-29Pu-4Am-2Np-30Zr) will begin irradiation testing in the Phénix reactor in France under the FUTURIX program in 2006.

One of the challenges associated with the fuel development program is a deficiency in the database of the fundamental properties and reactivities of actinide containing alloys. For example, of the 10 possible binary systems in the U-Np-Pu-Am-Zr system, only 7 have partial to full phase diagrams experimentally investigated with the rest having either only extremely limited data or having been studied from theoretical modeling aspects. In some cases there are conflicting experimental results. The scarcity of data in the ternary systems is even more pronounced and virtually nonexistent in the quaternary and higher systems. Although we have investigated the alloys for specific properties related to the fuel fabrication and irradiation testing (e.g. Am retention during fabrication and formation of low-melting Np phases), these studies have proffered some initial data points in the Pu-Np-Zr and Pu-Am-Zr ternary systems and, in conjunction with the quaternary and higher compositions studied, allowed an initial look at the influence and behavior of Np (itinerant f-electrons) and Am (localized f-electrons) on the Pu-Zr and U-Pu-Zr systems. In this short contribution, we will

![Figure 1](image)

**Figure 1.** Top: x-ray diffraction pattern of an as-cast Pu-40Zr arc-cast product. Bottom: theoretical pattern based on face-centered-cubic indexing.
compare the products of the Np bearing alloys Pu-10Np-40Zr and Pu-10Np-10Am-40Zr to the parent Pu-40Zr alloy, discuss the formation of low temperature melting phases and the consequence of oxygen contamination on the products. Finally, a brief discussion of the high Am volatility issue with respect to Am retention during processing will be presented.

The alloys were prepared from elemental feedstocks or, in the case of Am, from a Pu-19Am alloy. All of the feedstock materials except Np were high quality materials with low contamination levels. The Np metal was in the form of turnings that contained up to 5000 ppm oxygen contamination. Charges of the elemental feeds were arc melted and homogenized as buttons at least three times before being cast into 4mm diameter slugs using a modified arc casting method. As-cast samples of Pu-40Zr formed as a face-centered-cubic (fcc) structure which can be described as a solid solution of Zr dissolved in fcc δ-Pu (Figure 1). The effect of a 10% substitution of Np for Pu in Pu-40Zr is shown in Figure 2. Here, the as-cast product contains a mixture of a δ-Pu (fcc) Pu-Zr solid solution with a hexagonal indexed MZr$_2$ phase (UZr$_2$ structure). The Pu-10Np-10Am-40Zr sample is very similar to the Pu-10Np-40Zr.

![Figure 2](image)

**Figure 2.** Top: x-ray diffraction pattern of an as-cast Pu-10Np-40Zr arc-cast product. Bottom: combined theoretical patterns based on fcc δ-Pu solid solution (bold solid line) and hexagonal MZr$_2$ (dashed line) indexing. The unaccounted reflections are internal Al standard.

The presence of the fcc δ-Pu stabilized phase is due to the rapid cooling from the melt since the phase should be stable only between about 270°C and 640°C. The occurrence of the MZr$_2$ phase in the ternary is not surprising. Both studies on the Np-Zr system indicated formation of this phase and it has been observed in certain studies of the Pu-Zr system. It has been suggested, however, that the formation in the Pu-Zr system may be due to oxygen impurities. The phase was first observed in the U-Zr system and has been likewise reported for the Am-Zr system. The oxygen contaminated Np feedstock introduced oxygen into the ternary, which may have aided the formation of the MZr$_2$ phase. A comparison of the microstructures observed in the as-cast products of the Pu-40Zr and Pu-10Np-40Zr alloys is shown in Figure 2. Whereas Pu-40Zr has a generally homogenous microstructure with some pore formation, three phases can be observed in the Pu-10Np-40Zr alloy: a light contrast phase, a darker contrast phase and very dark contrast precipitate phase apparently associated with the darker contrast phase. X-ray maps indicate Np, Pu and Zr are present in all phases with the light contrast phase being enriched in Pu and Np, the darker contrast phases somewhat enriched in Zr and the precipitate phase being almost exclusively associated with the oxygen contamination. We interpret these results in terms of the light contrast phase representing the fcc solid solution, the darker contrast phase the MZr$_2$ solid solution and the darkest phase
oxide precipitates. The formation of the oxides as precipitates rather than as an oxide solid solution shows that the formation energies of the actinides dominate. Thus, both Np and Pu do not form solid solutions with oxygen but rather stoichiometric phases (NpO and PuO₂) as first formed line phases. Zr, on the other hand, forms a series of solid solutions with oxygen up to ZrO₂. Per mole of oxygen, the free energies of formation of NpO, PuO₂ and ZrO₂ are about equal, with the actinides slightly favored. Since at lower concentrations of oxygen the sub-stoichiometric Zr-O formed would have even smaller free energies, the actinides will determine the oxide and drive the formation of the discrete precipitate phase. The quantitative composition of this phase is still under investigation but may be either (Np, Pu, Zr₁₋ₓ)O or (Np, Pu, Zr₁₋ₓ)O₂ (although PuO and Np₂O₅ are not known).

**Figure 2.** SEM micrographs of as-cast Pu-40Zr (left) and Pu-10Np-40Zr (right).

The differential scanning calorimetry (DSC) heating curves for the two alloys are shown in Figure 3. Pu-40Zr (dashed line) shows the expected endotherm for the fcc to bcc transformation starting about 640°C. Pu-10Np-40Zr (solid line) shows two endothermic transitions with onset temperatures of about 500°C and 555°C. The low temperature transition represents the transition from fcc + MZr₂ to either (fcc + bcc), (fcc + α-Zr solid solution) or (fcc + bcc + α-Zr solid solution). The higher temperature transition is to the final sub-solidus bcc solid solution phase. It is concluded from the DSC measurement that no melting occurs in the ternary for the following reasons. A possible interpretation of the DSC measurement is that the 500°C includes a decomposition transition separating out Np or more probably a NpPu alloy and the higher temperature transition would include melting of the NpPu alloy eutectic at about 560°C. We rule this out on the grounds that under such a decomposition, a Pu-Zr (up to 50-50) alloy would be produced, which would undergo a transition to bcc at 620°C or higher (see Pu-40Zr plot). That no such transition is observed strongly suggests that no decomposition occurred. In addition, no clear evidence of melting was observed in other experiments including thermal expansion measurements and diffusion couple experiments. The details of the transitions will be discussed further.

**Figure 3.** DSC plots of Pu-40Zr (dashed line) and Pu-10Np-40Zr (solid line).
CONTRACTION OF ACTINIDES 3+ IONIC RADII AT THE END OF THE SERIE

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For the five heaviest members of the lanthanide series, the spacing between ionic radii of the adjacent elements decreases regularly from 1.3 to 1.0 pm (Table 1). Unexpectedly, in the case of end actinides the spacings between \( r_i \) of the neighbouring elements change irregularly. For example, the difference in \( r_i \) between Es\(^{3+}\) and Fm\(^{3+}\) is 1.7 pm, whereas that between Md\(^{3+}\) and No\(^{3+}\) only 0.2 pm.

In order to understand the sources of irregularity in the contraction of ionic radii of heavy actinides we compared the experimental \( r_i \) with the radii of the maximum charge density, \( R_{\text{max}} \), of the outermost orbital radii in these cations. Linear correlations of \( r_i \) on \( R_{\text{max}} \) and on expectation values of orbital radii \( <r^2> \), were found for cations of the same charge in many groups of the Periodic Table[1]. These correlations are suitable to predict \( r_i \) of ions in case when experimental measurements are difficult or impossible[2,3].

![Diagram](image)

Fig.1. The ionic radius as a function of the \( 2j+1 \) weighted \( R_{\text{max}} = \frac{2R_{\text{max,Lr}} + R_{\text{max,No}}}{3} \) in the heavy actinides. Triangles represent ionic radii determined from electron diffraction data and squares ionic radii from elution experiments.

Figure 1 presents the dependence of the ionic radius on \( R_{\text{max}} \) of the outermost shell in the ions of the heavy actinides. The orbital radii have been calculated by V. Pershina using the Dirac-Slater method[4]. As the outermost shell radii we used the \( 2j+1 \) weighted \( R_{\text{max}} \). As shown in Figure 1 a linear dependence of \( r_i \) on \( R_{\text{max}} \) of the outermost shell is observed for +3 actinides from Cm to Es. For these cations the experimental \( r_i \) were determined from electron diffraction on oxides. The chromatographically determined ionic radii of Lr\(^{3+}\) and No\(^{3+}\) also
fit the extrapolated part of the straight-line plot. As shown in Table 2, large differences exist between the extrapolated and experimental radii for Md$^{3+}$ and Fm$^{3+}$.

<table>
<thead>
<tr>
<th>An$^{17}$ ion</th>
<th>r$_e$(pm) experimental</th>
<th>r$_e$(pm) extrapolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fm$^{3+}$</td>
<td>91.1</td>
<td>91.5</td>
</tr>
<tr>
<td>Md$^{3+}$</td>
<td>89.6</td>
<td>90.3</td>
</tr>
<tr>
<td>No$^{3+}$</td>
<td>89.4</td>
<td>89.2</td>
</tr>
<tr>
<td>Lr$^{3+}$</td>
<td>88.1</td>
<td>88.1</td>
</tr>
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</table>

The ionic radii of Fm$^{3+}$, Md$^{3+}$ and Lr$^{3+}$ were determined only by the chromatographic method. The linear dependence of the logarithm of distribution coefficients, $K_d$, on $r_e$ for the tripositive ions of heavy lanthanides and actinides in α-hydroxyisobutyrate solutions was the basis for the $r_e$ determination of the heaviest actinides[5]. However, in complexing solutions strong deviations from linearity of the log $K_d$ vs. $r_e$ plot are observed[6,7]. This effect called double-doble or tetrarad consist in the division the lanthanide and actinide series into two subgroups by the f$^5$ configuration and further division of each subgroup into two segments by the f$^2$-f$^3$ and f$^0$-f$^1$ pairs[8]. Stabilization of the f$^3$, f$^4$, f$^5$, f$^{10}$ and f$^{11}$ configurations depends on the environment and decreases with increasing ability of the ligand to expand the $f$ electron cloud. In water, where the nephelauxetic effect is very low the delocalization of $f$ electrons is insignificant. In α-hydroxyisobutyrate solution where water molecules in the solvation sphere are exchanged for the ligand which shows high nephelauxetic effect, the cations with f$^2$, f$^3$, f$^4$, f$^{10}$ and f$^{11}$ configurations form less stable complexes than expected from ionic radii.

![Fig. 2 Dependence of the logarithm of the separation factor (α) on $r_e$ for the third segment (f$^2$-f$^{10}$) in lanthanide (Gd$^{3+}$-Ho$^{3+}$) and actinide (Cm$^{3+}$-Es$^{3+}$) series in the α-hydroxyisobutyrate – strong acidic cation exchange resin system.](image)

Figure 2 presents the dependence of the logarithm of the separation factor (α) on $r_e$ for the third segment (f$^2$-f$^{10}$) in both lanthanide (Gd$^{3+}$-Ho$^{3+}$) and actinide (Cm$^{3+}$-Es$^{3+}$) series in the α-hydroxyisobutyrate – strong acidic cation exchange resin system. The separation factor α is defined as $K_d$(Ln$^{3+}$)/$K_d$(Gd$^{3+}$) or as $K_d$(An$^{3+}$)/$K_d$(Cm$^{3+}$) for lanthanides and actinides, respectively. Figure 2 shows that for the third segment the dependence of log α on $r_e$ for lanthanides(III) does not deviate much from linear. However, in the case of actinides(III)
strong deviations from linearity due to the tetrad effect are observed. This is because greater 
radial extent of 5f in comparison with 4f orbitals results in stronger participation of 
5f orbitals in metal to ligand bonding. Similar effect should be observed in the fourth segment 
(f4f14) of the lanthanide (Er3+-Lu3+) and actinide (Fm3+-Lr3+) series. In the case of 
lanthanides(III) small deviations from linearity are indeed observed [9], whereas for Fm3+- 
Lr3+ strong tetrad effect is to be expected. This means that ionic radii of the heaviest actinides 
can not be determined from linear dependence of log Kd or log α on r in experiments based 
on the α-hydroxyisobutyrate –cation exchange system, as there is no way to get rid of the 
tetrad effect in the stability constants. The only way seems to be extrapolation of the linear 
dependence of r on (ionic radius based on crystal data) on Rmax which is valid for the Cm-Es 
interval, to the Fm-Lr interval, see Figure 1. From this extrapolation one gets r equal to 91.5 
and 90.3 pm for Fm3+ and Md3+, respectively.

The question remains, why the ionic radii of Lu3+ and No3+, determined from elution 
positions, are the same (Lu3+) or almost the same (No3+) as those calculated from orbital radii. 
In the case of Lu3+ participation of the f orbitals in the metal to ligand bonding is negligible 
because the 5f shell is filled and the nephelauxetic effect in 5f electrons does not affect 
the stability constant of the α-hydroxyisobutyrate complex. As far as the No3+ is concerned it 
should be noted that it has been determined chromatographically by comparison of its Kd 
with Kd of heavy lanthanides on cryptomelane-MnO2 cation exchanger[]. The selectivity of 
cryptomelane-MnO2 for the cations is due to steric effects and depends on the radii of the 
cations and of the tunnel (280 pm) in the sorbent[10]. Therefore, the selectivity of the 
cryptomelane MnO2 depends nearly linearly on the free energy of hydration which, in turn, is a 
linear function of the ionic radius. The linear dependence of the free energy 
of hydration on the reciprocal of the ionic radius for the whole Ln3+ series and for those 
actinides for which the ΔGhydration is available, indicates that in the hydration energy the tetrad 
effect is, as expected, insignificant.

The tetrad effect in complexion of actinide(III) cations by α-hydroxyisobutyrate gives 
derestimated values for Fm3+ and Md3+ ionic radii comparing with the ionic radii obtained 
from the linear dependence of ionic radii on orbital radii. With the calculated r for Fm3+ 91.5 
and Md3+ 90.3 pm, the ionic radii of An3+ at the end of the series decrease regularly like in 
the radii of the lanthanide (III) cations.

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URANIUM L-LINES EMISSION CHEMICAL AND ISOTOPE EFFECTS AND THE STATE OF URANIUM ATOM IN ITS COMPOUNDS

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Uranium compounds were studied by means of crystal-diffraction spectrometer (200mm, geometry of Cauchois and of Dumond). The chemical and isotope shifts of it's the most intensive lines (Lα2, Lα1, Lβ1, Lγ6...) were obtained. The complicated structure of chemical shifts of emission lines have been stated influenced both by the local atom charges and by the deviations of surrounding ligands from the spherical symmetry. No simple correlations observed between the oxidation states of atom and the chemical shifts of uranium L-emission lines. The most important observations may be formulated as follows: 1) distorted structures of uranium compounds and their signs in chemical shifts observed for them result in a remarkable collapse of spin-doublet splitting $\Delta E_{o}(\pm)$ shown to correlate with the distance values U - O1. 2) No similar effects were observed in the isotope effects. As a way of solving the problem of state identification of uranium (and perhaps other 5F-elements). Several versions of multivariate data analysis [1,2] have been considered. For practical needs own programs were composed and the account for the experimental errors realized. The most simple seemed to be a presentation of the data in the form of the single dimensional Minkovsky distances with respect to the center of gravity of all data (Fig.1). It may be expressed by the following formula:

$$R_i = \sqrt[3]{\sum_j (r_{ij} - r_{j}^0)^3}$$

where $R_i$ - Minkovsky distance for compound $i$ relatively to the gravity center of all chemical shifts, $r_{ij}$ - its chemical shift on line $j$, $r_{j}^0$ - gravity center coordinate.

The third degree should reflect sign variations in chemical shift.

The most important feature of such diagram is a wide range of the distribution, about 450 meV, which could be already considered as an indicator of the involved contribution of 5F-electrons. The mixed oxides occur in the negative part of the scale, the most reduced compounds (U(III), U(IV)) – in the positive part, together with U metal. And most of uranlys – in interval 0 - 100 meV.

Several possible diagrams were tested. It came out that the most promising presentation of the data (in terms of [1]) was the diagram of PC-2 plotted against PC-1 (Fig.2). Here we see three localities well separated from each other.

The remarkable thing here is: 1) the compounds of U(III), U(IV) and U metal are localized closely with each other, they occupy the positive part of PC-2, and the negative part of PC-1. 2) All mixed oxides occupy an intermediate area, rather close to 0. 3) Nearly all compounds of uranyl form rather tight clusters. The fact is that only
**Fig. 1.** One-dimensional arrangement of uranium compounds received by convolution of Ch.S. on four L-lines: a₁, a₂, b₃, b₄

**Fig. 2.** Arrangement in the space of two main components: PC-1 and PC-2

In this case the relative distribution of the compounds strictly shows the direction of oxidation of uranium: from the left to the right and the realistic scale of variation of the effects shown in upper corner.

**References**


NEW ORTHOPHOSPHATES MATRICES OF THE NZP-LIKE STRUCTURE FOR IMMOBILIZATION OF ACTINIDES

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This work presents the results of synthesis and X-ray diffraction analysis of new actinides orthophosphates A'M''^IV(PO_4)_3 where A' = Li, Na, K, Rb; and M''^V =U, Np and Pu. The compounds were obtained by the high-temperature synthesis.

Experimental

At present orthophosphate compounds are being studied actively and they are considered as future potential matrices for the creation of the first safety barrier for waste disposal. Among the structural types of orthophosphates one of the major places belongs to a structural type NaZr_2(PO_4)_3 (NZP), having a high chemical, thermal and radiation stability and ability to include a wide set of cations of various nature in the structure [1, 2].

Relatively large actinide (IV) ions have high coordination numbers (8, 9, 10) in the orthophosphates. U, Np and Pu orthophosphates were shown to have high-temperature rhombohedral modifications, in which the coordination number of actinide is lowered up to 6. This phenomenon is rather unusual, as the coordination number 6 is more typical of smaller cations of d-elements (Ti, Zr, Hf). To some extent, this phenomenon brings together crystal chemistry of d- and f-elements and provides the scientific ground for designing new compounds on the basis of the NZP structural type. In practice, it opens up the possibility of concentration and stabilization of long-lived actinides into homogenous matrices based on solid solutions, containing d and f-elements simultaneously, for example actinides and zirconium.

Results

The temperature polymorphism of the investigated series of orthophosphates was revealed and it was present, practically, in any combination "alkaline cation - actinide atom" [3]. At low temperatures of the synthesis (from 500-600 to 1100-1300 °C) most of them form monoclinic crystal structure NaTh_2(PO_4)_3 (NTP) (α-form). With increasing temperature up to 1500-1600°C one or two polymorphous transitions occur in the most cases. They result in the formation of NaZr_2(PO_4)_3 (NZP) structure of the hexagonal (rhombohedral) symmetry (β-form). The temperature of the α → β phase transformation depends on the nature of the alkali element and actinide atom combination. Some combinations (Li-Pu, Na-U, Rb —actinide) have individual distinctions of the phase formation when only one form (α or β) crystallizes and the other not at all or individual crystalline phases are formed.

For the first time crystallographic characteristics were identified for four monoclinic and eight rhombohedral orthophosphates by using powder X-ray diffraction data. The lattice parameters
and unit cell volumes depend on the ionic radii of alkaline metals and actinide atoms. For monoclinic phases these dependencies are irregular, while for rhombohedral ones–they are regular.

References

REFINED DATA ON THE PuO$_4$ VOLATILITY

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In thermochromatographic (TC) studies on the thermal oxidation of trace quantities of plutonium in a stream of He$^+$O$_2$ mixture, the formation of some volatile forms was observed [1,2]. The most volatile compound was adsorbed on a quartz surface at a negative temperature of about −100°C. In the ref. [3], we assumed that this adsorption zone could be related to the deposition of octovalent plutonium in the form of PuO$_4$. Later [4] the correctness of this assumption was shown. The deposition temperature of PuO$_4$ on quartz was determined with an accuracy of ±25°C and the calculated value of the adsorption enthalpy $-\Delta H^o_{m}$ for PuO$_4$ was accurate to ±6 kJ.mol$^{-1}$. The results presented allow the volatility of PuO$_4$ to be determined with a higher accuracy.

To take a thermochromatogram formed by an α-emitter, a TC column is cut into portions of a fixed length $l_n$ whose inner surfaces are treated with a suitable solvent; then α-sources are prepared from resulting solutions and α-spectrometric measurements are performed. The accuracy with which the temperature of the peak maximum $T_n$ is determined depends on the value of $l_n$. As the value of $l_n$ decreases, the accuracy of $T_n$ determination increases. This simple dependence served as a basis in the experiments in question.

Helium was used as a carrier gas and oxygen as a reagent, its concentration $c_{o_2}$ was equal to 50% (vol.). The values of $l_n$ were equal to 3 cm, 2.5 cm and 2 cm. The other experimental conditions as well as the procedure of producing and measuring α-samples were the same as in refs. [3,4].

It was found that, as in refs. [3,4], a significant portion of plutonium had passed into the gas phase and had been adsorbed in the form of volatile tetroxide, PuO$_4$, at a negative temperature close to −100°C. The data obtained are shown in the Table. The $-\Delta H^o_{m}$ PuO$_4$ values are calculated using equation 15 from ref. [5].

<table>
<thead>
<tr>
<th>$l_n$, cm</th>
<th>$-T_n$, °C</th>
<th>$-\Delta H^o_{m}$ PuO$_4$, kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>105±25</td>
<td>41±6 [3,4]</td>
</tr>
<tr>
<td>3</td>
<td>101±27</td>
<td>42±7</td>
</tr>
<tr>
<td>2.5</td>
<td>92±22</td>
<td>44±5</td>
</tr>
<tr>
<td>2</td>
<td>97±18</td>
<td>43±4</td>
</tr>
</tbody>
</table>

As can be seen, the presented results are in a good agreement with the literature data. The performed experiments allow the $T_n$ values for PuO$_4$ to be refined and more accurate value of $-\Delta H^o_{m}$ PuO$_4$ on quartz to be obtained. It is proved to be 43±4 kJ.mol$^{-1}$.
REFERENCES

THERMOCHROMATOGRAPHIC VOLATILITY STUDIES OF ACTINIDE OXIDES

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For more than 50 years PuO₂ has been recognized to be the highest plutonium oxide until Haschke et al. [1] reported the oxidation of PuO₂ with H₂O to a high-composition plutonium oxide phase, PuO₂ₓ, with x approaching 0.3. XPS data of the oxide formed were interpreted with substitution of Pu(IV) for Pu(IV) on cationic sites of PuO₂ₓ and the absence of Pu(V). Subsequent EXAFS measurements indicated the oxidation to Pu(V) [2]. Mass spectrometric measurements of effusing vapors over PuO₂ by Ronchi et al. [3] indicated the formation of volatile PuO₃(OH) in minor quantities. Thermochromatographic studies of plutonium compounds formed in an oxygen atmosphere were interpreted by Domanov et al. [4] with the formation of PuO₂ too and even PuO₄. PuO₂ was found to be volatile in the presence of humid oxygen already formerly by Krikorian et al. [5]. The Pu vapor pressure of about 10⁻¹⁶ bar at 1300 K was assigned to PuO₃(Oh) and PuO₃(OH)₂(Oh). The surprising and controversial reports motivated us to study the volatility of oxidic actinide species in trace amounts in the O₂-H₂O₃/SiO₂ system by thermochromatography. The enhanced volatility of trioxides in a moist atmosphere due to formation of volatile oxide hydroxides in reactions with water according to reaction (1) as established for uranium [6] and

\[ \text{MO}_x(\text{OH})_{3-x} \rightarrow \text{MO}_{3-x} + \text{H}_2\text{O} \quad (M = \text{Mo, W, U}) \] (1)

the group 6 elements [7] is indicative of the oxidation of PuO₂ to the trioxide, the more so as M(V)O₃ and M(V)₂O₅ oxides do not form volatile oxide hydroxides. Trace amounts of Mo and W have shown an analogous behavior in gas chromatographic experiments in silica glass columns which are governed by the surface reactions dissipative adsorption and associative desorption according to reaction (2), a special case of reaction (1) [8,9]:

\[ \text{MO}_x(\text{OH})_{2-x} \rightarrow \text{MO}_{3-x} + \text{H}_2\text{O} \quad (M = \text{Mo, W}) \] (2)

In the present work the actinides Th through Am were studied. Th and Pa oxides were considered as reference oxides of actinides having a maximal oxidation state of +4 or +5, respectively, uranium as a reference actinide reacting to the volatile UO₃(OH)₂(Oh).

The thermochromatography setup was equipped with the commercial gradient oven HTM LCRA 36. Empty silica glass tubes with an inner diameter of 3.5 mm were used as chromatography columns. The actinide isotopes ²³²Th, ²³³Pa, ²³³U, ²³⁷Np, ²⁴²Pu, and ²⁴¹Am were studied in quantities between 10⁻² (²³²Th, ²³³Pa) and 10⁻¹⁸ (²³³U, ²⁴²Pu) atoms per sample. The actinides were studied both in pairs and actinide by actinide. The actinide samples were prepared from nitric acid solutions by evaporation in silica boat. Prior to thermochromatography the actinide nitrates were converted into oxides by heating at 700 K for 10 min. A mixture of He and O₂ in the ratio of 1:1 was used as the carrier gas at a total flow rate of 100 cm³/min⁻¹.
The carrier gas was moistened by bubbling through water at defined temperatures. To start thermochromatography the hot oven was shifted into the working position. The temperature of the actinide sample at the starting position of thermochromatography was chosen between 1000 and 1475 K and kept for 30 to 120 min. To end a thermochromatography experiment the carrier gas flow was interrupted and the column removed from the oven within 10 seconds. Then, the column was cut into 1 or 2 cm long sections which were leached with hot nitric acid. Thin-layer samples were prepared from the acidic solutions by evaporation on glass disks. The actinide concentration of these samples was determined by alpha spectrometry. Gamma spectrometry was used to measure $^{233}$Pa.

![Graph showing counts per hour vs. column length](image)

**Fig. 1:** Thermochromatograms of $^{233}$U and $^{242}$Pu

Thermochromatograms of U and Pu after 30 min chromatography time at 1475 K at the starting position and a water vapor pressure of 2 kPa are depicted in Fig. 1. As can be seen from Fig. 1 U and Pu are well proven to be volatile in moist oxygen. In dry oxygen Pu remains nonvolatile. The peaks are relatively broad as typical for reaction gas chromatography, governed by surface reactions like reaction (2). In case of U the evidence of this data interpretation comes mainly from the strong dependence of the migration of the chromatographic peak on the water vapor pressure as the volatilization yield depends not only on the temperature but first of all on the water vapor concentration. A Monte Carlo simulation assuming reaction (2) resulted in an uranium chromatogram analogous to Fig. 1 with a reaction entropy $\Delta S_{\text{vol}} = -41 \text{ J/(Kmol)}$ and an enthalpy $\Delta H_{\text{vol}} = -71.5 \text{ kJ/mol}$. The plutonium volatility in moist oxygen is considerably lower than that of uranium. The volatilization of uranium starts at about 1175 K though plutonium becomes volatile only above 1300 K, presumably as PuO$_2$(OH)$_2$ formed according to reaction (3):

$$\text{PuO}_2(\text{OH})_2 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{PuO}_2(\text{OH})_2$$

The chromatograms represent the actinide fractions soluble in hot nitric acid. Not depicted are the actinide fractions removed from the gas chromatographic process due to reactions with silica to nonvolatile compounds or solid solutions and diffusion into the silica bulk. These processes compete with the volatilization reactions. The effective volatilization yield for uranium amounts to 90 % at maximum at 1375 K and a water vapor pressure of 2.5 kPa but remains considerably lower than 1 % for plutonium over the whole temperature range applied. Therefore, thermochromatography in silica glass columns is hardly suited for quantitative plutonium oxide chemistry studies. The alternative column materials Al$_2$O$_3$ and ZrO$_2$ proved to be even less suitable than SiO$_2$. However, even the low volatilization yield of Pu indicates the oxidation of PuO$_2$ to oxidic Pu(VI) species by the reactive carrier gas components O$_2$ and
H₂O. The behavior of Th and Pa supports this interpretation. As actinides in the oxidation state 4+ and 5+ which do not form volatile oxide hydroxides, they are quantitatively retained in the silicate host under conditions favorable for the volatilization of plutonium.

![Thermochromatograms of U and Np](image)

**Fig. 2:** Thermochromatograms of $^{233}$U and $^{237}$Np

Thermochromatograms of U and Np after 30 min chromatography time at 1375 K at the starting position and a water vapor pressure of 2.5 kPa are combined in Fig. 2. Np exhibits a broad distribution along the whole column with a small peak at 1000 K, about 200 K lower than the U peak. The broad distribution of Np is presumably a result of the diffusion of Np species into the silicate bulk. The volatilization yield of Np was about 1%, slightly higher than that of plutonium. The behavior of Np indicates the oxidation of NpO₂, presumably to NpO₂(OH)₂ in analogy to the oxidation of PuO₂. The position of the Np peak at lower temperatures than the U peak may result from a volatile Np(VII) oxide hydroxide. However, the evidence for this interpretation is very weak.

Americium was found to remain completely in the silicate host, obviously due to diffusion into the bulk too. Nevertheless, in spite of all these drawbacks our thermochromatographic volatility studies proved to be conclusive enough to give evidence for the oxidation of NpO₂ and PuO₂ to higher oxides by moist oxygen. This is in agreement with the experimental results published by Krikorian [5] and Haschke [1]. The oxidation to PuO₃ as claimed by Domanov [4] could not be confirmed.

**References**

UCa$_2$Si$_6$O$_{12}$ PHASES FOUND ON ANOXICALLY LEACHED UO$_2$ – EVIDENCE FOR U-EKANITE AS U(IV) SECONDARY ALTERATION PHASE

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The direct disposal of spent nuclear fuel, as foreseen in many European countries, puts up the need for investigation of the materials stability and reactivity under oxygen-free (anoxic) conditions. The reaction pathways of UO$_2$ under the conditions of oxygenated environments are well investigated and it is known that dissolving UO$_2$ forms a variety of uranyl minerals as secondary products, with their composition depending on groundwater chemistry and geochemical boundary conditions. However, in environments extremely depleted in oxygen, as it is expected for most of the European sites, UO$_2$ alteration pathways develop differently [1]. Recent studies in our laboratories showed that U(IV) silicate (USiO$_4$, in hydrated form known as coffinite) may be readily formed on the surface of UO$_2$ under simulated conditions of long-term storage at elevated temperature, possibly at the expense of other minerals, as a consequence of high silica concentrations in water. The examination of the products formed gave U/Si ratios of nearly constant 1:1.

Additional phases observed in small quantities gave evidence that further U(IV) compounds might be formed when reaction conditions are shifted. Together with U, we found Ca, Si, Ti, and Fe in these products. In order to investigate the spectrum of phases which are generated in solutions of differing compositions, an additional experiment studied the anoxic UO$_2$ dissolution in presence of the dissolving solids SiO$_2$, TiO$_2$, CaO, Fe$_2$O$_3$ / FeO. The solids were placed together with a pellet of UO$_2$ in groundwater solution ([Si]$_{sol}$ = 10$^{-2}$ mol/l) under Ar atmosphere and subsequently heated to 180 °C for 100 days. After ending the experiment, solutions were analysed with ICP-MS for element concentrations and the solids were investigated with SEM-EDX.

The UO$_2$ surface showed blue patches after the treatment and the SEM investigation revealed three separate areas formed by crystalline objects of different shape (Figure 1 a,b). Within the largest of the areas, a compound with almost constant compositional ratio of U/Ca/Si = 1 : 2 : 8 was measured. Measurements in the other fields resulted in USi = 1 : 1 or contained principally Si. No Ti or Fe were incorporated into the product.
The observed ratio of the elements does not coincide with the composition of any uranyl phase (Table 1); however it matches the composition of the Th/U(IV) mineral ekanite (Th,U)Ca₂Si₅O₂₀ with all Th substituted by U. This phase may be formed hydrothermally and was found to contain 21 % of Th replaced by U [2]. U and Th can substitute freely for one another in the ekanite structure, hence principally the formation of U-ekanite should be possible [3]; however, a member containing only U was so far not found in nature (which is probably due to the frequent appearance of Th and U together). XRD analysis is currently underway in order to confirm the structure of the compound.

Not enough is known about the newly formed minerals to know if they will make radioactive wastes more stable or less and it must be concluded that the models used to assess fuel corrosion are incomplete since the thermodynamics of U(IV) phase formation are mostly missing. Whether the end result will be an enhanced or decreased dissolution than without newly formed U(IV) phases covering the material, depends on a combination of thermodynamics and kinetics which need to be explored further.

Figure 1: Optical image (a) of a UO₂ pellet treated for 100 days at 180°C in anoxic groundwater solution with dissolving SiO₂, TiO₂, CaO, Fe₂O₃ / Fe(0) present; (b) EDX spectrum taken from a spot within the altered layer on the surface.
Table 1: mineral phases containing the elements U, Ca, and Si.

<table>
<thead>
<tr>
<th>Mineral phase</th>
<th>U oxidation state</th>
<th>Ratio U : Ca : Si</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Calciosilicate'</td>
<td>+6</td>
<td>8 : 4 : 10</td>
<td>(\text{Ca}_4(\text{UO}_2)_4(\text{Si}_2\text{O}_5)_5(\text{OH})_6\cdot15\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Ciprianite</td>
<td>+4</td>
<td>1 : 4 : 4</td>
<td>(\text{Ca}_4([\text{Th(U)}(\text{REE})]\text{Al}_2(\text{Si}_4\text{B}<em>4\text{O}</em>{22})(\text{OH},\text{F})_2)])</td>
</tr>
<tr>
<td>Ekanite</td>
<td>+4</td>
<td>1 : 2 : 8</td>
<td>((\text{Th},\text{U})(\text{Ca,Fe,Pb})_2\text{Si}<em>8\text{O}</em>{20})</td>
</tr>
<tr>
<td>Haiweeite</td>
<td>+6</td>
<td>2 : 1 : 5</td>
<td>(\text{Ca(UO}_2)_2[\text{Si}<em>5\text{O}</em>{12}(\text{OH})_2]\cdot4.5\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Lepersonnite-(Gd)</td>
<td>+6</td>
<td>24 : 1 : 4</td>
<td>(\text{CaO(\text{Gd, Dy})}_2\text{O}_2\cdot24\text{UO}_3\cdot8\text{CO}_2\cdot4\text{SO}_2\cdot60\text{H}_2\text{O})</td>
</tr>
<tr>
<td>'Meta-haiweeite'</td>
<td>+6</td>
<td>2 : 1 : 6</td>
<td>(\text{Ca(UO}_2)_2\text{Si}<em>6\text{O}</em>{15}n\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Uranophane</td>
<td>+6</td>
<td>2 : 1 : 1</td>
<td>(\text{Ca(UO}_2)_2[\text{SiO}_3\text{OH}]_2\cdot5\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Uranophane-beta</td>
<td>+6</td>
<td>2 : 1 : 1</td>
<td>(\text{Ca(UO}_2)_2[\text{SiO}_3\text{OH}]_2\cdot5\text{H}_2\text{O})</td>
</tr>
<tr>
<td>'Ursilite'</td>
<td>+6</td>
<td>4 : 4 : 11</td>
<td>((\text{Mg, Ca})_3(\text{UO}_2)_4(\text{Si}_2\text{O}_5)_5(\text{OH})_5\cdot13\text{H}_2\text{O})</td>
</tr>
</tbody>
</table>

References


COMPLEX FORMATION OF CURIUM WITH ADENOSINE 5’-TRIPHOSPHATE (ATP) STUDIED BY TRLFS

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We investigated for the first time the complex formation of curium(III) with adenosine 5’-triphosphate (ATP) by time-resolved laser fluorescence spectroscopy (TRLFS). The interaction between soluble species of curium(III) with ATP was studied at trace Cm(III) concentrations (10^{-7} M), at different concentrations of ATP and at different pH using 0.154 M NaCl as background electrolyte. Predominant 1:1 complex formation reactions were observed. Taking the dissociation of H_2ATP into consideration, we found evidence for the existence of three Cm – ATP species: CmH_2ATP^2, CmHATP and CmATP.

For a better understanding of the biosorption process of Cm(III) onto the cell envelope of the sulfate-reducing bacterial strain Desulfovibrio aspoensis on a molecular level we investigated the complexation of curium with selected bioligands of relevant functionalities as model compounds [1]. The spectroscopic studies of uranium and other actinide complexes in several biological systems like microorganisms [2-4] and plants [5] indicated that one functionality, most likely the phosphate group, might be responsible for complexation. ATP (scheme 1) is an important molecule in the life sciences, with the ability to transfer the phosphate and diphosphate groups between molecules. Heavy metals bound to ATP can influence the behavior of some enzymes which catalyze biochemical reactions.

![Scheme 1](image)

The ATP molecule can interact with metal ions via the nitrogen atoms of the purine nucleus (N-1, N-3 and N-7) and the oxygen atoms from the triphosphate chain. There is only one study exploring the coordination of a trivalent transition metal to ATP. Du et al. showed in the case of Fe(III) that besides the triphosphate chain the N-1 nitrogen is the predominant coordination site at pH 3 using ^1H and ^31P NMR [6]. Stability constants are not reported. However, the complex formation with trivalent actinides are unknown up to now. Therefore, we present the results of curium(III) complexation with ATP, obtained by TRLFS.

**Experimental**

Adenosine 5’-triphosphate disodium salt was purchased from ACROS ORGANICS (analytical grade). The stock solutions were prepared freshly for each experiment. A stock solution of the long-lived
curium isotope Cm-248 (t_{1/2} = 3.4 \times 10^7 \text{ years}) was used. This solution had the following composition: 97.5% Cm-248, 2.6% Cm-246, 0.04% Cm-245, 0.02% Cm-247, and 0.009% Cm-244 in 1.0 M HCO₃⁻. The experiments were performed in a glove box under N₂ atmosphere at 25°C. As a background electrolyte, 0.154 M NaCl was used. To avoid carbonate complexation of Cm(III) carbonate free water and NaOH solution was used. The Cm(III) concentration was fixed to 3 \times 10^{-7} M in all TRLFS measurements. The pH was changed between 1.5 and 7.0 by adding analytical grade NaOH or HClO₄. The ATP concentration was varied between 3 \times 10^{-7} and 3 \times 10^{-5} M. The TRLFS spectra were recorded at 25°C using a flash lamp pumped Ti:sapphire laser (Oslight, Tinana). Details on the experimental set-up are summarized in [1].

Results and discussion

We performed different sets of experiments. The complexation of Cm with ATP was investigated at fixed ATP concentrations of 3 \times 10^{-5} M (see Fig. 1A) and 3 \times 10^{-3} M (results not shown) between pH 1.5 and 7. Furthermore, the influence of the ATP concentration on the complexation reactions was studied at fixed pH values, e.g., 3.1 (results not shown), 4.5 (see Fig. 1B), and 6.5 (results not shown).

![Figure 1: TRLFS spectra of 3 \times 10^{-7} M Cm(III); a) as a function of the pH and b) as a function of the ATP concentration at pH = 4.5; the spectra are scaled to the same peak area.](image)

As depicted in Fig. 1, the complexation of Cm(III) by ATP is influenced by the pH and the ATP concentration. The TRLFS spectra (Fig. 1A) indicate the formation of Cm(III) – ATP species already at a pH of 2.0. Moreover, Fig. 1B gives evidence for interactions of Cm(III) with ATP already at a ligand concentration of 6 \times 10^{-5} M at pH 4.5. Starting at pH 2.0 the intensity of the 593.8 nm peak decreases with increasing pH and a second peak appears with a peak maximum at 600.5 nm. This peak dominates the emission spectra at pH > 4.0.

To describe the complex formation reactions in the system Cm(III) – ATP we applied the factor analysis program code SPECFIT [7]. The protonation constants of ATP determined from Oscarson et al. were used in the data fitting [8]. All data sets were used for the factor analysis calculations. As a result three different Cm – ATP species could be identified (see Fig. 2). Using the results of the SPECFIT calculations, we developed a preliminary model.
describing the ongoing processes in the Cm(III) – ATP system. Predominant 1:1 complexes were formed under the experimental conditions.

![Fluorescence emission spectra of the single components in the system Cm – ATP derived by peak deconvolution; the spectra are scaled to the same peak area.](image)

Figure 2:
Fluorescence emission spectra of the single components in the system Cm – ATP derived by peak deconvolution; the spectra are scaled to the same peak area.

The dependencies found in the TRLFS data could be expressed by the following equilibria:

\[
\begin{align*}
\text{Cm}^{3+} + \text{ATP}^{5-} + 2\text{H}^{+} & \leftrightarrow \text{CmH}_{2}\text{ATP}^{7-} \\
\text{Cm}^{3+} + \text{ATP}^{5-} + \text{H}^{+} & \leftrightarrow \text{CmHATP} \\
\text{Cm}^{3+} + \text{ATP}^{5-} & \leftrightarrow \text{CmATP}^{7-}
\end{align*}
\]

(1) (2) (3)

Preliminary formation constants for reactions (1) to (3) were calculated to be

\[ \log K_{1(12)} = 16.58 \pm 0.10, \log K_{1(11)} = 13.39 \pm 0.10 \text{ and } \log K_{1(10)} = 8.44 \pm 0.11, \text{ respectively.} \]

The hydrated Cm – ATP species showed fluorescence lifetimes in the range of 90 µs; whereas the CmATP complex has a longer fluorescence lifetime of 180 ± 10 µs. These lifetimes are significantly different from 68 µs measured for the Cm\(^{3+}\) aquo ion. Additional experiments are in progress to validate the stoichiometry, the complex formation constants and the characterization of the Cm(III) – ATP species.

Acknowledgements
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References
GAS-PHASE THERMOCHEMICAL STUDIES OF ACTINIDE OXIDES

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With the objective of contributing to a better thermodynamic characterization of species containing actinides (An) with relevance to the nuclear fuel cycle, as well as to the understanding of actinide chemistry at a fundamental level, we have recently made the first Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) studies of the gas-phase ion chemistry of the transuranium actinides Np, Pu, and Am [1-2].

As can be assessed in a recent review paper [3], prior to these studies, gas-phase ion chemistry experiments with the highly radioactive members of the actinide series Pa, Np, Pu, Am, Cm, Bk, Cf, and Es had been based on the use of the Laser Ablation with Prompt Reaction and Detection (LAPRD) technique, while FTICR-MS studies of An ions had been limited to Th and U.

Experimental

FTICR-MS is a technique that is specially suited to study the chemistry of ion-molecule systems in the gas phase. As a result of the applied magnetic and electrical fields, it is possible to trap ions for long periods of time and complex sequences of operations can be performed. To different event sequences correspond different types of experiments in which the structure of the ions can be probed, reagent/product sequences can be determined and kinetic and thermochemical studies can be made.

All the experiments were performed in a Finnigan FT/MS 2001-DT mass spectrometer equipped with a 3 Tesla superconducting magnet and with a Nd:YAG laser, which was used to produce the actinide ions from An-Pt alloys.

Results and Discussion

The study of oxidation reactions can provide actinide-oxygen bond energies. We studied the reactions of An⁺ and AnO²⁻ (An = Th, U, Np, Pu, Am) with several oxidants (N₂O, C₂H₂O, H₂O, O₂, CO, NO, CH₄O), which allowed us to estimate unknown An⁺-O and OAn⁺-O bond dissociation energies (BDE) and to verify literature values obtained by other methods.

We were able to determine that BDE[An⁺-O] ≥ 751.5 kJ/mol for An = Th, U, Np, in agreement with literature values, while BDE[Pu⁺-O] ≥ 631.6 kJ/mol, in accord with one of two reported values [1]. In the case of Am, we found that BDE[Am⁺-O] ≥ 532.2 kJ/mol, and an estimate of BDE[Am⁺-O] = 560 ± 30 kJ/mol could be made [2].

In the case of the dioxide ions AnO₂⁺, we determined that BDE[OAn⁺-O] ≥ 354.3 kJ/mol for An = Th, Am, BDE[On⁺-O] ≥ 498.4 kJ/mol for An = Np, Pu, and BDE[O²⁺-O] ≥ 631.6 kJ/mol. While the values for Th and U were in agreement with the literature, the value for Pu was significantly higher than the reported ones. The values for Np and Am were previously unknown. The following estimates were made: BDE[ONp⁺-O] = 580 ± 70 kJ/mol,
BDE[OPu^2-O] = 520 ± 20 kJ/mol, and BDE[OAm^2-O] = 390 ± 40 kJ/mol [1,2].

The study of electron transfer reactions can provide ionization energies (IE) by means of “bracketing” experiments, in which the ions in question are reacted with compounds with well-known IE. From the reactions of AnO^3- ions with several amines it was possible to determine IE(PuO_2) = 7.03 ± 0.12 eV [1], significantly lower than the literature values but in agreement with the results of the oxidation reactions, and IE(AmO_2) = 7.23 ± 0.15 eV [2], the first experimental determination of this quantity.

From the study of reactions of AnO^3- with dienes (1,3-butadiene and isoprene), and using a model developed by H. Schwarz and co-workers for the lanthanides [4], it was possible to determine IE(PuO) = 5.8 ± 0.2 eV and therefore recommend one of two discrepant literature values, and IE(AmO) = 5.9 ± 0.2 eV, that was in this way experimentally obtained for the first time [2]. These values have now been revised to IE(PuO) = 6.1 ± 0.2 eV and IE(AmO) = 6.2 ± 0.2 eV as a consequence of a recent accurate determination of IE(UO) = 6.0313 ± 0.0006 eV by M. C. Heaven and co-workers [5], which was ca. 0.3 eV higher than the literature value that we used to “anchor” the IE values for PuO and AmO. According to our experiments and to Heaven’s result, literature values for IE(ThO) and IE(NpO) should also be revised to IE(ThO) = 6.4 ± 0.2 eV and IE(NpO) = 6.1 ± 0.2 eV. A value of 6.4 eV for IE(ThO) makes this quantity amenable to scrutiny by electron-transfer “bracketing” experiments with amines and these experiments are currently under way.

Bond energies for the neutral species AnO(g) and AnO(g) can be derived from the estimated BDEs and determined IEs through the following equations:

\[
\text{BDE(An-O)} = \text{BDE(An}^\text{2-O}) + \text{IE(AnO)} - \text{IE(An)}
\]

\[
\text{BDE(OAn-O)} = \text{BDE(OAn}^\text{2-O}) + \text{IE(AnO}_2\text{)} - \text{IE(AnO)}
\]

In the sequence of these experiments with the singly-charged An ions and of a previous study with uranium [6], work in progress is focused on the oxidation reactions of doubly-charged An ions. Future studies will extend the work to other actinides, including Pa and Cm, as well as to other types of actinide species.

Acknowledgments
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References
LIMITING TRANSPORT PROPERTIES OF ACTINIDE IONS IN PURE WATER

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A procedure is proposed to calculate the transport properties in pure water, i.e. the limiting ionic conductivity ($\lambda^*$) and the limiting diffusion coefficient ($D^*$) of actinide ions at 298.15 K [1, 2]. The limiting ionic conductivity of actinide ions may be calculated by means of the microscopic version of the Stokes-Einstein law:

$$\lambda^* = \frac{F e z}{6 \pi \eta r_i}$$  \hspace{1cm} (1)

with $F$ as the Faraday constant, $e$ the elementary charge, $z$ the charge number of the ion, $r_i$ the ionic radius, $\eta$ the ion micro-viscosity, i.e. the viscosity of water molecules in the first hydration shell of the ion and $\theta$ a structural factor taking into account the deviations from the spherical geometry.

The limiting transport properties of the mono-atomic actinide ions $M^{z+}$ were calculated using the corresponding ionic radii and effective charge numbers $z_{\text{eff}}$ derived from the analysis of their structural and thermodynamics properties [3]. The effective charge number $z_{\text{eff}}$ reflects the contribution of the 4f and 5f orbitals to the chemical bonding, which might also lead to a certain extent to an affinity of the dynamics of water molecules in the vicinity of the ion. Considering a spherical geometry for the mono-atomic ions, $\theta$ was set to unity in Eq. (1). The micro-viscosity for the mono-atomic actinide ions was calculated using a model developed in [1] as

$$\left( \frac{1}{\eta^*} \right)_{M^{z+}} = \frac{1}{2} \eta^0 \arctanh \left( \frac{a e^{-b \sigma} + c e^{-d \sigma}}{2 - a e^{-b \sigma} - c e^{-d \sigma}} \right)$$  \hspace{1cm} (2)

where $a = 0.8704$, $b = 1.1453$ (m$^2$·C$^{-1}$), $c = 0.2404$ and $d = 5.5544 \times 10^3$ (m$^2$·C$^{-1}$) are numerical parameters, $\eta^0 = 8.903 \times 10^{-4}$ kg·m$^{-1}$·s$^{-1}$ is the viscosity of water at 298.15 K and $\sigma_i = z_{\text{eff}} e / 4 \pi r_i^2$ the surface charge density of the ion.

The limiting transport properties of the rod-shaped actinyl ions $MO_2^{z+}$ ($z = 1$ or 2) were derived by employing a geometric model in which the actinyl ions, firstly described by ellipsoids of revolution with the axis M-O-M as axis of revolution, were transformed into spherical ions. The equivalent spherical radius of actinyl ions was calculated as

$$r_i = \sqrt{r_M^2 (d_{M-O} + \delta)}$$  \hspace{1cm} (3)

where $r_M$ is the ionic radius of the central actinide ion M (CN = 6), $d_{M-O}$ the inter-atomic distance in the actinyl ion, and $\delta$ an additional length factor corresponding to the inter-atomic distance, taking into account the volume occupied by the oxygen atoms. The value of $\delta$ was estimated from the lattice parameter $a_0$ of the corresponding actinide dioxide $MO_2$ ($CaF_2$ type) [2].
The structural factor $\theta$ for actinyl ions was described by ellipsoids of revolution having a random orientation to their direction of migration [4]:

$$\theta = \frac{\sqrt{1 - \left(\frac{r_m}{d}\right)^2}}{(r_m / d)^{2/3} \ln\left(1 + \sqrt{1 - \left(\frac{r_m}{d}\right)^2}\right)}$$

with $d = (d_{MO} + \delta)$ the equatorial length. Note that for $d \rightarrow r_m$, relation (4) leads to $\theta = 1$, which corresponds to the spherical case for mono-atomic ions. The ion micro-viscosity of actinyl ions was calculated using the effective charge number $z_{eff}$ [5,6] of the central actinide on $M$ in $MO_{27}$ since it is well established that the water molecules in the first hydration shell are co-ordinated to $M$. On the other hand the water molecules close to the surface of the ion are attracted by the positive charge of the central actinide ion $M$ and somewhat repulsed by the negative charge of the oxygen atoms leading to a lose of orientational order for the water molecules i.e. a decrease of the viscosity of water molecules in the hydration shell. Additionally the non-spherical geometry of the actinyl ion may also affect the dynamics of exchange of the water molecules between the first hydration shell of the ion and the outer bulk water shell. Based on the consideration the ion micro-viscosity was calculated according to Eq. (2) as

$$\left(\frac{1}{\eta_i}\right)_{MO_{27}}^{\theta} = \frac{z_{eff}}{z} \cdot \arctan \left[ \frac{2}{\eta_0} \cdot \frac{ae^{-b\sigma_i} + ce^{-d\sigma_i}}{2ae^{-b\sigma_i} - ce^{-d\sigma_i}} \right]$$

where the ratio $z_{eff}/z$ is considered as a repulsion factor and $\theta$ is the structural factor given by Eq. (4). The expression in brackets in the right side of Eq. (5) corresponds to the ion micro-viscosity for the spherical geometry of the actinyl ion.

The limiting diffusion coefficient $D^\circ$ of the actinide ions was calculated according to the Nernst-Einstein relation.

The calculated values of the limiting transport properties of actinides are compared with the available experimental values in Table 1. The calculated values are close to the experimental data. The mean standard deviation between calculated and experimental data, 3.7±1.8 %, is comparable to the mean value for the experimental uncertainties, 3.1±1.7 %.

The model allows to calculate the limiting transport properties of an actinide for which experimental data are missing.
Table 1. Calculated and experimental limiting transport properties of actinide ions (T = 298.15 K). \( r_i \) is the ionic radius (equivalent spherical radius for the actinyl ions \( MO_2^{2+} \)), \( z_{\text{eff}} \) the effective charge number of the ion (of the central actinide ion in \( MO_2^{2+} \)), \( z \) the formal charge number, \( \eta_i \) is the ion micro-viscosity, \( \lambda^\circ \) the limiting ionic conductivity, \( D^\circ \) the limiting diffusion coefficient. a: mean value of available experimental data.

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<th>( r_i ) ( \times 10^{-10} \text{m} )</th>
<th>( z_{\text{eff}} )</th>
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<th>( \eta_i )</th>
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References
SORPTION OF URANYL ION ONTO GLUTARALDEHYDE DERIVATIVES OF CHITOSAN

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Though active uptake is a possibility in the uptake of metal ions by microorganisms, there is a distinct role of passive phenomena mediated by the functional groups present in the cell wall. Predominant constituents of polymers such as chitin or chitosan are the functional groups containing nitrogen donor atoms. Work on biopolymers such as chitosan is getting increasingly popular due to their eco-friendly nature, low cost and high abundance [1-2]. However, reports on their applications to metal ion sorption from waste solutions have been limited due to their slow kinetics and instability in acidic solutions. These have been overcome by preparing gel type resin beads and also by functionalizing / cross linking the chitosan biopolymers [3].

The sorption of uranyl ion from HCl, HClO₄ and HNO₃ medium was investigated in the present work using the glutaraldehyde derivatives of chitosan (chitosan-GA). It took nearly 3 hours for the attainment of equilibrium in HNO₃ medium while > 5 hours were needed for the same in HCl and HClO₄ medium. K₄ values were typically ~ 7000 for 10⁻⁴ M HNO₃ while much higher values were obtained (> 10,000) in 10⁻⁴ M HCl or 10⁻⁴ M HClO₄ (Fig. 1). Uranyl ion uptake was found to be affected by the acidity / pH of the medium. It appears that competition between metal ion and hydrogen ion to bind amino group increases with acidity. The monotonous decrease was observed in all the three mineral acids (up to 0.1 M). The lower K₄ values in HCl and HNO₃ medium as compared to those in the HClO₄ medium were due to increasing complexation in the former. Slight increase in the K₄ values in case of HCl medium is possibly due to the formation of anionic complexes of uranium which compete for the exchange sites.

Fig. 1: Distribution coefficient of uranium with chitosan-GA at various mineral acid concentrations
Total uptake capacity of uranyl ion at pH 4 was found to be 9.03x 10^{-8} mol/g. The kinetic study of adsorption indicated relatively faster rate of sorption as compared to that observed with unmodified chitosan alone. This is due to the higher surface area obtained after the derivatization done with glutaraldehyde and also due to the special nature of the gel type resin. In order to have an idea about the sorption isotherm, experiments were carried out at varying uranium concentration in the aqueous phase and the sorption capacity (q) was calculated for each concentration. It was not possible to obtain the isotherm data at pH 4 due to the precipitation and pH changes observed after equilibration. Fig. 2 shows adsorption isotherm obtained at pH 1 and 4 M HCl. The adsorption of uranium per unit mass of resin (q, mol/kg) at pH 1 first increases and then decreases with equilibrium uranyl ion concentration (Ce, M) where as it increases and then saturates in case of 4 M HCl solution. Therefore at higher uranium concentration, the concentration of anionic chloro complexes decreases and hence adsorption decreases at pH 1 but at 4 M HCl chloro complexes are always in excess and adsorption increases and then saturates with Ce.

The data shown in Fig. 2 are in conformity with the Langmuir adsorption isotherm as suggested by the following equation:

\[ q = q_m C_e / (1 + b C_e) \]  

The decrease in the q value at higher Ce was also observed earlier by Guibal et al., during their sorption studies carried out in the pH range of 4 – 6 [4]. The temperature did not have much effect on the adsorption of uranyl ion (Fig. 3). The sorbed uranium was stripped using 0.1 – 8 M HCl. It was difficult to strip uranium from the chitosan beads using higher concentration of acid and the best result was obtained using 2 M HCl as strippant. The resin beads were fairly stable at higher acidities and the desorption rate was much faster (< 10 min) as compared to the sorption rates.
The possibility of using the chitosan beads for the chromatographic separations was evaluated in a column study. A 50 mm (l) x 10 mm (d) column was made using 300 chitosan-GA resin beads (weight ~ 130 mg) and was used for sorption and elution studies. The bed volume was about 5 mL and a flow rate of 10 drops per minute was maintained in this study. The column was conditioned with pH 4 solution (dilute HCl) and U-233 activity was loaded at.

Due to the relatively slow sorption rate, about 15% of the activity broke through in 40 mL of the washings (pH 4 solution).

> 80% recovery was possible in 20 mL of 2 M HCl.

REFERENCES

SEPARATION OF Am\(^{3+}\) AND Eu\(^{3+}\) BY CYANEX-301 USING DIFFERENT TECHNIQUES

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Separation of trivalent actinides from lanthanides is a challenging problem due to the similarity in their chemical properties. The research in this area has gained momentum due to the emerging strategy of 'Partitioning and Transmutation' for the safe management of high level nuclear waste. Most of the ongoing research in this area involves development of solvent extraction methods using cyanex-301 (bis(2,4,4-trimethylpentyl)-di-thio phosphinic acid) as the organic extractant [1-5]. In the present study, the separation of Am\(^{3+}\) from Eu\(^{3+}\) was investigated using purified Cyanex-301 by solvent extraction (using toluene as the diluent), extraction chromatography as well as by bulk liquid membrane techniques. Cyanex-301 was purified using a literature method reported earlier [1] and was characterized by elemental analysis, NMR and GC-MS. All the experiments were carried out using \(^{241}\)Am and \(^{152,154}\)Eu tracers under varying experimental conditions.

Solvent extraction studies

The ligand concentration variation experiments have shown straight line behaviour with a slope value of 3.2 ± 0.1 for Am\(^{3+}\) in the entire range of Cyanex-301 concentration (Fig. 1). On the other hand, analogous experiment carried out for Eu\(^{3+}\) yielded a slope value of 1.7 ± 0.2 at lower concentration of Cyanex-301 which increased to 2.6 ± 0.2 beyond 0.3 M Cyanex-301. Experiments carried out with varying hydrogen ion concentration corroborate the observation. For both Am\(^{3+}\) and Eu\(^{3+}\), pH dependence of ~ 3 is observed using 0.5 M Cyanex-301 while pH dependence of ~ 3 and ~ 2 were observed for Am\(^{3+}\) and Eu\(^{3+}\), respectively with 0.1 M Cyanex-301. This indicates the extraction of the species of the type Am(Cyanex-301)\(_3\) and Eu(Cyanex-301)\(_3\) with 0.5 M Cyanex-301 while extraction of the species of the type Am(Cyanex-301)\(_2\) and Eu(Cyanex-301)\(_2\)(NO\(_3\)) with 0.1 M Cyanex-301.

The following extraction equilibria can be suggested for the extraction system comprising 0.5 M Cyanex-301 in toluene as the organic phase while the aqueous phase may or may not contain NaNO\(_3\):  
\[ M^{3+} + 3HA_{(o)} \rightleftharpoons MA_{3(o)} + 3H^+ \]  
(1)
where M = Am or Eu and HA represents Cyanex-301. Species with (o) as subscript are in the organic phase while those without any subscript are in the aqueous phase. In these studies, it is assumed that Cyanex-301 is present in the monomeric form. In presence of 1 M NaNO₃ at 0.1 M Cyanex-301 the following extraction equilibria seem to operate.

**Table 1: Extraction constants and separation factor (S.F.) values with purified cyanex-301 under varying experimental conditions**

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>log K_c,yₐ Am³⁺</th>
<th>log K_c,yₐ Eu³⁺</th>
<th>S.F. (D_Am / D_Eu)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase: 1.0 M NaNO₃ + 0.02 M sulphinic acid buffer, pH = 3.2; Organic phase: 0.1 M Cyanex-301; Temp. = 25°C</td>
<td>-10.58±0.34</td>
<td>-8.96±0.05</td>
<td>3500</td>
<td>Present work</td>
</tr>
<tr>
<td>Aqueous phase: 1.0 M NaNO₃ + 0.02 M sulphinic acid buffer, pH = 3.2; Organic phase: 0.5 M Cyanex-301; Temp. = 25°C</td>
<td>-10.58±0.27</td>
<td>-12.44±0.19</td>
<td>4900</td>
<td>Present work</td>
</tr>
<tr>
<td>Aqueous phase: 1.0 M NaNO₃ + 0.01 M sulphinic acid buffer, pH = 3.2; Organic phase: 0.5 M Cyanex-301; Temp. = 25°C</td>
<td>-7.72±0.07</td>
<td>-11.42±0.08</td>
<td>6000</td>
<td>Ref. [5]</td>
</tr>
<tr>
<td>Aqueous phase: 1.0 M NaNO₃, pH = 3.0 for Am and 4.1 for Eu³⁺; Organic phase: 0.5 M Cyanex-301; Temp. = 25°C</td>
<td>-7.75</td>
<td>-11.51</td>
<td>5800</td>
<td>Ref. [1]</td>
</tr>
</tbody>
</table>

a: conditional extraction constant, b: in toluene, c: in n-dodecane, d: S.F. values were calculated by extrapolating the D_Eu values to pH 3.0; e: in kerosene

**Table 2: Effect of nitrate ion concentration on the sorption of Am³⁺, Eu³⁺ and the corresponding S.F. values. Aqueous phase: 0.01 M Sulphinic acid; pH: 3.4**

<table>
<thead>
<tr>
<th>[NaNO₃]</th>
<th>K_d,Am</th>
<th>K_d,Eu</th>
<th>S.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>447</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>0.2 M</td>
<td>81</td>
<td>1.2</td>
<td>68</td>
</tr>
<tr>
<td>0.4 M</td>
<td>53</td>
<td>0.51</td>
<td>104</td>
</tr>
<tr>
<td>0.6 M</td>
<td>99</td>
<td>0.36</td>
<td>275</td>
</tr>
<tr>
<td>0.8 M</td>
<td>131</td>
<td>0.17</td>
<td>788</td>
</tr>
<tr>
<td>1.0 M</td>
<td>161</td>
<td>0.11</td>
<td>1434</td>
</tr>
</tbody>
</table>

Am³⁺ + 3HA(O) ⇌ AmA₃(O) + 3H⁺  ..................... (2)
Eu³⁺ + 2HA(O) + NO₃⁻ ⇌ Eu(A)₂(NO₃)O₃ + 2H⁺  ...... (3)

The extraction constants values were calculated and compared along with the S.F. values reported earlier [1,5].
Extraction chromatographic studies

Extraction chromatographic studies were carried out using cyanex-301 impregnated resin material prepared from chromosorb-W. Similar to the solvent extraction studies, there was a positive influence of nitrate ion on the separation behaviour of Am\(^{3+}\) from Eu\(^{3+}\). Table 2 shows the effect of increasing concentration of the nitrate ion on the K\(_d\) values as well as on the S.F. values. As expected, with the increase of nitrate ion concentration, the K\(_d\) values of both Am\(^{3+}\) and Eu\(^{3+}\) decreased due to aqueous complexation effect. On the other hand, on further increasing the concentration of nitrate ion, the K\(_d\) values of Am\(^{3+}\) alone increased due to the salting out effect. A separation factor of \(>1400\) was obtained at an aqueous nitrate concentration of 1 M.

Liquid membrane separation studies

Liquid membrane studies were carried out to understand the transport behaviour of Am(III) through a bulk liquid membrane made from 0.4 M cyanex 301 in toluene. The feed comprised of 1 M NaNO\(_3\) in 0.02 M sulphamic acid at pH 3.4 while 1 M nitric acid was used as the strippant. The experiments were carried out at varying stirring speed (100 rpm to 400 rpm). About 97% transport from the feed side was observed in 6 h irrespective of the stirring rate (Fig. 2). Under identical conditions, Eu transport was below detection limits. However, the activity in the receiver compartment was affected by the stirring speed. About 18% transport into the receiver compartment was observed after 22 h at a stirring speed of 100 rpm which increased to \(~80\%\) when the stirring speed was increased to 400 rpm. Counter transport of acid into the feed compartment is assumed to be the main reason for the slow transport rates.

From the results obtained in these experiments it is clear that the separation of Am\(^{3+}\) from Eu\(^{3+}\) is feasible by all the three methods. The solvent extraction method is fast and yielded very high S.F. value while the BLM method is very slow which may lead to reagent degradation. For a clean separation in a sample, however, one needs to go for chromatographic separation using a column.

REFERENCES

FORMATION AND STABILITY OF PU(IV) COLLOIDS IN AQUATIC SOLUTION

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The chemical reactions of aquatic Pu(IV) in dilute concentrations are of cardinal relevance for the appraisal of its thermodynamic solubility. Spontaneous colloid formation and disproportionation reactions hinder a straightforward approach and lead to a large number of controversial results in the past as summarized in [1].

The present work describes a combination of several complementary methods to investigate the solubility of Pu(IV) as a function of pH. At first, laser-induced breakdown detection (LIBD) [2] was applied for colloid quantification. Its sensitivity is higher than photon correlation spectroscopy (PCS) by 7 orders of magnitude (for colloids smaller than 50 nm) and applicable down to 5 nm-particles. To obtain optical absorption spectra for speciation a new diode array spectrometer with a 1m capillary cell (550 μm in diameter), which is 100 times more sensitive than a normal spectrometer, was applied. Its detection limit for Pu(III) and Pu(IV) is below μM. Additionally the capillary electrophoresis (CE) coupled with ICP-MS was used for speciation.

The chemical behaviour of the Pu(IV) is investigated below 10^{-4} mol/l at low pH (0.3 – 2.0). The results help evaluate the solubility of Pu(IV) colloids, which corresponds very closely to the solubility of Pu(IV) hydroxide or oxy-hydrate, as is the case observed on Np(IV) [3]. The 242Pu solution is prepared in 1 M HClO4 by electrochemical reduction of a mixture of oxidation states to Pu(III) and subsequent oxidation to Pu(IV). The Pu concentration is assayed by liquid scintillation spectrometry. The solution pH is varied from 0.3 to 2.0 by appropriate dilution with 0.5M HCl and 0.5 M NaCl.
The formation of Pu(IV) colloids is observed by LIBD [2] at a certain pH when increasing low pH gradually to higher pH. Once pH is reached to the point where Pu(IV) colloids are beginning to form, the breakdown events become distinctively noticeable (Fig. 1).

![Graph](image)

**Figure 1.** The concentration of Pu is decreased and pH increased by dilution with 0.5 M NaCl (top). Breakdown probability (BDP) at the same energy (2.5 mJ) is shown as a function of pH (bottom).

Pu(IV) colloid formation is investigated as a function of pH at different Pu(IV) concentrations and exhibits a slope of -2 in a pH - log([Pu(IV)]) plot (Fig. 2). This particular slope allows to infer the reaction: Pu^{4+} + 2H_2O ↔ Pu(OH)_2^{2+} + 2H^+, which further undergoes colloid formation and thus Pu(OH)_2^{2+} is in equilibrium with colloids. Knowing the hydrolysis constant of Pu(OH)_2^{2+} [1], the solubility product of Pu colloids is derived: \( \log K_{sp} = -59.0 \pm 0.4 \) extrapolated to zero ionic strength.
**Figure 2.** Solubility curve of Pu(IV). The calculations at 1.0 M ionic strength (dark line) and 0.1 M (light line) are well in line with the colloid onset as measured by LIBD.

The stability of Pu(IV) colloids was also investigated. It was observed by LIBD that Pu(IV) colloids dissolve with time. This is due to the decrease of Pu(IV) ionic species, which is in equilibrium with Pu(IV) colloids. Pu(IV) colloids are not formed quantitatively, i.e. there is still a considerable amount of Pu(IV) present in ionic state, which undergo disproportionation with time: $2\text{Pu(IV)} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pu(III)} + \text{Pu(V)} + 4\text{H}^+$. When Pu(V) is not stable, then it undergoes further disproportionation to Pu(IV) and Pu(VI): $2\text{Pu(V)} + 4\text{H}^+ \rightleftharpoons \text{Pu(IV)} + \text{Pu(VI)} + 2\text{H}_2\text{O}$. This reaction is observed in situ by the new capillary spectrometer. At low pH (0.3 – 2.0) the amount of tetravalent Pu decreases due to disproportionation, forming Pu(V), which is stable for months as observed by absorption spectrometry and CE.

**References**


SORPTION OF PLUTONIUM AND NEPTUNIUM ONTO
COLLOIDAL Fe- and Mn- OXIDES

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Sorption of actinides by mineral surfaces is considered as a geochemical barrier in a
radioactive waste repository system. However, minerals could be present as colloidal micro-
and nano-particles with enhanced mobility in the environment. Sorption of radionuclides to
such colloids can facilitate their transport in aqueous systems [1]. Molecular level description
of sorption processes as well as corresponding thermodynamic data enable predictive
modeling of radionuclide speciation and partitioning in the environment.

The sorption isotherms are provided for Pu and Np by two environmentally relevant Fe and
Mn oxyhydroxides - goethite α-FeOOH and manganese dioxide MnO₂. The solids were
synthesized and characterized by powder-XRD, SEM imaging, BET surface analysis and
potentiometric titration. The results are presented in Table 1 and Fig. 1.

Table 1. Characterization of solid phases

<table>
<thead>
<tr>
<th></th>
<th>α-FeOOH</th>
<th>MnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total specific surface area, m²/g</td>
<td>41.7</td>
<td>182</td>
</tr>
<tr>
<td>Specific micropore surface area, m²/g</td>
<td>7.23</td>
<td>32.9</td>
</tr>
<tr>
<td>Particle size, μm</td>
<td>-0.3</td>
<td>---</td>
</tr>
</tbody>
</table>

Fig. 1. SEM-photos of α-FeOOH (A) and MnO₂ (B).

The dependence of sorption of Np(V), Pu(V), Pu(IV) upon pH and ionic strength was studied
in NaClO₄ solutions at 25±1°C under N₂ atmosphere to prevent formation of carbonate
complexation. The corresponding sorption isotherms are presented in Figs.2-4. It was established that the sorption of either Np or Pu does not depend on ionic strength that indicates the formation of inner-sphere complexes with surface hydroxyl groups.

Fig.2. The pH dependence of Np ($5.6 \times 10^{-8}$ M) and Pu ($1.8 \times 10^{-8}$ M) sorption by α-FeOOH at 0.1 M NaClO₄ (initially actinides are taken in pentavalent forms).

Fig.3. The pH dependence of Np ($1.5 \times 10^{-7}$ M) and Pu ($1.8 \times 10^{-8}$ M) sorption by MnO₄⁻ at 0.1 M NaClO₄ (initially actinides are taken in pentavalent forms).

The redox speciation of actinides sorbed on solids was studied by solvent extraction technique (using TTA and HDEHP) [2]. In case of macroconcentrations of actinides the X-ray photoelectron spectroscopy (XPS) was used to determine the redox speciation of Pu or Np and discern molecular environment of the actinide surface complexes.

Fig.4. The pH dependences of Pu(IV) sorption by α-FeOOH (A) and MnO₂ (B) at 0.1 M NaClO₄.
According to the solvent extraction data and XPS no redox reactions occur with Np(V) either on the solid phase or in solution. In contrast, Pu(V) follows disproportionation to Pu(IV) and Pu(VI) upon sorption either by α-FeOOH or MnO₂ with no such effect in solution. This is probably due to high concentration gradient of Pu in the double electric layer of surface that favors disproportionation. In case of Pu(IV) sorption by MnO₂ the slow oxidation to Pu(VI) takes place (Table 2). The oxidation of Pu(IV) by rancieite (Ca, Mn³⁺)O₄ · Mn⁵⁺O₂ was confirmed by Duff et al [3] using micro-XANES spectroscopy.

<table>
<thead>
<tr>
<th>Initial valence state</th>
<th>Speciation after sorption</th>
<th>MnO₂</th>
<th>α-FeOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(V)</td>
<td>not changing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu(V)</td>
<td>disproportionation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>oxidation to Pu(V) and Pu(VI)</td>
<td></td>
<td>not changing</td>
</tr>
</tbody>
</table>

The Gibbs energy minimization software FITEQ (Ver.4.0 for MS Windows) was used to provide information on chemical equilibrium (reactions and corresponding equilibrium constants) for Pu and Np sorption by solid phases. It was found that diffuse layer model and formation of moderate, inner-sphere complexes fits the experimental equilibrium data. The strength of complexation follows the sequence: \( K_{(\text{Np-MnO}_2)} > K_{(\text{Np-α-FeOOH})} \) and \( K_{(\text{Pu(IV)-MnO}_2}) >> K_{(\text{Np(V)})} \) (Table 3). According to the XPS O1s spectra water molecules are coordinated in the outer-sphere of the surface complex.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MnO}_2 )</td>
<td></td>
</tr>
<tr>
<td>( =\text{Mn-OH} + \text{NpO}_2^- \leftrightarrow =\text{Mn-O-NpO}_2 + \text{H}^+ )</td>
<td>0.25</td>
</tr>
<tr>
<td>( \alpha-\text{FeOOH} )</td>
<td></td>
</tr>
<tr>
<td>( =\text{Fe-OH} + \text{NpO}_2^- \leftrightarrow =\text{Fe-O-NpO}_2 + \text{H}^+ )</td>
<td>-1.41</td>
</tr>
<tr>
<td>( =\text{Fe-OH} + \text{Pu}^{IV} \leftrightarrow =\text{Fe-O-Pu}^{IV} + \text{H}^+ )</td>
<td>2.64</td>
</tr>
<tr>
<td>( =\text{Fe-OH} + \text{Pu}^{IV} + \text{H}_2\text{O} \leftrightarrow =\text{Fe-O-Pu(OH)}^{IV} + 2\text{H}^+ )</td>
<td>-1.93</td>
</tr>
<tr>
<td>( =\text{Fe-OH} + \text{Pu}^{IV} + 2\text{H}_2\text{O} \leftrightarrow =\text{Fe-O-Pu(OH)}^{IV} + 3\text{H}^+ )</td>
<td>-5.87</td>
</tr>
<tr>
<td>( =\text{Fe-OH} + \text{Pu}^{IV} + 3\text{H}_2\text{O} \leftrightarrow =\text{Fe-O-Pu(OH)}^{IV} + 4\text{H}^+ )</td>
<td>-11.90</td>
</tr>
</tbody>
</table>

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References
CHEMICAL SHIFT AND WIDENING OF THE U $L_{\gamma_0}$-LINE AS PARAMETERS FOR IDENTIFYING THE CHEMICAL STATE OF THE URANIUM ATOM

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In the fields of radioecology, nuclear energetics, mining industry, geochemistry and radiochemistry many fundamental and applied problems need to be solved where it is necessary to know the chemical (valence, charge, magnetic) state of a uranium atom in complex synthetic and/or natural objects. One of the instrumental methods capable of providing adequate information about the chemical state of heavy atom is a method of chemical shift (ChSh) of hard X-ray emission lines.

A methodology has been proposed recently [1-3] for analyzing redox (valence) forms of uranium in natural oxides (naturans) on the basis of a correlation diagram of $L_{\gamma_1}$- and $L_{\beta_1}$-uranium lines ChShs. Synthetic oxides of the UO$_2$x (X=0-1) type were used as reference compounds in developing the diagram. Although formal calculations make it possible to determine U(IV), U(V), and U(VI) fractions in naturans, the problem whether it is correct to transfer the results obtained for synthetic oxides to the analysis of natural systems remains unsolved. It is necessary to obtain additional information which confirms the possibility of using the 2D space of $L_{\gamma_1}$- and $L_{\beta_1}$-lines ChShs for determining the oxidation state of uranium in natural oxides. This additional information may concern the magnetic properties of the uranium atom. These data can be obtained by studying other X-ray emission uranium lines.

We measured for the first time the values of ChShs and widening of $U L_{\gamma_0}$-line ($5d_{\gamma_0} \rightarrow 2p_{\gamma_0}$ X-ray transition) for synthetic oxides UO$_2$$_x$, seven natural naturans of different origins and ages [2], carnotite (K$_x$(UO$_2$)$_2$(V$_2$O$_5$)$_2$3H$_2$O), saytite (Pb$_2$(UO$_2$)$_3$O$_2$(OH)$_2$4H$_2$O), and uranophane (Ca(UO$_2$)$_2$SiO$_4$(OH)$_2$5H$_2$O). Results of measurements are given in Tables. The widening ($\Delta \Gamma$) of X-ray emission $L$-lines of uranium without changing its profile was detected first. It was shown, that the observed widening is due to the interaction between U 5d-orbital and the split (±) components of valent U 5f-orbital.

Table 1. Chemical shifts ($\delta$, in meV) and widening ($\Delta \Gamma$, in meV) of $L_{\gamma_0}$-line of uranium in uranium oxides and other uranium compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta U_{\gamma_0}$</th>
<th>$\Delta \Gamma U_{\gamma_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>U$_2$O$_3$</td>
<td>+142 ± 10</td>
<td>-407 ± 40</td>
</tr>
<tr>
<td>UO$_3$</td>
<td>-376 ± 10</td>
<td>-1004 ± 40</td>
</tr>
<tr>
<td>UO$_4$</td>
<td>+409 ± 9</td>
<td>-1133 ± 40</td>
</tr>
<tr>
<td>UO$_7$</td>
<td>+514 ± 11</td>
<td>-1620 ± 40</td>
</tr>
<tr>
<td>U$_2$F$_7$</td>
<td>+82 ± 6</td>
<td>+6 ± 22</td>
</tr>
<tr>
<td>CaU$_2$F$_7$</td>
<td>+120 ± 5</td>
<td>-42 ± 21</td>
</tr>
<tr>
<td>K$_2$UCl$_4$</td>
<td>+73 ± 5</td>
<td>-45 ± 22</td>
</tr>
<tr>
<td>K$_2$UCO$_3$</td>
<td>-51 ± 5</td>
<td>+140 ± 24</td>
</tr>
<tr>
<td>UO$_2$SO$_4$2.5H$_2$O</td>
<td>-540 ± 10</td>
<td>1614 ± 38</td>
</tr>
<tr>
<td>UO$_2$SeO$_4$2.5H$_2$O</td>
<td>520 ± 10</td>
<td>-1442 ± 61</td>
</tr>
</tbody>
</table>

92
Correlation between the experimental [4] values of effective magnetic moment on the uranium atom (μ_{\text{effect}}) and widening of $L\gamma_6$-uranium line ($\Delta \Gamma$ $UL\gamma_6$) in $UO_{2+x}$ oxides.

Furthermore, a linear correlation was observed between the values $\Delta \Gamma$ of $U L\gamma_6$-line and the experimental (literature [4]) values of effective magnetic moment on the uranium atom (μ_{\text{effect}}) in oxides of $UO_{2+x}$ series (the Figure). On the basis of this dependence effective magnetic moments (μ_{\text{effect}}) were found for seven natural nasturans:

$$\mu_{\text{effect}} = 0.00181 \cdot \Delta \Gamma UL\gamma_6 + 3.21663.$$  

For comparing the obtained values effective magnetic moments (μ_{\text{effect}}) of nasturans were calculated as linear combinations of experimental effective magnetic moments of redox uranium forms in $UO_2$, $U_2O_5$, and $UO_3$. The relative content was determined on the basis of the $La\gamma_1$- and $L\beta_1$-lines ChShs diagram:

$$\mu_{\text{effect}} = \mu^{(I)} + \mu^{(II)} + \mu^{(III)} + \mu^{(IV)} \approx \mu^{(I)} + \mu^{(II)} + 3.11 \mu^{(III)} + 1.57 \mu^{(IV)},$$

where μ^{(I)}, μ^{(II)}, and μ^{(IV)} are experimental [4] values of effective magnetic moments on the uranium atom in reference uranium oxides $UO_2$, $U_2O_5$, and $UO_3$: μ^{(I)}, μ^{(II)}, and μ^{(IV)} are fractions of uranium IV, V, and VI, calculated with the aid of the $La\gamma_1$- and $L\beta_1$-lines ChShs correlation diagram.

The close coincidence of (μ_{\text{effect}})_{1} and (μ_{\text{effect}})_{2} values obtained by two independent methods (correlation coefficient $R > 0.95$, see Table 2) showed that the use of the 2D-space correlation diagram of $La\gamma_1$- and $L\beta_1$-lines ChShs for identifying the valent state of uranium atom is correct over a wide range of natural uranium oxides.
Table 2. Results of investigating the magnetic state of uranium in natural objects.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Chemical shift (respect to UO$_2$), meV</th>
<th>Widening $\Delta$U$_{ij}$, meV</th>
<th>Relative content, %</th>
<th>Effective magnetic moment on uranium atom, $\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>U(L$_3$)</td>
<td>U(L$_2$)</td>
<td>U(L$_1$)</td>
<td>U(IV)</td>
</tr>
<tr>
<td>Exp. error</td>
<td>+3</td>
<td>+4</td>
<td>+8</td>
<td>$\pm 50$</td>
<td>+2</td>
</tr>
<tr>
<td>1</td>
<td>PD-3$^a$</td>
<td>-47</td>
<td>-10</td>
<td>+219</td>
<td>-539</td>
</tr>
<tr>
<td>2</td>
<td>PD-4$^a$</td>
<td>-63</td>
<td>-29</td>
<td>+240</td>
<td>-821</td>
</tr>
<tr>
<td>3</td>
<td>Ni-I$^a$</td>
<td>-72</td>
<td>-6</td>
<td>+224</td>
<td>-609</td>
</tr>
<tr>
<td>4</td>
<td>NH$^a$</td>
<td>-106</td>
<td>-14</td>
<td>+422</td>
<td>-1195</td>
</tr>
<tr>
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$^a$Natural uranium oxides (naturans) [2].

This work was carried out with the financial support of the Russian Foundation for Basic Research.

References


VALENCE STATE OF URANIUM ATOM IN UO$_{2}$X$_{1-x}$ OXIDES
ACCORDING TO DATA OF X-RAY EMISSION SPECTROSCOPY

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An unsolved problem of modern actinide chemistry originates from the participation of
valence 5f-, 6d-, and 7s-electrons in chemical bonding of heavy atoms. The main task is to
separate three principal interaction types of valence electrons in a multielectron system of a
heavy atom: Coulomb and spin-orbital interaction, and interaction with the crystalline field.
This problem may be solved by the method of chemical shift (ChSh) of hard X-ray emission
lines. It is very sensitive to changes in the chemical (valence, charge, spin) state of the
investigated atom. The aim of our work is to find the experimental parameter derivative of
chemical shift, with the aid of which it would be possible to describe both qualitatively and
quantitatively the process of chemical bonding (implementation of valence possibilities of
uranium atom) in the series of uranium oxides UO$_{2}$x$_{1-x}$ (x=0-1).

One of such parameters, in our opinion, may be the difference between ChShs of spin-doublet
uranium lines (∆δnl$_{z}$). This difference is a change in the energy of spin-orbital splitting (SOS)
of inner (core) nl-levels of uranium atom with changes in chemical state [1]. For UO$_{2}$x$_{1-x}$
oxides, a linear decrease in ∆δnl$_{z}$ (nl = 2p, 3p, 4p, 3d, and 4d) values was found with
increasing the x index. For compounds in which uranium is in the same valence form (e.g.
uranyl compounds), the range of ∆δnl$_{z}$ variation is less by an order of magnitude. It is shown
[1], that these facts are due to electron density redistribution on split 5f- and 5f-uranium
orbitals during chemical bonding. On the basis of atomic DHF-calculations the numbers of
electrons participating in this redistribution (Q$_{2p}$) were obtained. The values ∆δnl$_{z}$ or Q$_{2p}$
directly characterize the effect of SOS of 5f-uranium orbitals in chemical bonding.

We obtained for the first time partial effective charges of 5f- and 6d-electrons (Q$_{2p}$ and Q$_{6d}$)
on uranium atom in UO$_{2}$x$_{1-x}$ oxides with respect to UO$_{2}$ (see the Table) using the method [2]
of removal of the relativistic component of chemical shift (by transforming ChSh of single lines
in ChSh of the center of gravity of X-ray multiplets δ(2p-nl), n=3, 4).

| Table. Calculation of uranium atom valency in oxides as a sum of valence electron interactions. |
|---|---|---|---|---|---|
| Value | Q$_{2p}$ | Q$_{6d}$ | ΣQ = Q$_{2p}$ + Q$_{6d}$ | ΣQ from work [1] | ΔW$_{exp}$ = ΣQ + Q$_{2p}$ | ΔW$_{real}$ |
| Exp. error | ±0.03 | ±0.12 | ±0.12 | ±0.15 | ±0.2 | - |
| UO$_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| U$_{3}$O$_{8}$ | 0.10 | 0.00 | 0.10 | 0.26 | 0.4 | 0.5 |
| U$_{2}$O$_{5}$ | 0.18 | 0.02 | 0.20 | 0.70 | 0.9 | 1.0 |
| U$_{3}$O$_{8}$ | 0.21 | 0.01 | 0.22 | 0.90 | 1.1 | 1.33 |
| UO$_{3}$ | 0.25 | 0.28 | 0.53 | 1.10 | 1.6 | 2.0 |
Theoretical and experimental values of changes in SOS energy of 3d-uranium orbitals and values of ChSh of (2p-3d) multiplet center of gravity for $\text{UO}_2$ oxides.

The data in the Table show that $5f$-electrons are involved into bonding symbatly with increasing the oxygen coefficient $x$. However, partial populations of 6d-orbitals do not change ($Q_{6d}=0$) when uranium is oxidized up to $\text{U}_6\text{O}_{12}$. This phenomenon may be related to uranyl group formation during $\text{U}_3\text{O}_8\rightarrow\text{UO}_3$ transition and requires targeted study. It should be noted that the contributions of 7s-electrons to ChSh of 5-uranium lines are small. Therefore, $Q_{7s}$ is tentatively taken to be zero. The sum ($\Sigma Q$) of partial charges $Q_{5d}$ and $Q_{6d}$ is evidently the quantitative characteristic of the process of interatomic distribution of valence electron density between chemical bond participants. This sum can be used for the description of the Coulomb interaction between valence electrons during chemical bonding.

The role of crystalline field in the general scheme of interactions between valence electrons in $\text{UO}_2$ oxides can be indirectly evaluated from the character of the dependence of parameters $\Delta\delta_{3d_2}$ and $\delta(2p-3d)$ on $x$ (the Figure). The linear function observed in the former case, and the parabolic function observed in the latter case are in agreement with theoretical calculations in which the structural (radial) factor is not taken into account. Therefore, it may be concluded that the contribution of the crystalline field to chemical bonding in uranium oxides is rather small.

We have shown that the observed variations of $\Delta\delta_{5d_2}$ and $\delta(2p-nd)$ parameters are mainly caused by changes in uranium valency. Then the sum of $\Sigma Q$ and $Q_{6d}$ can be a measure of changes in valency ($\Delta W^{\text{val}}$) in units of electron charge. Some difference between our experimental values $\Delta W^{\text{exp}}$ and the actual values ($\Delta W^{\text{val}}$) can be explained by the
insufficiently precise choice of initial uranium atom configuration in the DHF-calculations. Moreover, we neglected some variations in \( Q_{2s} \) and \( Q_{3s} \) values.

Hence, we have shown that uranium chemical bonding (possibly, also that of other actinides) includes two processes:
1) *Interatomic distribution* of valence electron density between chemical bond participants. In other words, the non-relativistic removal of electrons from split valence orbitals is proportional to their statistical weights. It is this process that causes a change in the effective charge on the atom.
2) Relativistic *intraatomic redistribution* of electron density between split 5f\(_{-}\) and 5f\(_{+}\) components of uranium atom fine structure. This process does not change the charge on the uranium atom.

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References

TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROMETRY (TRLFS) APPLIED TO URANYL COMPLEXATION STUDIES

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Finding appropriate solutions for the treatment and storage of nuclear waste is a major environmental issue. Uranium is the main constituent of nuclear waste. Owing to the low solubility of U\(^{4+}\), uranium is dissolved in aqueous systems mainly in the uranyl hexavalent form U\(^{VI}\)O\(_2^{2-}\). An exhaustive knowledge of the uranyl coordination chemistry is hence required. Despite an intensive world-wide effort in this field, some parameters are still missing. For example, the identification of uranyl species formed in solution in the presence of ligands or other radionuclides is incomplete. In order to fill this gap, suitable analytical and spectroscopic tools have to be used and technical limitations such as high detection limits, interferences between species, lack of sensitivity, etc... have to be overcome. Time-Resolved Laser-Induced Fluorescence Spectrometry (TRLFS) is an already broadly used technique for uranyl species characterization [e.g. 1-8].

Using a conventional set-up (LASER Nd:YAG, \(\lambda = 266\) nm; monochromator, CCD detector), we have investigated new chemical and physical parameters influencing the UO\(_2^{2+}\)/ligand complexation behavior.

We selected the UO\(_2^{2+}\)/PO\(_4^{3-}\) well-known system, already studied by TRLFS, potentiometry and spectrophotometry [4]. After comparison of our results with the literature ones, additional parameters were introduced in order to monitor the uranium complexation behavior. The UO\(_2^{2+}\)/PO\(_4^{3-}\) system was investigated in the presence of Nd\(^{3+}\) in order to evidence the La\(^{3+}\)/UO\(_2^{2+}\) competition processes interfering with the metal-ligands complexes formation. Moreover, the UO\(_2^{2+}\)/PO\(_4^{3-}\) system was investigated as a function of the temperature, in order to evaluate the effect of temperatures higher than 25°C on uranyl speciation. This topic is of importance as such temperatures can be found in nuclear waste forms. The results obtained were compared with the ones deduced from other speciation methods such as capillary zone electrophoresis (CZE) and Electrospray Mass Spectrometry (ES-MS). In the future, we will apply the same methodology to other UO\(_2^{2+}\)/ligand systems, having weaker complexation constants and introduce some solids in the system in order to study the competition between sorption and complexation processes. In parallel, the methods used for chemometric studies will be applied in order to design a new reliable methodology to deconvolute the time-resolved multi-species spectra obtained by TRLFS, as already suggested in a recent paper [8].
References


POTENTIOMETRIC AND SPECTROPHOTOMETRIC STUDY OF THE TEMPERATURE EFFECTS ON COMPLEXATION. THE URANYL-SULPHATE (UO$_2^{2+}$/SO$_4^{2-}$) SYSTEM IN THE RANGE 5°C-85°C AT 1 AND 3 M IONIC STRENGTH.

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A large effort is under way in order to compile, select and improve the uranium thermodynamic database [1], however only few thermodynamic data are available at temperatures higher than 25°C [2]. This lack of data is mainly due to the experimental difficulties related to the complexation studies at high temperature. Theoretical methods to extrapolate thermodynamic data for high temperatures have been employed. They include Second Law Extrapolation (SLE), Isoelectric Model (IM), Isoconulcobic Model or One-Term Extrapolation Method (OTEM), the DEQUANT equation (Helgeson’s model), the revised Helgeson-Kirkham-Flowers Model (HKF) and finally the Ryzhenko-Bryzgalin Model (RBM) [3]. However experimental data are lacking in order to validate these models.

The complexation behaviour of uranyl cation (UO$_2^{2+}$) with sulphate (SO$_4^{2-}$) anions was studied by potentiometry and the changes in the visible absorbance spectrum monitored. This study was done for a 5-85 °C temperature range, in acidic media ([H$^+$] = 1 M), for several sulphate concentrations and two ionic strengths (I = 1; 3 M).

The experimental data obtained show how both sulphate concentration and temperature variations promote uranyl speciation changes. To describe clearly the system, the data needed to be modelled using different theoretical chemometric methods [4]. The second order absorbance data were analysed with a soft-modelling multivariate curve resolution procedure (Alternating Least Squares). This method evidenced the presence of several species (e.g. UO$_2^{2+}$ and UO$_2^{2+}$/SO$_4^{2-}$ species) present along the experimental conditions and allowed their pure spectrum calculation. The final refinement of equilibrium constants in the 5 °C to 85°C range has been done using the SQUAD program allowing the calculation of stability constants of UO$_2^{2+}$/SO$_4^{2-}$ formed species and the individual absorbivities. Values of both the reaction enthalpy ($\Delta H_m^\circ$) and entropy ($\Delta S_m^\circ$) of the formation of the UO$_2^{2+}$/SO$_4^{2-}$ species were determined using the Arrhenius model. The results obtained were compared with the ones obtained in the previous studies of the UO$_2^{2+}$/SO$_4^{2-}$ system [5-8]. It is now foreseen to apply the same methodology using the Time-Resolved Laser-Induced Fluorescence Spectrometry
(TRLFS) method in order to crosscheck the results and to work with lower uranium concentrations.

References
ELECTROCHEMICAL OXIDATION OF Am (III) AND Am (V) IONS IN NITRIC ACID SOLUTIONS CONTAINING POTASSIUM PHOSPHOTUNGSTATE K_{10}P_{2}W_{17}O_{61}

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Previously the authors of ref. [1-5] studied the oxidation of Am(III) to Am(IV) and Am(VI) in the mineral acids solutions (1-8 mol l⁻¹) in the presence of KPW by the chemical or electrochemical oxidation methods. It was of interest to experimentally measure the potentials of Am(IV)-Am(III), Am(VI)-Am(V) pairs and to study the kinetics of electrochemical oxidation on the platinum electrode in the HNO₃-KPW system.

1. Oxidation potentials of Am(IV)-Am(III), Am(VI)-Am(V) pairs and degree of electrochemical oxidation of Am(III) and Am(V)

Tables 1 and 2 present the results of E₀ values of Am(IV)-Am(III) and Am(VI)-Am(V) pairs versus the concentration of HNO₃ and KPW.

It is obvious that the change of C_{HNO3} practically does not influence the E₀ value of the Am(IV)-Am(III) pair, at the same time the increase of C_{KPW} causes the additional decrease of E₀ approximately by 100 mV. The oxidation potential of the Am(VI)-Am(V) pair (Table 2) in the studied concentration range of HNO₃ and KPW remains practically constant.

The observed shift of E₀ in the negative direction as compared to the standard values in the case of the Am(IV)-Am(III) pair makes up ~1.0 V. For the Am(VI)-Am(V) pair this shift is considerably lower and makes up ~50 mV.

The quantitative oxidation of Am(III) to Am(IV) is achieved up to C_{HNO3}=3 mol l⁻¹, if this concentration is higher, the oxidation degree of α_{Am(III)} decreases. At the same time the increase of the KPW concentration leads to the increase of α_{Am(III)}. During electrochemical oxidation of Am(V) the oxidation degree in all the studied experimental conditions remains practically constant and makes up 90% on average.

Table 1. E₀ values of Am(IV)-Am(III) pair, oxidation degree of Am(III) (α) and constant (k) of the reaction rate of Am(III)→Am(IV) + e⁻ (C_{0}^{6+}=0.92×10⁻¹ mol l⁻¹, S/V=1.87 cm²·mol⁻¹).

<table>
<thead>
<tr>
<th>C_{HNO3}</th>
<th>C_{KPW}×10⁻¹</th>
<th>E₀, V</th>
<th>α, %</th>
<th>k_{III}×10⁻⁴, s⁻¹</th>
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Table 2. $E_{a}^{\infty}$ values of Am(VI)-Am(V) pair, oxidation degree of Am(V) ($\alpha$) and constant (k) of the reaction rate of Am(V)→Am(VI) + e (C<sub>Am</sub>V=0.91×10<sup>-3</sup>mol·l<sup>-1</sup>, S/V<sup>o</sup>=4.36 cm<sup>2</sup>·ml<sup>-1</sup>)

<table>
<thead>
<tr>
<th>$C_{\text{HNO}_3}$</th>
<th>$C_{\text{KPF}}$</th>
<th>$E_{a}^{\infty}$</th>
<th>$\alpha$</th>
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<td>%</td>
<td>s&lt;sup&gt;-1&lt;/sup&gt;</td>
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*Selectrode area, cm<sup>2</sup>, V-solution volume, ml.

2. Kinetics of electrochemical oxidation of Am(III) and Am(V) ions

Fig. 1 presents the kinetic curves of electrochemical oxidation of Am(III) at the variable concentration of HNO<sub>3</sub>. The appearance of the kinetic curves formed when changing $C_{\text{KPF}}$ does not differ in principle.

![Kinetic curves](image1)

![Transformation of kinetic curves](image2)

In all cases there is a satisfactory transformation of the kinetic curves in the $\Delta C_{\text{Am(III)}}/\Delta t$ coordinates (Fig. 2). From this it follows that the electrochemical oxidation process of Am(III) proceeds according to the equation of the law of the reversible reaction rate.

$$\frac{dC_{\text{Am(III)}}}{dt} = k_{c}^{\infty} \times C_{\text{Am(III)}} - k_{a}^{\infty}$$

(1)

Thus, the electrochemical oxidation of Am(III) is complicated by proceeding of the reverse process — reduction of Am(IV). One of the reduction reactions of Am(IV) can be self-reduction under the influence of its own $\alpha$-radiation. We studied the self-reduction of Am(IV) at different concentrations of HNO<sub>3</sub>, KPF and dose rate. It is established that the process proceeds by the law of the first- and zero-order rate versus the concentration of Am(IV).
\[
- \frac{dC_{\text{Am}(IV)}}{dt} = k_a + k_i \times C_{\text{Am}(IV)}.
\]

If the reverse process is caused by self-reduction of Am(IV), the following equation is true
\[
k_i = k_a + k_i \times C_{\text{Am}(IV)}.
\]

However, the experimental results show that this equation is not obeyed. Therefore, the reversible process is not the consequence of self-reduction of Am(IV).

The investigation of electrochemical oxidation of Am(V) at different concentrations of HNO₃ and KPW demonstrated that oxidation of Am(V) proceeds by the law of the rate (1). The data analysis also demonstrated that the reverse process during Am(V) oxidation is not the consequence of self-reduction of Am(VI).

A comparison of electrochemical oxidation process of Am(III) and (V) allows a number of observations. The rates of electrochemical oxidation of Am(III) (k_{III}^{IV}) and Am(V) (k_{V}^{IV}) decrease with the growth of C_{HNO₃}. Probably, it is related to decrease of the fraction of Am(IV) and (VI) complexed with PW-ions and, thus, to their stability. The increase of C_{KPW} slightly affects the oxidation rate of Am(III) and (V). In this respect there is an analogy in the behavior of Am(III) and (V) ions during electrochemical oxidation. Yet, the growth of HNO₃ concentration the k_{IV}^{III} values increase, and the k_{IV}^{V} values decrease. This evidences a different mechanism of the reduction processes of Am(IV) and Am(VI). Evidently, reduction of Am(IV) proceeds as the result of its interaction with the products of electrochemical decomposition of HNO₃ formed during electrolysis at such a high oxidation potential (1.9 V). In the case of reduction of Am(VI) other oxidation-reduction reactions are also possible: disproportionation of Am(V), re-proportionation of Am(IV), reversible reaction of Am(V)+Am(IV)→Am(VI)+Am(III), laserable ions of Am(VI).

The obtained results of electrochemical oxidation of Am(V) and Am(III) ions in the concentrated HNO₃ solutions containing KPW show that for developing new effective processes of Am formation it is expedient to orient to electrochemical oxidation of Am(III) to Am(IV).

References

THERMOCHEMISTRY OF SELECTED SODIUM NEPTUNYL CARBONATES

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The present study is a continuation of earlier works from this laboratory aimed at better understanding the stability of lanthanide and actinide hydroxides, carbonates, hydroxycarbonates and related salts [1-6]. Most of these compounds are of utmost importance for the disposal of nuclear wastes in deep geological formations as they might emerge from the long-term interactions of natural waters with high-level nuclear wastes.

The molar enthalpies of dissolution in 1.00 M HCl of well characterized sodium neptunyl carbonates, namely NaNpO₂₃CO₃(cr), NaNpO₂₃CO₃·2H₂O(cr), and Na₂NpO₂₃(CO₃)₂·2H₂O(cr), were measured at 298.15 K. From these measurements, the following standard molar enthalpies of formation ΔH°ₚ (kJ · mol⁻¹) have been calculated as: NaNpO₂₃CO₃(cr), −(1885.4 ± 49); NaNpO₂₃CO₃·2H₂O(cr), −(2185.6 ± 5.2); Na₂NpO₂₃(CO₃)₂·2H₂O(cr), −(3340.5 ± 5.0).

In this study, use was made of an improved version of a sealed solution micro-calorimeter described previously [2]. The new calorimetric cell [5,6] made of 18-carat gold alloy is well suited for redox sensitive solutions such as those of Np(V).

No experimentally measured entropy of any solid neptunium(V) carbonate is available in the literature. The value S°(NaNpO₂₃CO₃, cr, 298.15 K) = (179 ± 15) J · K⁻¹ · mol⁻¹ was obtained when (a) using the estimate S°(Np₂O₇, cr, 298.15 K) = (174 ± 20) J · K⁻¹ · mol⁻¹ [7], (b) assuming that the entropy change for the reaction

\[ \text{Np}_2\text{O}_7 \text{(cr)} + \text{CO}_2 \text{(g)} = \text{(NpO}_2\text{)}_3\text{CO}_3 \text{(cr)} \]

is the same (with increased uncertainty limits) as that of the better known [8] system

\[ \text{UO}_3 \text{(cr, γ)} + \text{CO}_2 \text{(g)} = \text{UO}_2\text{CO}_3 \text{(cr)} \]

ΔS° (reaction 2, 298.15 K) = −(165.7 ± 0.4) J · K⁻¹ · mol⁻¹ and, (c) accepting a negligible entropy change for reaction (3) between solids

\[ 0.5 \text{Na}_2\text{CO}_3 \text{(cr)} + 0.5 \text{(NpO}_2\text{)}_3\text{CO}_3 \text{(cr)} = \text{NaNpO}_2\text{CO}_3 \text{(cr)} \]

Similarly, taking into account the presence of one water molecule [9], we calculated S°(NaNpO₂₃(CO₃)₂·H₂O, cr, 298.15 K) = (219 ± 15) J · K⁻¹ · mol⁻¹ and S°(Na₂NpO₂₃(CO₃)₂·2H₂O, cr, 298.15 K) = (354 ± 19) J · K⁻¹ · mol⁻¹.
The solubility products, \( \log K_{sp} \), corresponding to the general reaction (4) at infinite dilution in water, were then calculated.

\[
\text{Na}_x\text{NPo}_2\text{(CO}_3 \text{)}_{0.5(x+1)}^y\text{H}_2\text{O} \text{ (cr)} = \{x\text{ Na}^+ + \text{ NPo}_2^+ + 0.5(x+1) \text{ (CO}_3 \text{)}^2\text{(aq)} + y \text{ H}_2\text{O(l)} \quad (4)
\]

Our results are in good agreement with values recently assessed [10] from solubility measurements. Our values \( \log K_{sp} \)(NaNPo2CO3, cr) = \( -9.8 \pm 1.2 \) and \( \log K_{sp} \)(NaNPo2CO3·2H2O, cr) = \( -10.8 \pm 1.3 \) agree with that for a more hydrated compound, \( \log K_{sp} \)(NaNPo2CO3·3.5H2O, cr) = \( -11.00 \pm 0.24 \). Our value \( \log K_{sp} \)(NaNPo2CO3·2H2O, cr) = \( -14.2 \pm 1.3 \) compares with \( \log K_{sp} \)(NaNPo2CO3·2H2O, cr) = \( -14.22 \pm 0.50 \) where water molecules were not specified.

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References
3. Transactinides
CHEMISTRY OF THE TRANSACTINIDE ELEMENTS

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The knowledge and understanding of the chemistry of the superheavy elements, especially of the early transactinides Rf, Db, and Sg and their compounds, both experimentally and theoretically, is nowadays quite extensive as documented by the first textbook entitled "The Chemistry of Superheavy Elements" edited by M. Schädel [1]. While rapid chemical separations in aqueous solution were (and are) the method of choice for detailed investigations of Rf and Db, the development of gas-phase chemical separation methods have allowed first chemical studies of increasingly heavier transactinide elements.

The spectacular results obtained at Flerov Laboratory in Dubna using $^{60}$Ca ion beams and targets of $^{238}$U, $^{240}$Pu, $^{243}$Am, $^{245}$Cm and $^{249}$Cf to synthesize isotopes of elements 112 [2], 114 [3,4], 115 [5], 116 [6], and 118 [7] give chemists the perspective to experimentally investigate the chemistry of even the heaviest known elements. Especially since some of the nuclides and their decay products attributed to elements Rf, Db, Sg, Bh, Hs, Ds, 111, 112, 113, and 114 seem to have half-lives of the order of seconds to even hours.

In the last couple years, chemists have made a quantum leap and are now working with nuclides that can be produced with picobarn ($10^{-24}$ cm$^2$) cross sections only. One of the highlights of NRC5 was the announcement of the first gas-phase chemical isolation of bohrium (Z=107) as volatile BrO$_2$Cl using the OLGA technique [8]. The nuclides $^{289}$Bh and $^{297}$Bh were produced in the reaction $^{208}$Bk($^{22}Ne$, 4,5n) with maximum cross sections of about 100 pb [9]. Even though the experiment was successful and deserved highest scientific merits, the outlook to apply the same technique to the investigation of even heavier elements was bleak, since the overall efficiency to detect a correlated mother-daughter α-particle decay chain was only about 4%. The experimental chemical investigation and characterization of the next heavier transactinide element hassium has, for some years, constituted a daunting task even though from the very beginning the selection of a volatile compound was absolutely clear. Hassium, as a presumed member of group 8 of the Periodic Table and thus a homologue of Fe, Ru, and Os, should form stable and at the same time very volatile HsO$_x$ molecules, very similar to OsO$_x$. However, in order to gain access to hassium (Z=108) the overall efficiency of the experiment had to be improved by at least one order of magnitude. By developing a completely new approach of separation (IVO) [10] and detection (CTS, COLD) [11] and also by introducing the rotating target set-up ARTESIA [12], which allowed the use of much higher beam intensities, the first chemical characterization of Hs became reality [13].

This spectacular progress however is limited to a few selected cases which chemically are extremely favorable. One such case is also element 112 in its elemental state. First experiments done in Dubna [14,15] and recently at GSI [16] seem to indicate a quite spectacular difference in chemical behavior between element 112 and its lighter homolog Hg in the elemental state. Compared to chemical investigations of the early transactinide elements Rf through Hs, where always the highest possible oxidation state was investigated, now with
elements 112 through 118, which are expected to be moderately to highly volatile in the elemental state, the influence of relativistic effects of the valence electrons should become noticeable in direct experimental investigations. These relativistic effects might be responsible for some quite dramatic differences in chemical behavior as this seems to be the case in the adsorption properties of element 112 compared to its lighter homologue Hg [17].

Experiments on the aqueous chemistry of transactinide elements focused mainly on a much deeper understanding of the properties of Rf in solution [18]. A fully Automated Ion exchange apparatus coupled to a Detection system for Alpha-particle spectroscopy (AIDA) developed at JAERI, was used to extensively study the behavior of Rf in pure HCl solution [19]. Future experiments with Db using the reaction $^{248}\text{Cm}^{3+} + 5n \rightarrow ^{253}\text{Db}$ are planned [19]. A series of trendsetting experiments were performed by the SISAK collaboration [20]. The radionuclide $^{257}\text{Rf}$ was produced in the reaction $^{267}\text{Pb}^{6+} + 1n \rightarrow ^{257}\text{Rf}$, separated in the Berkeley Gas-filled Separator (BGS) and transferred to a gas jet using the Recoil Transfer Chamber (RTC) [21]. The activity delivered by the gas jet was dissolved in nitric acid and Rf was extracted into dibutyl-phosphoric acid in toluene. The decay of Rf nuclides was registered on-line by flow-through liquid scintillation counters. This was the first time a transactinide element was extracted and unequivocally identified by the SISAK system. The use of the BGS provided the necessary reduction of background from interfering by-products of the nuclear reaction.

Another approach to extend liquid-phase chemical studies to heavier transactinides is the so-called Multi Column Technique (MCT) [22]. In this continuous on-line chromatography, the solution containing the dissolved transactinide element passes through a series of columns. The transactinide element of interest passes a first column where only its actinide daughter nuclei (and other actinides) are retained. The transactinide element is then retained on a second column. However, its actinide decay daughters pass this column and are retained on a third column from which they are eluted after completion of the experiment and assayed by alpha-particle spectroscopy. This technique is very efficient and allows to access relatively short-lived nuclei. However, a breakthrough even of a small fraction of actinides in the first column can ruin the experiment. Also, all information about the nuclear decay properties of the transactinide element is lost.

What are the prerequisites to achieve the ultimate goal of chemically identifying a new, superheavy element? Due to the very low production cross sections of 1 pb or less highest possible beam intensities must become available in the near future. This ultimately calls for a new accelerator capable of delivering a continuous beam of up to $5 \times 10^{13}$ ions/s. Evidently, this also calls for improved target irradiation facilities, since target thicknesses of the order of 1 to 1.5 mg/cm$^2$ are useful. Nevertheless, the experiences with ARTESIA clearly demonstrated, that this setup already today allows accepting a 3 to 4 fold higher beam intensity if a DC beam were available instead of a pulsed beam.

Chemical separation procedures need to be improved with respect to sensitivity and speed. Here, gas phase chemical separations will play an important role, since many of the superheavy elements with atomic numbers between 112-118 may be moderately or even highly volatile in their elemental state. Thus future experiments point to investigations of elements 112 and 114 in their elemental state. However, a particularly difficult problem is constituted by some Rn isotopes, since their Po daughter nuclides decay with $\alpha$-decay energies which strongly interfere with the detection of heavy transactinide nuclides. Especially element 112 seems to exhibit a very similar volatility as Rn. A possible solution to
this problem, although not yet available, may constitute a dedicated kinematical pre-separator
which is coupled to chemical set-ups. A workshop held a GSI in 2002 clearly demonstrated
the future need for such an instrument.

Even more challenging than the investigation of elements 112 and 114 is probably the
chemical identification of elements Mt through 111, the heavy analogs of Ir, Pt, and Au. Here,
o no obvious chemical properties or compounds, as for instance with group 8 elements, are at
hand. Again, the use of a kinematic preseparator of nuclear reaction products might
considerably facilitate chemical investigations.

To conclude it is fair to say that chemists have made enormous progress in investigating
the chemical properties of transactinide elements and certainly the successful haxium experiment
will serve as a text book example for years to come. With the synthesis of relatively long-
lived superheavy elements with Z=112-118 chemists are facing an extremely challenging but
also rewarding future. The possibility to experimentally characterize the complete 7th row of
the periodic table has never become more real than starting with today.

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CHEMICAL IDENTIFICATION AND PROPERTIES OF ELEMENT 112


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1. Introduction

We present the results of two experiments on the chemical identification of element 112 [1, 2]. Chemical studies of element 112 (E112) are of great interest. They might test the predicted strongly pronounced "relativistic effects" in chemical properties of the element and provide an independent determination of its atomic number and decay properties. E112 has been obtained directly in the $^{238}\text{U}$ ($^{40}\text{Ca}; \alpha n$) reaction and also as the daughter of E114 produced in the $^{242,244}\text{Pu}$ ($^{40}\text{Ca}; \alpha n$) reaction [3]. According to its ground state electronic structure, E112 belongs to group 12 of the Periodic Table of the Elements (PTE), and is the nearest homologue of Hg. Based on classical extrapolations; E112 can form stronger bonds with surfaces of some metals, than between E112 atoms in the hypothetic metallic phase [4]. At the same time, relativistic quantum chemistry predicts increasingly strong "relativistic effects" in the chemistry of superheavy elements (SHE) [5-9]. The calculated contraction stabilizes the spherical $s$ and $p_{1/2}$ electron orbitals, which more efficiently shield the nuclear charge and thus destabilize the $p_{3/2}$ and $d$- orbitals. This may strongly influence the chemical behavior of the 7s and 7p$_{1/2}$ elements, E112 and E114. They are sometimes predicted to approach noble gases in volatility and chemical inertness [8]. The expected enhanced volatility of E112 makes it an ideal object for the study of its chemical behavior in the elemental state by gas-phase chemical methods. Hence, one has to investigate the volatility and adsorption behavior of E112 in comparison with those of Hg and Rn.

2. Experimental

In the first experiment [1] we tried to detect E112 assuming that the behavior of 112-atoms is "Hg-like", in a second experiment, we achieved a higher beam dose and tried to detect E112 atoms as a homologue of Hg which strongly adsorbs on the metallic surface of the PIPS detectors, or as a homologue of Rn. For that case, a special flow-through ionization chamber was built to register decays of Rn-like E112. The experiments were performed at JINR, FLNR at the U-400 cyclotron. The target was a 2 mg/cm$^2$ thick layer of $^{233}\text{UO}_2$ which contained also about 35 μg/cm$^2$ of $^{144}\text{Nd}$. The target material was deposited onto a 2 μm HAVAR foil as a circular spot, 20 mm in diameter (working area). In the second experiment we used a wobbler device, which distributed the beam projectiles uniformly over the target; it allowed us to accept 0.6 μA of $^{40}\text{Ca}$ ions. The original energy of the $^{40}\text{Ca}$ beam, 262 MeV, was degraded
to 242 MeV after passing through the HAVAR foil and became 224 MeV at the exit of the target layer. Some short-lived Hg isotopes were simultaneously produced in the fusion reaction $^{197}$Nd$(^{238}$U,xn)$^{197}$Hg, and multinucleon transfer reactions of projectiles with uranium yielded Rn isotopes among other nuclides. The nuclei recoiling from the target were thermalized in a 45-cm$^3$ chamber, which was continuously flushed with pure He gas at a pressure of about 1000 mbar. The chamber was connected to the detection unit of the setup by a 25 m long PTFE capillary with 2 mm i.d., i.e. 80 cm$^3$ in volume. Three flow rates of He gas (250 cm$^3$/min, 500 cm$^3$/min and 1000 cm$^3$/min) were used during the experiment to compensate for the considerable uncertainty in the half-life of $^{252}$Hf [10]. Volatile atoms were transported by the He carrier gas into a disk chamber with 16 PIPS detectors. Each of them had a working area of 3.25 cm$^2$ coated with 30 μg/cm$^2$ of Au. They were arranged in 8 pairs, in which they faced each other across a gap of 1 mm. After the PIPS detectors, the carrier gas flow merged with some Ar and CH$_4$, passed through an aerosol filter and was admitted into the cylindrical ionization chamber (i.d. 9 cm, 75 cm in length). The PIPS detectors and the ionization chamber were placed inside a 1 m long assembly of 126 $^3$He-counters, each inserted in a plastic moderator block. Observation of a fission fragment signal in the PIPS detectors or in the ionization chamber triggered a special regime aimed at the registration of prompt neutrons within the following 128 μs. For each registered neutron, the pulse amplitude and the counter number (i.e. its position in the assembly), as well as the time elapsed since the trigger signal were measured. The detection efficiency of a single neutron was about 35%. Measurements of the fission fragment energies and of the characteristics of the accompanying neutrons allowed us to significantly increase the reliability of registering rare SF events.

3. Results and Discussion

After 22.5 days of bombardment, a total beam dose of $2.8 \times 10^{13}$ $^{48}$Ca ions was accumulated (taking into account the transparency of the supporting grate). The behavior of Hg and Rn atoms in the PIPS detector assembly was traced by registering the α-decays of $^{197}$Hg ($T_{1/2} = 49$ s) and $^{220}$Rn ($T_{1/2} = 55$ s). At a He flow rate of 500 cm$^3$/min, as much as 95% of the 49.5 $^{197}$Hg was adsorbed already in the first detector pair. In contrast, only a minute part of the Rn activity decayed within the PIPS detector assembly and was distributed practically evenly over all the 8 pairs of the PIPS detectors. The excellent purification from non-volatile species was confirmed also in the present experiment by measurements of long-lived activities after a long run. We measured also the background of the PIPS detectors and ionization chamber during 15 days before and 100 days after the experiment, in working conditions (same neutron flux) but with the gas flow stopped. The PIPS detectors did not register even a single fission fragment, while the ionization chamber signaled four events. The expected average number of background SF-like events in the ionization chamber during the experiment, which lasted 22.5 days, was slightly less than 1 event.

Towards the end of our E112 experiment, eight SF events had been observed (Table 1), characterized by a high pulse amplitude in coincidence with one, two or three neutrons. All these events were observed in the ionization chamber, none by the PIPS detectors. The time distribution of the neutrons is consistent with their lifetime in our detector. The probability of random coincidence between a fragment pulse and one, two or three background neutrons is negligible, $10^{-7}$, $10^{-4}$, and $10^{-6}$, respectively. As the average expected background rate for the duration of the experiment was less than one fission event, the mean counting rate for "net" spontaneous fissions of a volatile element formed in the $^{48}$Ca+$^{238}$U reaction is $7\pm 3$.
(68% c.i.). The observed detection yields were 2.4 events/10^{18}^{48}Ca at a flow rate of 250 cm³/min and 500 cm³/min, and 6.7 events/10^{18}^{48}Ca at a flow rate of 1000 cm³/min, respectively. The half-life of the SF activity could be from a few seconds up to a few minutes having in mind the low statistics and the operating speed of our technique. Measured yield corresponds to the cross section σ = 2.4 ± 0.7 pb (68% c.i.) for production 3-min SF activity. Based on most recent results from Dubna,^{203}12 has a shorter lifetime (T_{1/2} ≈ 6 s), and in that case the cross sections should be about 7 pb.

<table>
<thead>
<tr>
<th>He/Ar/methane</th>
<th>max/mean</th>
<th>Duration</th>
<th>Beam dose, particles x10^{18}/SF events</th>
</tr>
</thead>
<tbody>
<tr>
<td>flow rates, cm³/min</td>
<td>intensity, pA</td>
<td>days</td>
<td></td>
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<tr>
<td>250/250/50</td>
<td>0.6 / 0.3</td>
<td>10.5</td>
<td>1.25 / 3</td>
</tr>
<tr>
<td>500/500/100</td>
<td>0.6 / 0.4</td>
<td>9</td>
<td>1.25 / 3</td>
</tr>
<tr>
<td>1000/1000/100</td>
<td>0.6 / 0.3</td>
<td>3</td>
<td>0.3 / 2</td>
</tr>
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</table>

Using the model of mobile adsorption for the description of migration velocity of species in chromatographic column and a Monte Carlo simulation we evaluated the adsorption enthalpies of Rn and E112 on the gold surface of the PIPS detectors. For Rn ΔH_{ads}(Rn) = −36 kJ/mol was evaluated. In the case of the 3-min ^{203}112, from the estimated upper limit of the retention time we calculated the upper limit to be ΔH_{ads}(3-min ^{203}112) = −60 kJ/mol. If the half-life is shorter, this upper limit is lower, ΔH_{ads}(6-s ^{203}112) = −48 kJ/mol. The adsorption enthalpy of Hg is much higher ΔH_{ads}(Hg) = −114 kJ/mol[11]. Since, the limit ΔH_{ads} is less than the sublimation enthalpy of Hg, ΔH_{sub}(Hg) = 62 kJ/mol. Also macroscopic amounts of E112 must be more volatile than Hg. Thus, in the atmosphere of an inert gas in contact with PTFE and SS, the atoms of E112 behave in accordance with the predicted enhanced volatility of the element. In addition, they do not form strong metal-metal bonds when interacting with the Au surface. In other words, E112 behaves more like the noble gas Rn rather than Hg. Such a pronounced difference in the chemical properties of a transactinoid and its nearest homologue in the PTE was observed for the first time.

References

ATTEMPT TO CHEMICALLY CHARACTERIZE ELEMENT 112

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Due to relativistic effects within the electron shells, deviations from that predicted by the periodicity of chemical properties are expected to increase along rows of the Periodic Table, thereby influencing most strongly the highest elements of each row. In this context element 112 with its electronic configuration \([\text{Rn}]5f^{14}6d^{10}7s^2\) is exceptional. The expected relativistic stabilization of the closed-shell electronic ground state led to the prediction of noble gas like properties for element 112 [1]. Other prediction methods yielded a volatile noble metal character [2,3]. First chemical investigations yielded indication that element 112 does not behave like Hg at room temperature [4]. An upper limit for the adsorption enthalpy of element 112 on Au was deduced as \(\Delta H_{\text{ads}}^{\text{Au}}(E112) < 60\ \text{kJ/mol.}\)

Our experiment was designed to determine thermochemical data for element 112 by measuring its adsorption enthalpy on Au to understand whether a metallic bond or a van der Waals interaction is observed. So far, the only directly produced isolate of element 112 with a sufficiently long half-life to be chemically characterized is $^{238}$U$^{(49}\text{Ca}\_3)n$, with a cross-section of $\sim 2\ \text{pb}$ [5-7]. $^{238}$U$^{(49}\text{Ca}\_3)n$ decayed in all these studies via spontaneous fission with $T_\text{f} \approx 5\ \text{min.}$

Based on the expected inertness of element 112 a modified IVO (In-situ Volatilization and On-line technique) was applied for its chemical investigation. At GSI a 1.6 mg/cm$^2$ $^{238}$U target was irradiated with a beam-dose of about $2.8 \times 10^{18}$ particles of 222-239 MeV $^{48}$Ca covering an excitation energy range between 27 MeV and 40 MeV. Products recoiling out of the target were thermalized in dried 1 l/min He carrier gas. The inner surface of the recoil chamber was completely covered by a quartz insert to prevent adsorption of volatile metallic reaction products. All gaseous products were swept out of the recoil chamber through an open quartz column to an oven with a quartz wool filter heated to 850°C. Aerosol particles produced e.g. by beam particle induced sputtering processes in the beam dump were stopped in this filter. Separation factors of about 10$^3$ have been determined for lanthanides (model elements for heavy actinides) in test experiments with Yb, produced in the reaction $^{142}$Nd($^{208}$Ne,6n)$^{206}$Yb. Volatile products that passed this filter were transported through a 10 m long PFA capillary to a getter oven containing Ta and Ti and operated at 1000°C in order to
remove trace amounts of water and oxygen from the carrier gas. It was experimentally verified that the transport of carrier free amounts of Hg and Rn occurred with almost no loss through the PFA or quartz capillary tubes and through the hot Ta/Ti-getter. Finally, after a separation time of about 25 s gaseous products were injected into the modified detector COLD (Cryo On-Line Detector) [8]. This device consists of an array of 32 silicon PIN-photodiodes (10 x 9.8 mm² active area) mounted in a Teflon coated copper channel at a distance of 1.6 mm opposite to a Au covered surface, forming a rectangular gas chromatographic column. The Au surface was produced by vapor deposition of Au on a copper frame. A negative temperature gradient from +35°C to -187°C (see Fig. 1, black line) was established along this chromatographic channel using a thermostat heating and a liquid nitrogen cooling. The whole detector set-up was placed in a vacuum tight steel box kept at 900 mbar to isolate it thermally against ambient air. The adsorption behavior of element 112 in the COLD detector was measured simultaneously with that of 185Hg produced in the nuclear reactions of 144Nd (admixture to the target) with 48Ca and of 220Rn, a transfer-product of the reaction of 238U and 48Ca. The measured distribution of 185Hg and 220Rn is presented in Fig. 1.

![Thermochromatogram of 185Hg and 220Rn](image)

**Fig. 1** Thermochromatogram of 185Hg and 220Rn (bars) measured along the detector array. Monte-Carlo simulations (dashed lines) are in good agreement with the experimental results. The temperature gradient is indicated (solid line).

Applying a kinetic Monte-Carlo model of gas adsorption chromatography, the adsorption enthalpy of Hg and Rn may be determined. The diffusion controlled deposition pattern of Hg on Au yielded a lower limit of \(-\Delta H_{\text{ads}}(\text{Hg}) > 80 \text{ kJ/mol}\), in good agreement with literature values [9]. For 220Rn \(-\Delta H_{\text{ads}}(\text{Rn}) = (22 \pm 1) \text{ kJ/mol}\) is obtained. This value agrees well with data for Rn on ice [10] but not for Rn on Au [11]. Moreover, analysis of the \(\alpha\)-resolution yielded evidence for the formation of an ice layer at temperatures below about -90°C (see Fig. 2). 11 high energy (E > 35 MeV) events were measured during 16.8 days of experiment, at 3 expected background events. Their distribution along the detector array is presented in Fig. 2. A clear accumulation of 7 events was observed in the detectors #29-31. Because of the ice coverage of the detectors the spontaneous fission fragment spectroscopy was hampered. No indication for SF-decaying actinide nuclides – possible transfer products of the 238U with 48Ca
reaction was found in the spectra accumulated with the COLD nor in  measure-ments of the leached quartz wool filters behind the recoil chamber.
If the 7 events are tentatively assigned to the decay of $^{283}$122
- $\Delta H_{\text{sub}}^{\text{st}}(E112) = (25 \pm 5)$ kJ/mol (95% c.i.) may be calculated. From the observed non adsorption on Au down to temperatures of -90°C, an upper limit for the enthalpy of element 112- $\Delta H_{\text{sub}}^{\text{Au}}(E112) < 48$ kJ/mol can be determined.

![Graph showing distribution of SF-fragments](image)

Fig. 2 Distribution of SF-fragments (black bars, right-hand scale) measured along the COLD. Monte-Carlo simulation is shown (dashed line, left-hand scale).

This value allows to estimate an upper limit of the standard sublimation enthalpy of $\Delta H_{\text{sf}}^{\text{st}}(E112) = 33$ kJ/mol [12]. This low value indicates that element 112 should be gaseous under standard conditions.

Recently, unpublished results from the Flerov Laboratory in Dubna (Russia) point to an $\alpha$-decaying $^{283}$122 with $T_{1/2} \approx 5$ s followed by a SF $^{279}$Ds ($T_{1/2} \approx 0.2$ s). Therefore, a new experiment will be conducted soon at GSI with an improved faster IVO set-up that will allow for detection of gaseous products with half-lives of a few seconds.

References
RATIONALE FOR ESTIMATING VOLATILITY CHARACTERISTICS OF TRANSACTINOID HALIDES FROM ADSORPTION ENTHALPY DATA

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Volatility – adsorption enthalpy correlations
The adsorption enthalpies $\Delta H_a$ ($<0$) of trace quantities of metal halides evaluated [1] from gas-solid (thermo)chromatography data correlate with the vaporization or sublimation characteristics of bulk compounds [2,3,4]. The mere fact is widely used to judge the characteristics of macro volatility of the compounds of transactinoids. This situation with such important quantities can hardly give intellectual satisfaction and calls for search of the physicochemical grounds of the regularity.

To date, most researchers have preferred the correlations with sublimation enthalpy, $\Delta H_s$, because its values are better known. But $\Delta H_s$ is the sum of the enthalpies of vaporization, $\Delta H_v$, and melting. The latter is often quite large and very sensitive to details of the structure of the solid compound, while the neighborhood of a single molecule adsorbed on a foreign substrate can hardly be similar. We believe that, first, one must understand the regularities in $\Delta H_v$ or absolute normal boiling points, $T_b$, values (at $T_b$, the two quantities are just proportional – the Trouton's rule).

New formula for boiling points
Recently, when continuing some past attempt [5], we semiempirically found a better, more general, and still surprisingly simple formula for $T_b$ of the compounds MX$_n$ where M is, in particular, an element of transition metal groups 4 to 8 in the highest oxidation state; $n$ is 4 to 7; and the ligand X is a halogen or oxygen:

$$T_{b,calc}=2(n-2)a^{1/3}/\lambda_{(\text{radii}, n)}.$$  

The parameters are: the polarizability of $X^-/X^{2-}$ ions $\alpha$ and certain commonly used additive radii of M$^{n+}$ and $X^-/X^{2-}$ ions. The radii serve to calculate $\lambda$, the "reduced" (divided by the X$^-$/X$^{2-}$ radius) minimum possible distance between the surface of M$^{n+}$ and that of $X^-/X^{2-}$ of a neighboring molecule. It was calculated within the touching hard sphere model for the "corner to face" configuration, i.e. from strictly geometric relations born in MX$_n$ with regular polyhedral root structure. The formula contains just one adjustable parameter – the proportionality/scaling coefficient.

As shown in the Figure, the formula proved valid to $\pm10\%$ for some 50 "regular" compounds:
(Ru,Os)O; (Si/Ge)F; (Si/Ge/Sn/Ti/Zr/Th)(Cl/Br/I); Hf(Cl/I); (P/As/V/Bi)F; (P/Sb/Nb/Ta/PaCl; (Sb/Nb/Ta)Br; (Nb/Ta)I; (S/Se/Te)F; (Mo/W/U)(F/Cl); WBr; (Ir/Ir)F; (Ru/Os)O. Oxohalides and mixed halides, if characterized by averaged parameters, also reasonably comply with the regularity.

The term \(2(n-2)\) in the formula suggests that \(T_b\), as well as \(\Delta H\), is proportional to the number of faces of the molecular root polyhedron. Also, \(T_b\) is inversely proportional to \(\lambda\). This may indicate that of the possible electrostatic interactions the ion – ion ones mostly contribute to the value of \(\Delta H\), because the bond dipoles of touching molecules cannot closely interact due to spatial hindrance.

![Figure. Ratio of the experimental to calculated \(T_b\) versus the experimental b.p.](image)

**Actual column surface in chromatographic experiments**

The experiments on gas solid (thermo) chromatography of transactinoid compounds are usually performed using carrier gases with halogenating constituents. The latter can modify the column surface, usually fused silica or glass, by attaching to it halogen atoms or molecular fragments. The original centers available for modification can be as numerous as 5 per 100 Å²; in other words they are some 5 Å apart which is the molecular diameter of ZrCl₄ in our hard sphere model. Thus, if the modification is deep enough, the adsorbed molecule must experience interactions qualitatively similar to those in bulk liquid. Then, one would expect \(-\Delta H\) to be only a fraction of \(\Delta H\) on smooth homogeneous surfaces because fewer faces of the molecule are exposed. But surfaces of fused silica columns often have a microstructure developed down to the atomic scale [6] probably including micropores. So, undoubtedly, the surface is heterogeneous in adsorption properties and at some sites the adsorbed molecule may be surrounded by so many halogen atoms that \(-\Delta H\) will become comparable with \(\Delta H\).

A heterogeneous surface can be characterized by probability density distribution (spectrum) of the \(-\Delta H\) values. In any gas chromatography experiment, the molecules experience numerous adsorption - desorption events when passing down the column. Hence, in the simplest model of retention in an isothermal column, one can evaluate an effective, now temperature dependent adsorption enthalpy \(\Delta H_t\) obeying...
\[ \exp\left(\frac{\Delta H_s}{RT}\right) = \int_{\Delta H_{\text{min}}}^{\Delta H_{\text{max}}} \exp\left(\frac{\Delta H_{\rho}}{RT}\right) \rho(\Delta H_{\rho}) d\rho. \]

We traced how does \( \Delta H_s \) depend on the form of \( \rho \) for several kinds of realistic distributions between the limits -\( \Delta H_{\text{min}} = 0.5 \Delta H_s \) to -\( \Delta H_{\text{max}} = \Delta H_s \). The value of -\( \Delta H_s \) always proved to be quite close to the upper limit, \( \Delta H_s \), the difference being of the order of \( RT \). This is not surprising in view of the exponential dependence of the retention time on -\( \Delta H_s \). It follows that experimental adsorption enthalpies must more or less approach \( \Delta H_s \). The problem has never been discussed from this point of view. As for the experimental observations, indeed, already at the very beginning of the gas phase transactinoid studies, we evaluated [2] some \( \Delta H_s \) values and saw that they differ from \( \Delta H_s \) by not more than 20-30 \%. A recent plot [3] of the known adsorption enthalpies versus bulk boiling points of the compounds yielded the regression equation

\[ -\Delta H_s / \text{kJ mol}^{-1} = (0.087 \pm 0.005)T_b + 32.9 \pm 6.4. \]

According to the Trouton's rule \( \Delta H_s /RT_b = 10.5 \) and by substituting \( T_b \) into the correlation we obtained

\[ -\Delta H_s / \text{kJ mol}^{-1} = (0.99 \pm 0.06)\Delta H_s + 32.9 \pm 6.4, \]

thus revealing a component equal to \( \Delta H_s \).

**Conclusion**

The above considerations represent a sound base to expect that at certain, more or less standard conditions of experiments, the effective adsorption enthalpy will approach the vaporization enthalpy. As the values are obtained by the "quasi-3d-law" method [1], more attention is to be paid to their accuracy (systematic errors). The author analyzes some experimental data on the transactinoid elements and outlines an experimental program aimed at better understanding of the volatility – adsorption parallels.

**References**

STATUS AND FUTURE DEVELOPMENTS OF THE AQUEOUS HEAVY-ELEMENT CHEMISTRY

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Recently, the status of the liquid-phase chemistry of the transactinide elements has been reviewed extensively in a number of reviews and book contributions [1-4]. In the Table below, an attempt is made to summarize the chemical systems studied with elements 104, 105, and 106, so far. The chemical techniques involved include manual techniques, the multi-column technique (MCT), the automated rapid chromatography apparatus (ARCA), the online liquid-liquid extraction system SISAK, and the automated ion-exchange separation apparatus coupled with the detection system for α-spectroscopy (AIDA). Critical comments [1] have been addressed to the results and conclusions presented in Refs. [8-12], and [14].

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Chemical technique</th>
<th>Chemical system studied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>104, Rutherford</td>
<td>260Rf</td>
<td>manual</td>
<td>Cation exchange/α-hydroxyisobutyrate</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>manual</td>
<td>Aliquat 336/12 M HCl, 6 M HCl</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>manual</td>
<td>Tri-isooctyl amine/12 M HCl</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>manual</td>
<td>Thenoyltrifluoroacetone/0.05 – 0.24 M HCl</td>
<td>8</td>
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<td>manual</td>
<td>Tributyl phosphate/8 M – 12 M HCl</td>
<td>9</td>
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<tr>
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<td>260Rf</td>
<td>manual</td>
<td>Tributyl phosphate/9 M – 12 M HBr</td>
<td>10</td>
</tr>
<tr>
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<td>manual</td>
<td>Co-ferrocyanide/&lt;6 M HCl</td>
<td>11</td>
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<tr>
<td></td>
<td>260Rf</td>
<td>Manual</td>
<td>Tri-isooctyl amine/0.4 M HF</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>MCT</td>
<td>Anion exchange/0.2 M HF</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>MCT</td>
<td>Anion exchange/0.27 M HF, 0.2 or 0.1 M HNO₃</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>ARCA</td>
<td>Tributyl phosphate/6 M HCl</td>
<td>15</td>
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<tr>
<td></td>
<td>260Rf</td>
<td>ARCA</td>
<td>Cation exchange/0.1 M HNO₃, var. HF</td>
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<tr>
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<td>257Rf</td>
<td>SISAK</td>
<td>Dibutyl phosphoric acid/6 M HNO₃</td>
<td>17</td>
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<tr>
<td></td>
<td>260Rf</td>
<td>AIDA</td>
<td>Anion exchange/8 M HNO₃&lt;4 – 11.5 M HCl</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>260Rf</td>
<td>Manual</td>
<td>Cation exchange/α-hydroxyisobutyrate and Tributyl phosphate/9 M HCl</td>
<td>19</td>
</tr>
<tr>
<td>105, Dubnium</td>
<td>262Db</td>
<td>Manual</td>
<td>Glass surfaces/fuming with HNO₃</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>262Db</td>
<td>ARCA</td>
<td>Tri-isooctyl amine/12 M HCl, 0.02 M HF/10 M HCl, 0.025 M HF/4 M HCl, 0.02 M HF/0.5 M HCl, 0.015 M HF</td>
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</tr>
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<td></td>
<td>262Db</td>
<td>ARCA</td>
<td>Diisobutyl carbinol/conc. HBr/6 M HCl, 0.0002 M HF/0.5 M HCl</td>
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<tr>
<td></td>
<td>262Db</td>
<td>ARCA</td>
<td>Cation exchange/α-hydroxyisobutyrate</td>
<td>24, 25</td>
</tr>
<tr>
<td></td>
<td>262Db</td>
<td>ARCA</td>
<td>Aliquat 336/10 M HCl/6 M HCl/6 M HNO₃, 0.015 M HF</td>
<td>26</td>
</tr>
<tr>
<td></td>
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<td>Aliquat 336/0.5 M HF/4 M HF/6 M HNO₃/0.015 M HF</td>
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106, seaborgium  

<table>
<thead>
<tr>
<th>256\text{Sg}</th>
<th>ARCA</th>
<th>Cation exchange/ 0.1 M HNO₃, 5x10⁻⁵ M HF</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>256\text{Sg}</td>
<td>ARCA</td>
<td>Cation exchange/0.1 M HNO₃</td>
<td>28</td>
</tr>
</tbody>
</table>

Technical developments are going on in several directions: The MCT has been coupled to the aerosol collection device ALOHA on which 2-s collection and dissolution cycles are performed so that the dissolved activity can be fed rapidly onto a sequence of chromatography columns in a quasi-continuous mode. The optimized conditions for on-line experiments with seaborgium are discussed in which $K_d$ values on an anion exchange resin in 0.1 M HNO₃/5x10⁻⁵ M HF are planned to be measured via the long lived descendant of 260\text{Sg}, 20-d 253\text{Es}. It is also planned to reduce seaborgium to a lower oxidation state by contacting its aqueous solution with a hot aluminum surface and by distinguishing anionic seaborgium(VI) from cationic seaborgium(III) on a cation exchange column using the MCT.

Continuous efforts have been devoted to improvements of the on-line liquid-liquid extraction system SISAK coupled with liquid scintillation counting (LSC). Analog pulse-shape discrimination (PSD) has been used to reduce the $\beta$ background in the $\alpha$ spectra by a factor of > 1000. Without this technique, the $\beta$- and $\gamma$-induced background from activities produced in the target will interfere with the $\alpha$ spectrum to such an extent that it becomes useless. However, in the past, when feeding the He/KCl jet directly into the SISAK system, the PSD alone was insufficient to unequivocally identify transactinides with the SISAK-LSC system. Omtvedt et al. [17] have overcome this limitation by producing 257\text{Rf} in the 208\text{Pb}(58\text{Ti}, 1n) reaction, separating it in the Berkeley Gas-filled Separator (BGS), and transferring it to the gas jet using the Recoil Transfer Chamber (RTC). This was the first time that a transactinide was extracted and unequivocally identified by the SISAK-LSC system and also the first experiment to use preseparation in a transactinide chemistry investigation. Another improvement comes from the digital recording of the LSC pulses with a fast transient recorder and the pulse-shape analysis by an artificial neural network (PSD-NN) [29]. This has been proven to eliminate pileups to the extent that identification of transactinides even without preseparation becomes feasible. Its ability to recognize $\alpha$-$\gamma$ and $\alpha$-conversion-electron-coincidence summing which is known to cause shifted $\alpha$ energies may be used in the future to do nuclear spectroscopy [29].

A new development in the field of liquid-liquid extraction is MicroSISAK based on the use of microsystem components [30]. Such a system provides separation times on the order of seconds at considerably reduced flow rates as compared to the conventional SISAK system. For mixing of the aqueous phase with the organic phase, a micro mixer is used where the phases are conducted through 2 mm long and 50 $\mu$m broad channels to a common outlet. The so-produced emulsion is subsequently separated in a filter apparatus on a filter membrane of 0.5 $\mu$m pore size. At a pressure differential of 10 mbar across the membrane and a flow rate of 0.5 ml min⁻¹, the aqueous phase is completely retained by the hydrophobic membrane while the organic phase penetrates the filter. The goal is to eventually spray the organic phase onto a moving tape where it is evaporated to dryness and assayed for $\alpha$ activity by silicon detectors thus avoiding the drawbacks of LSC. In collaboration with the Institut für Mikrotechnik, Mainz, IMM, extraction yields are being optimized for flow rates below 0.1 ml min⁻¹ [31].

For a future application to the spherical superheavy elements 112-114, the electrodeposition of these elements has been proposed [32]. It is well known that the electrochemical deposition of radionuclides in metallic form from solutions of extremely small concentrations depends strongly on the choice of the electrode material. The associated “underpotential” can deviate considerably from the Nernst potential. In a macroscopic model [32], the interaction between
the radionuclide and the electrode material has been described by the partial molar adsorption enthalpy and entropy, and a potential has been calculated that characterizes the electrode process at 50% deposition. Model calculations for Ni-, Cu-, Pd-, Ag-, Pt-, and Au-electrodes and the microcomponents Hg, Tl, Pb, Bi, and Po have confirmed the decisive influence of the electrode material on the deposition potential. The experimental determination of "underpotentials" for some of these elements [33] is in qualitative agreement with the model predictions [32]. Parameters relevant for a fast kinetics of the electrodeposition are discussed. Plans for its application to the spherical superheavy elements are presented.

References
[33] H. Hummrich, J.V. Kratz, contribution to this Conference.
DEVELOPMENT OF AN ON-LINE HOT CATCHER FOR TRANSACTINIDE RESEARCH AT PSI

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One of the most exciting results of the transactinide research within the last 5 years was the observation of isotopes of transactinide elements 112-116, in 166Ca-induced nuclear fusion reactions with actinide targets (see for review [1,2]). However, the assignment of the observed nuclides to new elements is performed only via the determination of their masses and according to their measured decay properties. Thus, the unambiguous assignment of the observed nuclides to specific elements is problematic. Chemical investigations of these nuclides may help to determine indirectly their atomic number Z. Hereby, difficulties may arise from the increasing strength of the influence of the relativistic principle on the electron structure with the increasing nuclear charge of the heaviest elements (for review see [3-6]). The amount of these so-called relativistic effects determines the chemical behavior of the transactinide elements. Due to the uncertainty of this influence, the predictions of volatility for the superheavy elements 112-118 yield broadly ranging values [7-11].

Already during the 1970-s and 1980-s it was suggested to use gas phase adsorption chromatographic methods to study the elemental transactinide s- and p-elements [12]. The extreme volatilities, predicted for some of the transactinide elements (e.g. elements 112, 114, and 118) require gas phase chromatographic techniques to run down to temperatures of about 70 K. Cleaning procedures of the carrier gases applied in gas chromatography are still not effective enough in order to provide clean chromatographic surfaces at these temperatures [13]. Therefore, working under vacuum conditions would be advantageous in terms of clean chromatographic surfaces, which are required for the determination of adsorption properties of these elements. A coupling to physical pre-separation devices, which perform also at low gas pressure conditions or even at vacuum conditions, will be comfortable. Coupling of high temperature chromatographic devices to low temperature detection techniques is also feasible in vacuum. Additionally, α-SF-fragment spectroscopy has excellent energy resolution in vacuum. An on-line hot catcher system was suggested to serve for transfer of nuclear reaction products from heavy ion induced fusion reactions to vacuum chromatographic set-ups [14,15]. The reaction products recoiling out of the target surface are implanted into the solid catcher heated up to about 1800 K. Due to thermo-diffusion, implanted atoms drift towards the surface of solid catcher and are desorbed from the catcher surface. These processes are closely related to the material constants of the solid catcher, to diffusion coefficient, and to the adsorption enthalpy of the species in or on the catcher material, respectively. In the presented experiments, several catcher materials were tested off-line in order to find out the proper catcher with high release efficiency for volatile p-elements such as Tl, Pb, Bi, and Po. Isotopes of 209210Tl and 209210Pb produced in the reaction 2389W(20Ne,xn)206Po as decay products from the Po nuclides are implanted into the catcher foil mounted just behind the target. At ISOLDE-CERN, radioactive ion beams of 222Rn and 212212Bi were implanted into various foils. The release experiments were performed in the model set-up for the PSI Hot Catcher for Transactinide Research (HOTCAT) device [15]. A detailed description will be
given in the presentation. The results of the release experiment are summarized in Figure 1. We observed that Tl, Pb, Bi, and Po were completely released from the Pt and Rh catcher at a working temperature of about 1800 K, and partly remained in the Ta-, Ti-, and graphite catchers. The release enthalpies $\Delta H_{\text{f}}^M$ were calculated from the sum of the formation enthalpies of solid solution based on the Miedema model [12] and of the desublimation enthalpies. The measured release efficiencies are closely connected to the release enthalpies (Figure 1), suggesting the applicability of the semiempirical model for such predictions. Rh revealed the best properties regarding oxidation stability under irradiation conditions and release yield for all p-elements at the given working conditions. Very stable compounds of Rh with actinide elements are known. Hence, the metal chemistry inside the catcher material will be valuable for a chemical pre-separation already in the catcher.

![Fig. 1](image.png) Release efficiencies for the p-elements from various catcher foils (at 1800 K) plotted versus the calculated release enthalpies $\Delta H_{\text{f}}^M$.

However, the connection of a hot catcher having a working temperature of about 1800K to a heavy ion target is problematic. Moreover, the handling of Be foils under vacuum conditions is critical due to overheating under strong beam intensities. Therefore, we suggest to use a hot target serving both, as target and as catcher. For the production on transactinide elements actinide targets are irradiated by $^{48}\text{Ca}$. Hence, a target backing material has to be found, which retains these actinides and which releases efficiently the transactinides. Semi-empirical calculations of the release enthalpies of various elements from a Rh matrix have been calculated based on the Eichler-Miedema model [12] (Figure 2). Radioactive tracers of various elements ($^{166}\text{Yb}$, $^{199}\text{Th}$, $^{105,106}\text{Ag}$, $^{113}\text{Sn}$, $^{23}\text{Na}$, $^{167}\text{Tm}$, $^{171}\text{Lu}$) have been produced in Rh-foils or have been implanted into Rh at the PSI Philips Cyclotron. The Rh foil was heated stepwise from 298 K to 1498 K (4 h each temperature) in a quartz apparatus in a pure H$_2$ gas flow (100 ml/min). In between the heating steps the remaining activity in the Rh catcher was determined by $\gamma$-spectroscopy. Afterwards, the Rh catcher was placed into the off-line Model-HOTCAT device and heated at vacuum conditions to about 1800 K. The resulting release yields of the tracers from the Rh catcher are presented in Figure 3.

A comparison of the release yields of the investigated elements at 1800 K (Figure 3) with their calculated release enthalpies (Figure 2) is excellent. Yb, Ag, and Te are released almost completely. Sn is released to 40%. As expected, Tm and Lu remained in the Rh metal. The only exception is Na. Having a very low release enthalpy, it is obviously the large atomic volume, which hinders its efficient diffusion within the lattice of Rh. This is a hint for an interstitial diffusion pattern of Na in Rh. Such effects have to be taken into account working with hot catcher materials. However, the beginning release of Tm from Rh allowed us to mark a lower limit release enthalpy, at which a remarkable release from Rh starts at working condi-
tions of HOTCAT (Figure 2, dashed line). Hence, except of Sm, Eu, Yb, and heavy actinides beginning from Bk, all lanthanide and actinide elements are suitable as hot targets with a Rh carrier matrix. This will be verified by further tracer studies using radioactive isotopes of lanthanides and actinides produced in heavy ion induced nuclear reactions at the PSI Philips cyclotron.

![Graph showing calculated release enthalpies](image)

**Fig. 2** Calculated release enthalpies from a Rh matrix. The dashed line indicates the beginning release at 1800K. The sublimation enthalpy of Rh (solid line) is included. Elements studied in this work are marked (black triangles).

![Graph showing measured release yields](image)

**Fig. 3** Measured release yields for various elements from Rh matrix.

**References**

CHEMICAL STUDIES OF RUTHERFORDIUM AT JAERI

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Chemical studies of element 104, rutherfordium (Rf), at JAERI (Japan Atomic Energy Research Institute) are reviewed. To perform chemical experiments of transactinide elements with single atoms on an atom-at-a-time scale, we have developed some experimental apparatuses: a beam-line safety system for the usage of the gas-jet coupled radioactive target and recoil chamber, a rotating wheel catcher apparatus for the measurement of α and spontaneous fission (SF) decay of transactinides, and an automated rapid ion-exchange separation apparatus based on high performance liquid chromatography coupled with an on-line α-particle detection system [1].

The transactinide nuclide, 78-82^{201}Rf which is commonly used for recent chemical studies of element 104, has been produced through the reaction of ^249Cm(^16O,5n) at the JAERI tandem accelerator. An excitation function of the reaction has been measured with the newly developed rotating wheel catcher apparatus MANON (Measurement system for Alpha particle and spontaneous fission events ON-line), and the maximum production cross section has been determined to be about 10 nb at around 94-MeV ^16O [2].

On-line anion-exchange experiments of Rf together with the group-4 elements Zr and Hf in acidic solutions have been conducted with AIDA (Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy). The adsorption behavior of Rf as a function of HCl concentration was quite similar to that of the group-4 elements Zr and Hf, while it was different from that of the tetravalent pseudo-homologue Th in HCl concentration of > 8 M. The results indicate that the anionic chloride complexes of tetravalent Rf, Zr, and Hf were formed in concentrated HCl. Another interesting feature was observed in the adsorption order on the anion-exchange resin among Rf, Zr and Hf. The adsorption order that reflects the stability of chloride complexation was Rf ≈ Zr > Hf [3].

Non-Th(IV)-like and non-Pu(IV)-like behavior of Rf was also probed with anion-exchange experiments in 8 M HNO₃ with AIDA. Although Th(IV) and Pu(IV) formed anionic complexes and were adsorbed on the anion-exchange resin, Rf was eluted from the column with 8 M HNO₃ as expected for a typical group-4 element [3].

Recently, we have obtained quite interesting result on the anion-exchange behavior of Rf in hydronium fluoride acid (HF) solution [4]. Variation of the adsorption behavior of Rf, Zr and Hf as a function of HF concentration was thoroughly measured. The adsorption of Zr and Hf was absolutely equal in the studied HF concentration of 1.9 – 13.9 M and it decreased steeply with HF concentration above 8 M, while that of Rf decreased over 4 M HF [4]. The lower adsorption of Rf indicates that the fluoride complex formation of Rf would be weaker than that of Zr and Hf. The observed large difference in adsorption behavior between Rf and its homologues Zr and Hf suggests that the relativistic effect strongly influences the fluoride
complex formation of Rf [4]. Presently, we are conducting relativistic molecular orbital calculations to understand the present results and to see whether the anion-exchange behavior of Rf is affected by relativistic effects.

Plans for further chemical studies of Rf and element 105, dubnium (Db), will be also discussed.

Acknowledgments
The present study at JAERI has been carried out in collaboration with RIKEN, Niigata University, Osaka University, Tokyo Metropolitan University, University of Tokushima, Kaaazawa University, Tsukuba University, Gesellschaft für Schwerionenforschung (GSI), and Mainz University.

References


PREDICTION OF IONIC RADIUS AND BINDING ENERGY OF HYDRATION FOR THE No$^{2+}$ ION BY RELATIVISTIC DENSITY FUNCTIONAL CALCULATIONS

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Since Seaborg predicted [1] that element 102 might exist in a divalent state due to the special stability of the filled 5f$^{14}$ shell configuration, nobelium received considerable attention in the actinide chemistry. Maly and co-workers performed cation-exchange chromatography and coprecipitation experiments of $^{252}$No [2]. Their experiments showed that nobelium behaves like divalent alkaline-earth elements, Sr, Ba and Ra. Silva et al. reported cation-exchange with Dowex 50 and bis(2-ethylhexyl) phosphoric acid extraction chromatography of nobelium [3]. They obtained two different behaviors of No$^{2+}$; The No$^{2+}$ ion eluted from Dowex 50 resin exactly at the Ca$^{2+}$ elution position, while the results of HDEHP extraction chromatography showed that the No$^{2+}$ ion eluted between the position of Ca$^{2+}$ and Sr$^{2+}$. Earlier theoretical calculation [4] of the radius of maximum charge density gave the calculated ionic radius of No$^{2+}$ 1.1 Å, which is located between the radii of Ca$^{2+}$ (0.99 Å) and Sr$^{2+}$ (1.13 Å). By adopting this theoretical information, Silva et al. concluded that the ionic radius of No$^{2+}$ must be between those of Ca$^{2+}$ and Sr$^{2+}$.

To discuss the chemical properties of No$^{2+}$ in solution, the ionic radius and the stability of hydration are quite informative for the evaluation of the results of one atom-at-a-time experiments. In this presentation, we will address the binding energy profiles of the hexahydrated Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and No$^{2+}$ ions. We applied the recently developed relativistic density functional calculation method [5-7] to this system. Figure 1 shows the relation between binding energy and bond distance of M$^{2+}$ - OH$^-$ [where, M = Mg, Ca, Sr, Ba and No] calculated by the relativistic density functional method with PW91 exchange and correlation functionals. As shown in Fig. 1, No$^{2+}$ behaves like Ca$^{2+}$ and the binding energies of these ions are lower than that of Sr$^{2+}$. The optimized bond distance of No$^{2+}$ is very close to that of Ca$^{2+}$ and is slightly shorter than that of Sr$^{2+}$.

Fig. 1. Potential energy curves for the hexa-hydrated Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and No$^{2+}$ ions calculated by the relativistic density functional method with PW91 exchange and correlation functionals.
DEVELOPMENT OF A GAS-LOOP SET-UP FOR THE INVESTIGATION OF THE CHEMICAL PROPERTIES OF ELEMENTS 112 AND 114

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The prediction of the chemical properties of element 112 is difficult. From the position of element 112 in the periodic table a noble and volatile metallic character (similar to Hg) is expected. On the other hand, theoretical calculations showed, that the direct relativistic effects [1] may affect the electron shell of element 112 very strongly, resulting in a very inert character, similar to a heavy noble gas (e.g. Rn) [2].

So far, experiments to investigate the chemical properties of element 112 have been performed at the FLNR in Dubna, Russia [3] and at the GSI in Darmstadt, Germany [4]. The results indicated a non Hg-like and inert behavior. In all studies the only directly produced long-lived isotope of element 112 with the mass number 283 (T_{1/2} = 5 min, SF) was used. $^{283}_{112}$ was synthesized by the nuclear fusion reaction: $^{268}_{48}$U($^{48}$Ca,3n)$^{281}$112. The disadvantage of this nuclide is its unspecific spontaneous fission (SF) decay mode, which complicates its unequivocal identification. In the GSI experiment the chemical investigation and on-line detection of element 112 was done using the thermochromatographic device Cryo On-Line Detector (COLD) [4]. The experimental results are valued as an indication for a very noble and volatile behavior for element 112. The observed high volatility of element 112 requires to run the gas chromatographic technique as low as -200°C. Difficulties rise from contaminations in the carrier gas which are deposited on the chromatographic surfaces at these low temperatures. Therefore, for the next experiments large efforts are needed in order to provide exceptional cleanliness of the carrier gas.

The next steps towards second generation experiments should be:
1. Increase the speed of the method to be able to measure the $\alpha$-particle decay ($T_{1/2} \approx 4$ s), which was recently measured for $^{283}_{112}$ [5];
2. Decrease the water vapor content in the carrier gas;
3. Improve the COLD-device to a $4\pi$-detection system, to be able to measure SF-coincidences as well as correlated $\alpha$-decay chains.

In order to speed up the transport of the nuclear reaction products to the chemical separation device, a smaller recoil chamber was designed. Therefore, a reduction of the thermalization volume is needed in which the nuclear reaction products are stopped. An Ar/He mixture is used since Ar has a much higher stopping power compared to He. The developed recoil chamber is lined inside by quartz glass and can be heated up to approx. 800°C. This heating is a mandatory for future experiments with element 114. At the outlet a getter oven is placed to collect sputtered target material and actinides that are produced in nucleon transfer reactions. In order to achieve a higher purity of the carrier gas, a gas loop is used, which can be evacuated prior to the experiment. Once the system is filled with Ar/He-gas, the metal bellow bag pump provides a constant gas flow up to 1.5 l/min. The getter oven (Ta/Ti, 1000°C) is
used to keep the gas loop dry during the experiment. The buffer is used for a reduction of the pulsations in the carrier gas caused by the pump. A trap filled with charcoal is used, in order to trap all Rn isotopes, which are able to pass the COLD detector (see Figure 1).

Fig 1 : Gas-loop set-up for future experiments with element 112

Presently, a 4π-thermochromatography detector based on the COLD technology for the efficient detection of time correlated α-decay chains and SF is under construction. It consists of an array of 32 sandwiched detector pairs, based on PIN-diodes. One side of the sandwiches will be covered by a thin layer of Au. For the identification of correlated α-α-decay chains of transactinides the interfering decay properties of the 220Rn daughters 212Bi and 212Po are problematic. 220Rn is produced in vast amounts as a transfer reaction product. Its chemical separation is not possible in the currently designed setup. However, this separation is not required for the detection of pure SF- decay or of very short α-SF correlations (t < 500ms), which is expected for 237112 (α) → 239110 (SF, T1/2 = 0.2 s) [5]. In order to suppress these interferences in further chemical investigations, e.g. of the element 114, either a coupling of the chemical experiments to physical recoil separation devices, or the development of an electronic β,α-pile-up suppression is envisaged.

We will present first results of test experiments with the described improved setup. 180Pb (Eα = 6.33 MeV; T1/2 = 4.83 s) → 182Hg (Eα = 5.87 MeV; T1/2 = 10.83 s), produced in the 152Gd(40Ar,6n)180Pb nuclear reaction at the PSI Philips-Cyclotron will be used as model system. In addition 210Rn from a 222Rn-source will be added to the carrier gas.

References

[4] S. Soverna et al., Contribution to this conference
ELECTROCHEMICAL DEPOSITION - A TOOL FOR THE INVESTIGATION OF SUPERHEAVY ELEMENT CHEMISTRY?

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The electrochemical deposition of a carrier-free radiotracer A on an electrode B leads to an electrode coverage that is much smaller than a monolayer. If the interaction of A with B is thermodynamically more advantageous than that of A with A, the deposition takes place at more positive potentials compared to the Nernst potential. This phenomenon is called underpotential deposition (upd). Calculations with a modified Nernst equation basing on physical properties of the deposited atom and the electrode metal lead to predictions for electrode potentials for the deposition of 50% of A on B (E_{50%}-values) for the element 112 to 116 [1] and their homologs Hg, Tl, Pb, Bi and Po [2]. According to these predictions, an electrochemical deposition of the probably very noble elements 112-116 might be possible.

To compare the predicted E_{50%}-values with experimental data, the potential dependence of the electrochemical deposition of Pb, the homolog of element 114, was investigated. As radiotracer, \(^{212}\)Pb was used. The deposition experiments were performed at constant electrode potentials by using a potentiostatic three electrode system with a working electrode (Cu, Pd, Ag), a Ag/AgCl reference electrode, and a Pt counter electrode. The area of the working electrode was 1 cm\(^2\). The electrolyte (1 ml 0.1 M HClO\(_4\)) was agitated with a magnetic stirrer at 600 rpm during electrolysis. Starting at positive potentials, electrolysis was continued for 10 min. After that time, the maximum possible deposition for the given potential was achieved. The working electrode was then removed under voltage and the deposited activity was determined by \(\gamma\)-spectrometry. Thereafter, the electrolysis was continued at a lower potential etc.

![Deposition graph](image)

Fig 1: Deposition of \(^{212}\)Pb on Pd, Ag and Cu from 0.1 M HClO\(_4\). The crossings of the tangents with the x-axis give the critical potentials, the dashed lines indicate the potentials at 50% deposition.

Starting at a critical potential (E_{crit}), the deposition sets in and approaches eventually 100% (Fig. 1). Apart from E_{crit}, from the potential curve, the potential for 50% deposition (E_{50%}) can be deduced. The E_{crit} and E_{50%} values for the different electrode materials differ considerably.
The comparison with the Nernst potential of about -560 mV (assuming a Pb concentration of 10<sup>4</sup> mol/l, due to inactive Pb impurities) shows unpotential deposition in all cases.

In order to use electrodeposition as a separation method for short lived radioisotopes, the electrochemical deposition must occur rapidly. Therefore, it is necessary to investigate the relevant parameters determining the deposition kinetics.

According to Joliot [4], the electrochemical deposition of radiotracer is determined by

\[
\frac{dN_{dep}}{dt} = \frac{DF}{\delta V} (KN_{tot} - N_{dep})
\]

Here, \(dN_{dep}/dt\) is the number of deposited atoms per time unit, \(N_{tot}\) is the total number of atoms in solution, \(D\) is the diffusion coefficient, \(\delta\) the thickness of the Nernst diffusion layer, \(F\) the area of the electrode, and \(V\) the volume of the electrolyte. \(K\) stands for the maximum fraction of atoms that can be deposited at a given potential. A fast deposition can apparently be achieved by a large ratio of the area of the electrode to the volume of the electrolyte, a small Nernst diffusion layer (achievable by intensive convection) and by a large diffusion coefficient. After integration and replacing the diffusion coefficient according to the Stokes-Einstein equation, Fahland [5] comes to an expression for the time after which 50% of the atoms in solution are deposited \((t_{50\%})\):

\[
t_{50\%} = \frac{\ln 2 \cdot 6 \cdot \pi \cdot V \cdot a \cdot \delta \cdot \eta}{F \cdot k \cdot T}
\]

Here, \(a\) is the hydrodynamical radius of the ion, \(\eta\) the dynamic viscosity of the solution, \(k\) the Boltzmann constant, and \(T\) the absolute temperature.

![Graph showing deposition of Pb on Pd electrodes](image)

Fig. 2: Deposition of <sup>212</sup>Pb on Pd electrodes from 0.1 M HClO<sub>4</sub> as a function of the duration of the electrolysis and the temperature of the electrolyte.

The deposition of <sup>212</sup>Pb on Pd from 0.1 M HClO<sub>4</sub> was chosen to study the temperature dependence of the deposition kinetics. The potential was fixed by a potentiostat at -500mV (vs. Ag/AgCl) which allows for a maximum deposition with \(K=1\). At given time intervals, the working electrode was removed under voltage and measured by \(\gamma\)-spectrometry. The electrolysis was repeated at different temperatures.
The $E_{30\%}$ value decreases with increasing temperature, as expected (Fig. 2). It is the influence of the viscosity that dominates; a rise of the temperature from 20°C to 90°C corresponds to an increase in the absolute temperature by a factor 1.2 (293 K $\rightarrow$ 363 K), but leads to a decrease of the viscosity by a factor of 3.2 (1 mPas $\rightarrow$ 0.32 mPas).

Underpotential deposition can also be studied by cyclic voltammetry [6]. Here, underpotential deposition becomes visible by a current peak occurring upon the deposition (re-dissolution) of the first monolayer on the electrode which is shifted positively relative to the peak associated with the deposition (re-dissolution) of the bulk.

![Cyclic Voltammogram](image)

Fig. 3: Cyclic voltammogram of the Pb deposition on Ag. $10^{-4}$ mol/l Pb$^{2+}$ in 0.1 M HClO$_4$.
Scan: 10 mV/s, (1) deposition of dissolved Ag$^+$, (2): deposition of the Pb monolayer, (3) deposition of the bulk (4) dissolution of the bulk (5) dissolution of the Pb-monolayer.

In order to compare underpotentials determined by cyclic voltammetry and the radiochemical method, the deposition of Pb on Ag was investigated. The cyclic voltammograms were recorded using a BANK M- Lab 100 potentiostat with a Ag/AgCl reference electrode and a Pt-counter electrode, that was shielded by a glass frit. The area of the Ag electrode was 2 cm$^2$, the electrolyte was 25 ml 0.1 M HClO$_4$. In Fig. 3, one observes the upp potentials for the deposition (+280mV) and dissolution of the Pb monolayer (-254mV). These values agree roughly with the radiochemically determined $E_{30\%}$-value (-230mV, see Fig. 1).

Future studies will focus on the determination of further $E_{30\%}$ and $E_{50\%}$ values for different analyte/electrode/electrolyte systems and on the comparison of the radiochemical and the cyclic voltammetric method. Additionally, the kinetics of the electrolysis kinetics will be improved. It is planned to perform online experiments with $^{206}$Pb at GSI with an automated electrodeposition and detection system.

**References**

MICROSISAK – A NEW DEVICE FOR FAST AND CONTINUOUS LIQUID-LIQUID-EXTRACTIONS ON A MICROLITER SCALE

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1. Introduction

The investigation of the chemical properties of the heaviest (transactinide) elements is of great interest in order to assess the significance of relativistic effects on the electron configuration of the transactinide elements [1]. The main problems in studies of the transactinide elements are small production cross sections ranging from the nb-level down to a few pb and their decay properties, predominantly α-particle emission or spontaneous fission (SF) with half-lives in the order of seconds. Thus, efficient and very fast separation techniques in combination with suitable detection systems have to be applied. So far, on-line gas chromatography as well as liquid chromatography and surface barrier detectors have successfully been used to study the chemical properties of Rf (Z=104), Db (Z=105), Sg (Z=106), Hs (Z=108) [2,3] and, very recently, element 112 [4,5].

Another approach in this field is the fast centrifuge system SISAK-3 [6] combined with an on-line detection system based on liquid scintillation counting (LSC) of α-particles and SF-events [7]. Flow rates between 0.3 and 3 ml/s can be adjusted to optimize the hold-up time in the detection unit with respect to the half-life of the nuclide to be investigated. However, experiments at the Paul-Scherrer-Institute (PSI) to investigate 78-s 261Rf produced in the reaction 248Cm(15O,5n) and at the Gesellschaft für Schwerionenforschung (GSI) with 4.3-s 251Rf produced in the reaction 249Cf(12C,4n) failed, mainly due to the large surplus of βγ-activity. In a recent experiment at the Lawrence Berkeley National Laboratory (LBNL), 257Rf was produced in the reaction 208Pb(110Ti,In) and the reaction products were pre-separated by means of the Berkeley Gas-filled Separator (BGS) and subsequently transferred to the SISAK centrifuges. In this way, the βγ-background was reduced significantly, thus enabling the unambiguous measurement of Rf with SISAK [8].

2. MicroSISAK

From the high flow rates inherent in the application of SISAK-3 various drawbacks result:

- High consumption of organic solvents (0.5-2 ml/s) and extracting agents. Thus, continuous recycling of chemicals during a long-term experiment is irrevocable
- LSC is the only suitable detection method for α-particles or SF-events in combination with SISAK. Other measuring techniques require either dry samples or very thin liquid films. No method was found to produce such samples in acceptable time. Furthermore, LSC suffers from poor energy resolution (about 300 keV FWHM at 7 MeV α-energy) and is also sensitive to β-particles and γ-rays interfering with the detection of α-particles.
In order to overcome these problems, a new device for continuous liquid-liquid-extraction on a microliter scale has been developed in cooperation between the Chalmers University of Technology in Göteborg, the Institut für Mikrotechnik Mainz (IMM), and the Institut für Kernchemie in Mainz. In figure 1, a schematic view of the new MicroSISAK set-up is shown. MicroSISAK consists of a stack of micro-structured discs sealed in a Ti-housing. For mixing the aqueous phase with the organic phase, a micro-mixer unit fabricated at IMM is used where the phases are conducted as two counter-flows through 2 mm long and 20-50 μm broad interdigital channels (see fig 1a). The laminated flow leaves the device perpendicular to the direction of the feed flows and - due to the small thickness of the lamellae - fast mixing takes place through diffusion [9]. The mixer can be made of titanium, stainless steel, or SiO₂. The mixed phases are then fed into a filter unit (see fig. 1b) for instant phase separation by means of a teflon filter with a pore size of 0.5-1 μm. Here, the aqueous phase is completely retained from the hydrophobic filter, while the organic phase penetrates the filter. A small differential pressure (10-50 mbar) must be applied across the membrane [10]. Table 1 comprises the dimensions and volumes of the mixer- and the filter- unit. The system is designed to provide a separation time of about 1 s at a flow rate of 0.02 ml/s.

<table>
<thead>
<tr>
<th>Overall diameter</th>
<th>Mixer unit</th>
<th>Filter unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructure</td>
<td>2 x 15 channels (20-50 μm)</td>
<td>20 x 0.4 x 0.3 mm³</td>
</tr>
<tr>
<td>Inner volume</td>
<td>2 x 1.5 mm³</td>
<td>2 x 2.5 mm³</td>
</tr>
</tbody>
</table>

Currently, experiments are performed to investigate the performance of the MicroSISAK set-up. Phase separation is checked with an aqueous NaCO₃-solution and toluene as organic phase. Aliquots of the outgoing phases are irradiated at the research reactor TRIGA Mainz. The ⁶⁰Na-activity in the two phases delivers the phase purity. It could be shown that, at flow rates of 0.002-0.04 ml/s, less than 0.5% aqueous phase contamination is in the organic phase. Next, the D-values of Gd extracted into toluene with 2-ethyl-hexyl-phosphoric acid (HDEHP) from 0.050 M HNO₃ and of Hf into toluene with dibutylphosphosphate (DPB) from 6 M HNO₃ will be determined.

The performance of the system with respect to phase separation as well as the extraction of Gd and Hf will be reported. Further experiments are planned to measure the total hold-up time of the system and to optimize the extraction yield for flow rates below 0.002 ml/s. Under these conditions, a new detection system can be applied where the outgoing organic phase is evaporated to dryness and assayed for activity by silicon detectors to overcome the limits of LSC-detection.
Figure 1: Schematic view of the new MicroSISAK-device with a microstructured unit for intense mixing of phases (1a) and a filter unit for subsequent phase separation (1b)

References

RELATIVISTIC ELECTRONIC STRUCTURE CALCULATIONS
FOR THE HEAVIEST ELEMENTS

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Recent discoveries of elements 112, 114 and 116 [1] have reinforced attempts to design sensitive experiments to identify these elements chemically. Gas-phase chromatography [2] and electrochemical depositions from aqueous solutions [3,4] are very promising techniques. From the chemical point of view these elements are very interesting since they should exhibit properties close to those of the noble gases due to the very strong relativistic effects on their electronic shells.

Though a number of predictions for these elements were made via extrapolations of properties from the lighter homologs and various semi-empirical models [5], theoretical works on the basis of fully relativistic quantum-chemical calculations were missing. They have become nowadays possible due to the developments in accurate calculational algorithms and hardware. First relativistic calculations were performed for the systems containing element 112 and Hg and the influence of relativistic effects on various properties has been elucidated.

Fully relativistic (four-component) density-functional calculations were performed by us for dimers of the element 112 and its lighter homolog Hg, M-X (M=Hg and element 112; X = Pd, Cu, Ag and Au). A relatively small decrease of about 15-20 kJ/mol in bonding was found from the HgX to 112X compounds. Accordingly, the bond lengths were increased by 0.06 Å on the average. The Mulliken population analysis has shown this effect to be a result of a decreasing contribution of the relativistically stabilized 7s-AO of element 112 to bonding. The following trend in the binding energies was predicted for 112X as a function of X: Pd > Cu > Au > Ag, in agreement with the trend obtained experimentally for adsorption of Hg on the corresponding metal surfaces.

The influence of relativistic effects on atomic properties and the volatility of element 112 and its homolog Hg has been studied using results of relativistic atomic and molecular calculations. Volatility was considered as sublimation of macro-amounts or adsorption of single atoms on inert and metal surfaces. For predictions of adsorption on metal (gold) surfaces, fully relativistic and nonrelativistic density functional theory calculations were performed for various intermetallic compounds of Hg and element 112: dimers and metal-gold cluster systems. Results show that the influence of relativistic effects on volatility is different, depending on the process. For element 112 as metal the sublimation enthalpy will be drastically decreased by relativistic effects, so that it will be the most volatile in the group, probably a gas. Upon adsorption on an inert surface, element 112 will have the strongest dispersion interaction with the surface in group 12 and hence the least volatile. On the contrary, upon adsorption on transition metal surfaces, e.g. gold, element 112 will be more volatile than Hg, though the influence of relativistic effects on
the adsorption energy is different depending on the adsorption position. For example, relativistic effects do not increase (or could even decrease) the adsorption energy of element 112 when adsorbed in on-top position, while for the hollow position, relativistic effects substantially increase the interaction energy, so that relativistically element 112 will be less volatile than nonrelativistically. Calculations have shown that the relativistic and nonrelativistic properties have opposite trends from Hg to element 112.

Thermodynamics of adsorption of Hg and element 112 in the elemental state on the gold surface of detectors of a chromatography column for gas phase chromatography experiments is considered on the basis of knowledge of the metal-metal bonding obtained from relativistic density-functional calculations. Relevant equations stemming from models of mobile and localized adsorption are offered which allow the adsorption temperature of an element to be predicted on the basis of the knowledge of the adsorption temperature of a homologous element. The present results suggest that the adsorption temperature of element 112 should be somewhere a hundred degrees below that of Hg. This relation should be valid provided experiments are conducted in the same set up under the same conditions. According to the predicted temperature, the reactivity of element 112 is expected to be somewhere between those of Hg and Rn.

Various other compounds of element 112 and Hg with various halides are also considered. The strength of complexes of element 112 in relation to that of Hg is shown to be dependent of the coordination number and the type of ligand. For high coordination compounds of element 112, relativistic effects increase bonding, while for low coordination compounds, they decrease it. As Mulliken analysis shows, it is related to different contribution to bonding of valence 6d orbitals on the one hand and 7s orbitals on the other hand.

References
FINAL RESULT OF THE CALLISTO-EXPERIMENT: FORMATION OF SODIUM HASSATE(VIII)


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Hassium, element 108, was discovered in 1984 [1] through identification of $^{263}\text{Hs}$ with a half-life of 1.5 ms. The much longer lived isotope $^{265}\text{Hs}$ with a half-life of about 10 s was observed in the two $\alpha$-decay chains of $^{277}\text{Hf}$ [2]. This half-life is sufficiently long to allow for the chemical identification of hassium. A suitable reaction for its direct production is $^{243}\text{Cm}$ (from $^{208}\text{Mg}$, Sn) $^{263}\text{Hs}$ with an estimated formation cross-section of a few picobarn.

As a member of group 8 in the periodic table, Hs should behave chemically similar to its homologues Ru and Os, which form highly volatile tetroxides. A very volatile HsO$_4$ was expected to be suitable for gas-phase separation even though earlier attempts to isolate HsO$_4$ failed [3]. More recently, several groups have adapted the in-situ production of volatile group-8 tetroxides directly behind the target [3] by adding oxygen to the He carrier gas that contains no aerosol particles [4-7]. Typically, the reaction products were transported with the carrier gas through a quartz column containing a quartz wool plug heated to some 600 °C at the exit of the recoil chamber providing a hot surface at which the oxidation of the group-8 elements to their tetroxides was completed. All volatile products were further transported through a Teflon capillary to a deposition and detection system.

In the present work, the final result of the CALLISTO project (Continuously Working Arrangement For CLusterLess Transport of In-Situ Produced Volatile Oxides) [8], started in 1998, will be presented. It was developed independently from the other major project to
investigate the chemical properties of hassium [9]. Both projects use the ability of hassium to form in-situ a volatile oxide, presumably the tetroxide, which can be transported through PTFE capillaries at room temperature. In the CALLISTO project, its tendency to undergo a chemical reaction with a substrate involving the solid and the gaseous phase was investigated. The tetroxide of osmium is well-known to behave as an acid anhydride, forming with aqueous Na$_2$OH sodium osmate (VIII) of the stoichiometry Na$_2$[OsO$_4$(OH)$_2$]. Already J.M. Jakob Berzelius described in 1828, that the gaseous OsO$_4$ can be adsorbed on humid KOH. This behaviour can be used for the deposition of OsO$_4$ on a thin layer of hydroxide directly from the gaseous phase in the presence of water, which was introduced into this system via a well-defined amount of moisturized He, since water cannot be added directly to the deposition system. The reactive layer was prepared as a thin coating onto small stainless steel plates, which were placed into a deposition and detection system. The alkaline layer was analyzed at a distance of 1 mm by an array of 16 PIN-diodes in a set-up especially developed for this experiment and described in [10]. The advantage of the latter arrangement is the combination of a continuously operating system with the possibility to change the deposition material on a regular basis without interrupting the experiment. Preliminary experiments with metallic sodium surfaces and extremely dried transport gases showed, that Os can be deposited effectively for $\gamma$-spectroscopy, but the resolution for $\alpha$-spectroscopy was not sufficient, perhaps because of fast diffusion into the surface. During a beamtime at the UNILAC November 2002 we observed one correlated $\alpha$-$\alpha$-decay chain and 5 $\alpha$-SF decay chains.

The spatial distribution of simultaneously produced Os and Hs suggests a lower reactivity of HsO$_4$ compared to OsO$_4$; but the statistics of only 6 events need to be improved by further experiments.
References
Additional information and illustrations are available in the internet at http://www.callisto.ws

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ZIRCONIUM AND HAFNIUM EXTRACTION USING CROWN ETHERS -
A MODEL SYSTEM FOR THE STUDY OF RUTHERFORDIUM

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Introduction

Recently, the fast, automated liquid-liquid extraction system SISAK was successfully used to
study the chemical behavior of element 104, rutherfordium [1]. This was made possible by
coupling the SISAK system to the Berkeley Gas-filled Separator (BGS). The BGS was used to
achieve a physical pre-separation of the desired species from the beam and unwanted reaction
products. This pre-separation reduced the background due to the scattered beam and other
reaction products substantially, and allowed for an easier detection of rutherfordium atoms.
The lack of interfering reaction products offers several advantages for the design of chemistry
experiments with transactinides. In addition to simplifying the detection and data analysis, it
allows the use of different classes of extraction systems in future experiments with SISAK or
other automated systems, as well as manual extraction experiments.

In the past, it was necessary to select extraction systems that removed all interfering reaction
products and left only the element of interest. Consequently, a very high decontamination factor
between the element of interest and interfering nuclides had to be favored over a high selectivity
between the different homologs within the group being studied. When using a physical pre-
separator, selectivity between the members of the same group of the periodic table can now be
favored over efficient separation from elements belonging to other groups when designing
extraction systems for future experiments [2]. As a result the usefulness of previously used
extraction systems should be reevaluated and other classes of extraction systems can now be
considered as well.

Based on the first successful experiments with pre-separated rutherfordium isotopes, it was
decided to start searching for different highly selective extraction systems that could be used to
study the chemistry of rutherfordium. Some of the extraction systems under investigation use
macrocyclic ligands, such as crown ethers. The high selectivity of these systems is used in a
multitude of applications in analytical and technical chemistry. The coordination chemistry of
macrocyclic ligands and alkali and earth alkali metals has been studied in depth [3], and these
ligands are commonly applied for the separation of various metal ions [4].

The kinetic of the reaction is in important factor in developing suitable extraction systems for
chemistry experiments with transactinide elements. The reaction should reach equilibrium as
fast as possible. The size of the organic molecules used as ligands can have a large effect on the
kinetics of the reaction. The use of different crown ethers, e.g., dibenzo-18-crown-6 and dicyclohexano-18-crown-6, for the separation of zirconium and hafnium has been reported previously in the literature [5, 6], but none of these studies were conducted on a time scale short enough to ensure that the reaction kinetics is fast enough to allow the study of rutherfordium.

**Experimental**

In this work, the extraction of zirconium and hafnium with dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DC18C6) from various concentrations of hydrochloric acid was studied using isotopes with short and medium half-lives. The distribution ratios for the elements were determined as a function of acid and ligand concentration. The kinetics of the reaction was studied by varying the contact time during mixing and the time allowed for phase separation. The online experiments were performed at the 88-inch cyclotron at LBNL using the short-lived isotopes $^{88}$Zr ($T_{1/2} = 7.9$ m) and $^{183}$Hf ($T_{1/2} = 3.25$ m). The isotopes were produced by bombarding a $^{150}$Gd with an $^{18}O^+$ beam and a $^{125}$Sn target with a $^{50}$Ti$^{19}$ beam, respectively. The two beams were delivered by the cyclotron as a cocktail beam. The use of this ion cocktail allowed for the fast switching between the two beams. It ensured together with the use of an adjustable target ladder in the BGS that experiments with zirconium and hafnium could be performed almost simultaneously and under virtually the same experimental conditions.

The zirconium and hafnium isotopes produced were separated from the beam and interfering reaction products using the BGS. After traveling through the BGS, the products passed through a thin Mylar window into the Recoil Transfer Chamber (RTC) [7]. Inside the RTC, the recoils were thermalized in helium and transported to the chemistry setup using a potassium chloride aerosol gas-jet. The gas-jet was operated with an average flow rate of 1.8 L/min and a pressure of 1.2 bar.

The aerosols containing the radionuclides were transported over a distance of ~15 meters and deposited on platinum foils. The aerosol residue was dissolved in 50 μL HCl of appropriate concentration and transferred to a centrifuge cone containing additional 3950 μL of the same acid. The aqueous phase was mixed with an equal volume of crown ether diluted in dichloromethane. Phases were vigorously mixed for 20 seconds and centrifuged for 20 seconds. Afterwards a 3-mL aliquot was taken from each phase and assayed using a HPGe γ-ray detector. Offline experiments were performed using $^{88}$Zr ($T_{1/2} = 83.4$ d) and $^{183}$Hf ($T_{1/2} = 70.0$ d) as radioisotopes to study the effect of longer mixing times on the distribution ratio.

**Results**

Figure 1 shows the yield for the extraction of Zr and Hf with 0.900 M DB18C6 from 8.0 – 10.5 M HCl. Both elements are extracted, the extraction yield increases with increasing acid concentration. Zr extraction starts at HCl concentrations above 8.0 M and reaches a maximum of 89%. Hf extraction begins between 8.5 and 9.0 M and reaches a maximum value of 84%. The separation factor, defined as the ratio of extraction yields for the two elements, has its maximum at the lowest acid concentration studied and decreases with increasing acid concentration.

The yield for the extraction of Zr and Hf with 0.025 M DC18C6 from 7.0 – 10.5 M HCl can be seen in figure 2. Zr and Hf are both extracted with the extraction yield increasing sharply between 7.0 and 8.5 M. It generally reaches higher values than with DB18C6. As with DB18C6
the Hf extraction starts at higher acid concentration compared to Zr. The extraction yield reaches a maximum of 91% for Zr and 88% for Hf. Both crown ethers investigated show great potential as extractants for the study of the chemical behavior of rutherfordium. They show a stronger tendency to form complexes with Zr than with Hf. Suitable experimental conditions can be chosen to separate Zr from Hf. Using similar conditions when studying the chemistry of rutherfordium, should answer the question whether Rf behaves more like Zr or Hf in this chemical system. Additional data on the extraction behavior of Zr and Hf, the influence of the ligand concentration, and the results of the study of the reaction kinetics will be presented at the conference.

![Graphs showing extraction yield vs. HCl concentration](image)

**Figure 1.** Zr and Hf extraction from 8.0 – 10.5 M HCl into 0.900 M DB18C6 in CHCl3. **Figure 2.** Zr and Hf extraction from 7.0 – 10.5 M HCl into 0.025 M DC18C6 in CHCl3.

**Acknowledgement:**

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TOWARD VOLATILE METAL COMPLEXES OF RUTHERFORDIUM - RESULTS OF TEST EXPERIMENTS WITH Zr AND Hf

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Introduction

The chemical investigation of the transactinide elements (TAN, Z ≥ 104) is a topic of great interest in recent nuclear chemistry research. The highly charged nucleus accelerates the innermost electrons to relativistic velocities thus causing contraction of spherical (s, p1/2) orbitals and expansion of the others (p3/2, d, and f), which directly affects the chemical behavior of these elements. Deviations from trends established in the periodic table may therefore occur due to these so-called relativistic effects [1,2]. In gas phase experiments, mostly volatile inorganic compounds (e.g., halides or oxides) of TAN were investigated. We refer to [3] for a recent review. For reasons such as low production cross-sections or short half-lives, but also technical challenges, more sophisticated chemical studies have not yet been possible. One restriction in present TAN research is the plasma behind the target caused by the intense heavy ion beam. "Weak" molecules (e.g., organic ligands) are immediately destroyed, thus limiting the possibilities of synthesizing chemical compounds directly behind the target to "simple" and robust inorganic compounds. It is highly desirable to expand the knowledge on the chemical behavior of the TAN to other compound classes, e.g., volatile metal complexes. The use of the Berkeley Gas-filled Separator (BGS) [4] as a physical pre-separator makes such studies possible by separating the beam from the desired TAN isotopes.

Volatile β-diketonate metal complexes

A compound class that appears suitable for such studies are the β-diketonates, i.e., coordination compounds of a metal with ligands of the structural type shown in Figure 1. The β-diketone anions are well known to act as bidentate ligands forming neutral complexes, some of which can be transferred to the gas phase without decomposition. It has been observed that the introduction of fluorine atoms leads to more volatile species [5]. In studies of Hf β-diketonates using long-lived (T1/2 ~ h) carrier-free isotopes, Fedoseev et al. demonstrated that single molecules of Hf-hfa complexes deposited at temperatures below 100°C in a temperature gradient tube [6]. Therefore, we used the hfa system for first studies of a volatile metal complex. As a first system, rutherfordium (Rf, Z=104) was chosen since 257Rf (T1/2=4.7 s) can be produced at a relatively high rate of 1-2 atoms/min at the BGS. Here, we report on experiments with the lighter homologs of Rf, zirconium (Zr) and hafnium (Hf).
Experimental and Results

Production of short-lived Zr and Hf isotopes using a heavy ion cocktail

To rule out the role of differing experimental conditions in the measurement of chemical properties, it is desirable to investigate isotopes of all homologs simultaneously. Due to their different magnetic rigidities, BGS can not forward them to the chemistry setup simultaneously. The next best approach is to switch quickly between short-lived isotopes of these elements without having to open the chemistry setup. Short-lived Zr and Hf isotopes have therefore been produced in the nuclear reactions \(^{116}\text{Ge}(^{19}\text{O},x_{n})^{139}\text{Zr}\), \(^{74}\text{Se}(^{16}\text{O},\alpha 3n)^{107}\text{Zr}\) and \(^{112,116,120,124}\text{Sn}(^{109}\text{I},x_{n})^{158,161,165,169}\text{Hf}\). Using a heavy-ion cocktail [7] of \(^{92}\text{O}^{+}\) and \(^{50}\text{Ti}^{12+}\) and a target ladder holding up to 5 targets, which can be remotely introduced into the path of the beam, allowed for a quick switching between Zr and Hf. Magnetic rigidities for all produced isotopes were measured as well as the residual range of \(^{169}\text{Hf}\) and \(^{92}\text{Zr}\) in Mylar, which is used as the BGS exit window.

Formation of volatile hfa compounds of Hf

A schematic of the experimental setup is shown in Figure 2.

![Setup schematic](image)

Figure 2: Setup used to chemically investigate volatile metal complexes at the BGS.

The beam, delivered by the 88-inch cyclotron, induced nuclear reactions in the target at the irradiation position. The beam was deflected using the BGS and did not reach the focal plane of the separator. The evaporation residues (EVR) entered the recoil transfer chamber (RTC) [8] through a 3.6-μm thick Mylar window. The RTC was flushed with 1.3 l/min He that was enriched in hfa by passing part of the gas through a bubbler containing hfa. Hfa is a liquid at room temperature. The thermalized recoils were transported to a nearby oven where the volatile complexes were formed. These were forwarded through a PFA Teflon transfer capillary to a thermochromatography (TC) setup located at a distance of 5 m. The gas-flow rate, temperature of the RTC-oven and hfa concentration in the He carrier gas were optimized to produce maximum yields. The following partial yields were measured for \(^{169}\text{Hf}\): Formation of volatile complexes: >95% of the Hf present in the RTC; transport to the chemistry setup: >95%; giving an overall yield of more than 90% for this 3.24-min isotope.

Thermochromatography experiments

The adsorption behavior of the formed compounds was investigated in on-line TC experiments by introducing them into an open quartz column with a negative longitudinal temperature gradient from +75 to -50°C. It is not possible to use a lower minimum
temperature because macroamounts of Hf present in the carrier gas deposit at about -65°C. Deposition of Hf and Zr isotopes along the temperature gradient was determined by scanning the column with a HPGe γ-detector using a lead collimator with a window of 2-cm width. Each section was counted for 2 min. A considerable fraction of the transported 169Hf passed through the chromatography column and reached an activated charcoal (ACC) trap that was installed after the exit of the column. Such traps absorb 100% of the formed species. The reminder of the 169Hf deposited at temperatures between 0 and -20°C. This is in contradiction to a deposition temperature of 40°C as reported in [9].

These first results are very encouraging and can be considered as a proof that it is indeed possible to form fragile compounds containing short-lived radionuclides produced in heavy-ion induced fusion reactions when the beam is separated. Further experiments are under way and the results will be presented at the conference.

Acknowledgements

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References

CHLORIDE COMPLEXATION OF RUTHERFORDIUM
– X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY
OF Zr AND Hf IN HCl

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1. Introduction
Chemical behavior of the first transactinide element, rutherfordium (Rf), in hydrochloric acid has been investigated by ion-exchange and solvent extraction methods together with the group-4 homologues Zr and Hf [1–5]. Recently, relativistic molecular density-functional calculations of electronic structure were performed for hydrated, hydrolyzed, and chloride complexes of Rf, Zr, and Hf [6]. The chloride complexation and hydrolysis of Rf have been discussed so far, but there are no detailed structural data of Zr and Hf in HCl that are essential to discuss the experimental results of Rf and to perform the theoretical calculations. The Extended X-ray Absorption Fine Structure (EXAFS) measurements can provide information on the local environment around the central atom such as the atomic number (Z) and the number of neighboring atoms (N) and their distance from the central atom (R). In the present work, we have measured EXAFS spectra of Zr and Hf complexes systematically in 1.0–11.9 M HCl. A change in the complex structure with the HCl concentration is discussed by referring to the anion-exchange behavior of Rf as well as Zr and Hf [5].

2. Experimental procedures
Commercially available ZrCl4 and HfCl4 powders were dissolved with 1.0–11.9 M HCl solutions to obtain 0.01 M concentration of Zr and Hf. EXAFS spectra were measured using a Si (111) monochromator at the BL27B beam line of the High Energy Accelerator Research Organization Photon Factory (KEK-PF). Measurements were performed in the fluorescence mode with a 7-element Ge detector at the Zr K edge and the Hf L edge. Curve-fitting amplitudes and phases were calculated by the FEFF7 code [7].

3. Results and discussion
Fourier transformed EXAFS spectra of the Zr and Hf complexes in 9.0, 9.5, 10.0, 11.0, 11.5, and 11.9 M HCl, which represent radial distribution functions of the atoms surrounding the central atom, are shown by solid curves in Fig. 1 together with the simulations by the FEFF7 code [7] by dotted curves. Note that the spectra shown in Fig. 1 are not corrected for the EXAFS phase shifts, δ, so that each peak position does not correspond to the real distance R. As shown in Fig. 1, two peaks for shells M-O and M-Cl with the R values of 2.21 and 2.43 Å, respectively, are shown as indicated by vertical dashed lines. At 9.0 M, only the M-O peak for M-OH2 and/or M-OH bonds (M = Zr and Hf) is seen and the octahedral complex structure of M(OH)2, 2H2O is deduced. With an increase of [HCl], the coordinated OH- or H2O are replaced with Cl- and the anionic hexachloride complex of MCl6- is finally formed at ~11.0
M for Zr and −11.5 M for Hf. It is noted that the onset of the chloride complexation for Zr is
~9.5 M, and this is lower than that for Hf (~10.0 M), indicating that the chloride complexing
strength for ZrCl$_6^{2-}$ is stronger than that for HfCl$_6^{2-}$.

Fig. 1. Fourier transformed EXAFS spectra of the (a) Zr and (b) Hf complexes in 9.0,
9.5, 10.0, 11.0, 11.5, and 11.9 M HCl (solid curves) and the simulations by the FEFF7

Previously, we measured the distribution coefficients ($K_d$) of $^{88}$Zr and $^{178}$Hf on the
anion-exchange resin CA08Y in 1.0–11.5 M HCl by the batch method [5]. In the [HCl] range
of < 8 M, the $K_d$ values of Zr and Hf are almost constant, < 10 mL g$^{-1}$, while at the higher
[HCl], the $K_d$ values increase steeply up to 1.5×10$^4$ mL g$^{-1}$ for Zr and 4.5×10$^5$ mL g$^{-1}$ for Hf
at 11.5 M. This variation of the $K_d$ values of Zr and Hf is reasonably consistent with the
change in the complex structure, M(OH)$_2$2H$_2$O $\rightarrow$ MCl$_6^{2-}$, deduced above from the EXAFS
measurements. The $K_d$ values of Zr are higher than those of Hf, reflecting the different onset
of the chloride complexation. On the other hand, the percent adsorptions (%ads.) of Rf on
CA08Y were determined in the 1893 anion-exchange experiments at 4.0–11.5 M based on the
186 α events from $^{221}$Rf and its daughter $^{217}$Rn [5]. The %ads. values of Rf increase with an
increase of [HCl] from 4.5.32 to 57.9% at 4.0 M to 97.39% at 11.5 M. This adsorption behavior
of Rf is typical of the group-4 elements Zr and Hf; and the adsorption order is Rf ≥ Zr > Hf [5].
It is expected that Rf forms the same complex structure as Zr and Hf and that the chloride
complexing strength for $\text{MCl}_n^{2-}$ is $\text{Rf} \geq \text{Zr} > \text{Hf}$.

References
ELUTION BEHAVIOR OF RUTHERFORDIUM (Rf) IN
ANION-EXCHANGE CHROMATOGRAPHY IN A HYDROFLUORIC
ACID SYSTEM

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Recently, the anion-exchange behavior of Rf in 1.9-13.9 M hydrofluoric acid (HF) solution was studied together with its homologues, Zr and Hf [1]. It was shown that the slope of the logarithm of the distribution coefficients ($K_d$) against the logarithm of the HF concentration was -2.0±0.3 for Rf that differs from the slope of -3.0±0.1 for the homologues, suggesting that the different anionic fluoride complexes are formed. The $K_d$ values of Rf were derived from the transformation of the percent adsorption (\%ads) values, which represent the percentage of the activity adsorbed on the anion-exchange column which a constant volume of solution was fed into, with the help of the relationship between $K_d$ and \%ads of the homologues. The purpose of this study is to directly measure the $K_d$ value of Rf from its elution curve in the anion-exchange chromatography with HF solution by using the modified AIDA (the Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy) [2].

The isotope $^{26}$Rf was produced in the $^{248}$Cm($^{18}$O,5n) reaction with the 94-MeV $^{18}$O projectiles delivered from the JAERI tandem accelerator. The target included 39.3%-enriched $^{152}$Gd for the simultaneous production of the short-lived $^{150}$Hf isotope. The reaction products recoiling out of the target were transported to the collection site of AIDA by a He/KCl gas-jet system. After the collection, the site was moved onto a micro-column packed with an anion exchange resin (MC1 GEL, CA08Y, 1.6 mm i.d.×7 mm). Hydrofluoric acid solution of 5.4 M
was then fed to the column with a flow rate of 0.82 mL/min. The effluent was consecutively
collected on three separate Ta disks so that a volume of 130 µL might be recovered on each of
the three. Each fraction was evaporated to dryness with hot He gas and halogen heat lamps.
Two hundred sixty microliter of 4.0 M HCl solution was thereafter fed to the column to elute
the $^{261}$Rf and $^{166}$Hf remaining in the column. The effluent was collected on a Ta disk as the 4th
fraction and evaporated to dryness. These 4 Ta disks were in turn transferred to the
$\alpha$-spectrometry station equipped with eight 600 mm$^2$ PIPS detectors, followed by
$\gamma$-spectroscopy with Ge detectors to monitor the isotope $^{169}$Hf.

The anion-exchange experiments were performed 511 times and 8, 20, 12, and 8 $\alpha$-events of
78-s $^{261}$Rf and its daughter “25-s $^{257}$No” were registered in the energy range of 8.0-8.3 MeV in
the 1st to 4th fractions, respectively. The peak volume of the elution curve for $^{261}$Rf was
observed around 200 µL while $^{169}$Hf was eluted only in the 4th fraction. In the dynamic
column method, the $K_d$ value is described as

$$K_d = \frac{v}{m_r},$$

(1)

where $m_r$ is the mass of the dry resin and $v$ is the peak volume corrected for the dead volume
of the columns. The preliminary $K_d$ value of Rf was evaluated to be 20-40 mL/g which was
approximately consistent with the previous results [1].

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SORPTION ON ANION-EXCHANGE RESIN OF DUBNIIUM AND ITS HOMOLOGUES IN HF SOLUTION

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Several experiments have been made to study the aqueous chemistry of element 105, dubnium [1]. Although difference of the complex formation strength among Db and its lighter homologues was deduced from some of the experiments in HF solution [2], enough data have not been accumulated to discuss in detail the fluoride complexations and/or relativistic effects. In the present work, we have investigated the chemical behavior of Db together with its group-5 homologues by anion-exchange chromatography in HF.

We are interested in fluoride complexing strength of Db and its group-5 homologues, Nb and Ta, and pseudo-homologue Pa on the anion-exchange resin. The sorption sequence of Ta\(\rightarrow\)Nb\(\rightarrow\)Pa in 2-15 M HF solutions was observed in the batch experiment. The adsorption on the anion-exchange of Db together with Ta in a 14 M HF solution was investigated. \(^{262}\)Db and \(^{169}\)Ta were produced in the \(^{248}\)Cm\((\text{Fr}, 5n)\) and \(^{154}\)Gd\((\text{Fr}, xn)\) reactions, respectively, at the JAERI tandem accelerator [3]. On-line anion-exchange separations of Db and Ta were performed using the Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [4]. AIDA enables us to perform cyclic discontinuous chromatographic separations in aqueous phase and automatic detections of \(\alpha\)-particles within a typical cycle time of 1 min. The reaction products recoiling out of the target were transported by a He/KCl gas-jet system to AIDA, and were dissolved with 115 \(\mu\)L of 14 M HF and fed onto the anion-exchange column (MCI GEL CA08Y, 1.0 mm i.d. \(\times\) 3.5 mm) at a flow rate of 1.2 mL/min. The effluent was collected on a Ta disk as Fraction 1 and evaporated to dryness with hot He gas and a halogen heat lamp. The products remaining in the column were eluted with 150 \(\mu\)L of 6 M HNO\(_3\)/0.015 M HF. This effluent was collected on another Ta disk and
evaporated to dryness as Fraction 2. Each pair of Ta disks, Fractions 1 and 2, was automatically transferred to an α spectrometry station equipped with eight 600 mm² PIPS detectors. After the α-particle measurement, some pairs of Ta disks were assayed by γ-ray spectrometry to evaluate the adsorption of the activities $A_1$ and $A_2$ observed in Fractions 1 and 2, respectively, and the percent adsorption ($\%_{\text{ads}}$) on CA08Y was evaluated: $\%_{\text{ads}} = 100A_2/(A_1 + A_2)$. 1702 anion-exchange separations were conducted using AIDA. 6 α singles in the 14 M HF (including one α-α-pair of correlated mother-daughter decay) and 4 in 6 M HNO$_3$/0.015 M HF (including one correlation) were registered with life times compatible with the 34 s half-life of $^{263}$Db and its daughter $^{259}$Lr. From this distribution the $\%_{\text{ads}}$ values of 45 ± 1 % for Db and >80% for Ta were obtained. The $\%_{\text{ads}}$ values of Db and Ta were converted into the distribution coefficients ($K_d$) using the relation between elution positions and the $K_d$ values examined in detail with the batch tracer method for Ta, Nb, Zr and Hf. From this relation the $K_d$ value of about 35 for Db in 14 M HF was deduced. Figure 1 shows the $K_d$ value of Nb, Ta, Pa and Db as a function of the HF concentration. The $K_d$ value of Db is larger than that of Pa (18) and smaller than those of Nb (150) and Ta (175), and the adsorption sequence Pa$<$Db$<$Nb$<$Ta was determined. The present result shows a notable difference in the sorption behavior between Db and its homologues Ta and Nb.

![Graph showing $K_d$ vs HF concentration](image)

**Fig. 1** Distribution coefficients of Nb, Ta, Pa, and Db fluoride complexes on CA08Y as a function of the HF concentration. The data from the batch experiments for Nb, Ta, and Pa are shown by closed circles, open squares and open circles, while the on-line data for Db and Ta at 14 M HF are indicated by closed triangles and arrow, respectively.
References


4. Radioanalytics
ULTRATRACE ANALYSIS OF LONG-LIVED RADIONUCLIDES BY LASER MASS SPECTROMETRY (RIMS)

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Ultrasensitive analysis of long-lived radionuclides is required in various scientific and technological fields. Traditionally, radiometric methods were and are still used for these determinations with the disadvantages of long measuring times and insufficient selectivities. Therefore, mass spectrometric techniques using ion counting are getting more and important. Accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS) have been applied [1-4], when extremely high sensitivities and isotopic selectivities are required and isobaric interferences must be prevented. Drawbacks of AMS are the high experimental expenditure and the limitation in the number of elements addressable in routine operation. These drawbacks are not valid for RIMS which has the advantages of: i) nearly complete suppression of atomic or molecular isobaric interferences; ii) good overall sensitivity with detection limits in the fg range; iii) excellent isotopic selectivity by combining the optical isotope selectivity in the laser excitation process with the isotope abundance sensitivity of a mass spectrometer.

The concept of RIMS for ultratrace analysis consists of three steps. In a first step a chemical separation of the element under investigation is performed and the isolated fraction is thermally evaporated from an atomic beam source. Multistep resonance excitation and ionization is then carried out on the atoms in the gas phase by irradiation with tunable laser light. The resulting ions are accelerated in an electric field and transmitted through a mass spectrometer with subsequent ion detection. For RIMS experimental limits of detection as low as \(10^6\) atoms per sample and isotopic selectivities of \(5 \times 10^{12}\) have been obtained.

In those cases where an extreme isotopic selectivity is not required, RIMS with pulsed laser excitation and a time-of-flight (TOF) mass measurement is used. This approach has been applied for the determination of smallest amounts of actinides, mainly plutonium, and technetium in environmental and biological samples [5]. Very recently a new laser system consisting of a commercially available intracavity doubled Nd:YAG pump laser with a repetition rate of up to 25 kHz and three titanium-sapphire lasers has been set up. This unit is coupled to a TOF mass spectrometer and is now routinely employed for isotope selective ultratrace analysis of plutonium.

The high selectivity of RIMS in collinear geometry on a fast atomic beam has been used for the fast and sensitive determination of Sr-89 and Sr-90 in environmental samples [6], as needed, e.g., in case of a nuclear accident. In this mass region the isotope shifts are small and the required selectivity cannot be reached, even with high resolution continuous wave lasers. Therefore, the velocity dependent Doppler-shift of optical resonance lines of the different isotopes together with conventional mass spectrometry is utilized.

High resolution multistep RIMS with narrow-band continuous wave (cw) lasers in combination with a quadrupole mass spectrometer (QMS) is becoming the most versatile
RIMS method [7]. The advantages of this RIMS arrangement are the excellent elemental and isotopic selectivity, the good overall efficiency, the compactness of the apparatus as well as the low instrumental efforts and operating costs. The potential of high resolution RIMS is demonstrated for the determination of Ca-41 [8,9] which has a half-life of 1.04 x 10^5 a. Ca-41 is of interest as a biomedical tracer in studying the human calcium kinetics, in meteorite investigations, and in concrete from nuclear reactors for integrated neutron dosimetry as well as for radiodating covering a time window of 10^4 to 10^5 years before present.

Single cw lasers are used for isotope selective excitation of a thermal atomic beam of calcium produced from a graphite furnace. After far-infrared laser ionization, the ions are analyzed in a quadrupole mass spectrometer with low background ion detection.

The major advantages of RIMS, namely good elemental and isotopic selectivity, low detection limits, short measuring times (~ 1 h) and easy-to-use and reliable solid state or diode laser systems allow the application of this technique for routine analysis in the ultratrace level for long-lived radioisotopes and also for other species [10].

References


RECENT DEVELOPMENTS IN PROMPT GAMMA ACTIVATION ANALYSIS

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Although early trials of this analysis method were made in the 1950s, Prompt Gamma Neutron Activation Analysis (PGAA) began to proliferate as a useful technique only during the 80s, when neutron beam facilities at research reactors became common and also the large volume, high-purity germanium gamma detectors first appeared. In spite of several apparent advantages of the method, it mainly has been used till now as a supplementary tool to other instrumental analytical techniques. The major reasons for this have been the difficulties in the evaluation of prompt gamma spectra and the lack of any proper analytical library [1].

Since both neutrons and gamma rays are highly penetrating, PGAA in most cases can be regarded as matrix-independent. That is why it does not require any sample preparation. It is also non-destructive. Practically every element can be analyzed with it, though the sensitivities of the elements vary over several orders of magnitude. Some elements (like B, Cd and many rare-earths) can be determined at very low detection limits (0.01–0.1 ppm) and most transition metals still show considerable analytical sensitivities. One of the major strengths of PGAA is in the analysis of light elements (Ca and below). In particular, hydrogen (or water) can be detected in almost any matrix in trace amounts. Due to the recent developments – partly performed by the Budapest group under the leadership of Gábor Molnár who tragically passed away in January --; more and more laboratories begin to apply this powerful technique.

PGAA facilities worldwide

The PGAA facility at the collimated thermal beam at NIST in the USA started its operation in the early eighties and has been used mainly in the analysis of food samples [2]. Another PGAA system was installed there at a guided cold neutron beam at the end of the eighties. [3] After several modifications, both systems are still in regular operation. Both neutron beams are filtered to reduce the fast neutrons and the direct gamma radiation. The spectrometers are equipped with Compton-suppressed HPGe detectors.

The PGAA facility operating on either the thermal or the cold beam at JAERI in Japan started in the early nineties. The spectrometer consists of a Compton-suppressed HPGe detector and the carefully designed shielding enables counting with a low radiation background. [4, 5]

About twenty reactor-based PGAA facilities used for analytical applications have become operational since 1982 all over the world [6]. At least six other countries have recently proposed or begun to build PGAA facilities.

Budapest PGAA facility

The PGAA facility at the Budapest Research Reactor was placed in operation in 1996. A medium size HPGe detector serves for the detection of the gamma rays; its active Compton-shielding reduces the room background by more than two orders of magnitude. As a result of
the low background environment and the sophisticated calibration procedures, high quality gamma-ray spectra can be acquired with this system. After the installation of a liquid hydrogen cold neutron source in 2000, the flux increased by more than an order of magnitude, lowering the detection limits significantly. A beam chopper has also been installed to enable counting short lived radioactive products separately [7, 8, 9].

**PGAA data library**

Our major project to date has been the establishment of a new spectroscopic library of prompt gamma lines and an atlas of spectra for every stable element from H to U (also including $^{99}$Tc). A systematic series of measurements has been performed on pure elements or simple compounds (mainly oxides) to determine the energy and intensity values of prompt gamma rays for every element. The absolute partial gamma ray production cross sections have been determined using internal standardization on stoichiometric compounds and homogeneous mixtures [10, 11].

**Applications**

The PGAA method has been validated at most of the thermal- and cold beam systems (at NIST, JAERI, KAERI, Budapest) through Certified Reference Materials (CRMs) and Standard Reference Materials (SRMs) [12]. The PGAA method has been used successfully at the thermal and cold neutron beams at the Budapest Research Reactor (BNR) for the analysis of archeological artifacts, geological, environmental and biological samples, as well as in inactive tracing of melting processes in industrial furnaces and in almost all fields of radiochemistry. For instance, the H-, Cl- and active metal content of different catalysts have been determined with this technique [13]. It has also been used in the analysis of nuclear materials. A method has been developed for the determination of the enrichment of $^{235}$U isotope, as well as the U-concentration in uranium containing samples [14]. It proved to be a unique technique in boron-geochemistry, where the analysis of B in trace amounts provides important information on the genetics of minerals. One of the major fields until now has been archeometry, e.g. the analysis of Roman silver coins, Roman bronze fibulae and Neolithic polished stone tools [15].

**References**


Isotope ratio measurements and determination of radionuclide concentration with high precision and accuracy are required for quite different applications, such as environmental monitoring and health control, age dating or applications in the nuclear industry, (e.g., quality assurance and determination of the burn-up of fuel material in a nuclear power plant, reprocessing plants, nuclear material accounting and radioactive waste control). Of the analytical techniques, inductively coupled plasma mass spectrometry (ICP-MS) possesses excellent sensitivity and precision and good accuracy for isotope ratio measurements and determination of long-lived radionuclide concentration at the ultratrace level [1,2]. ICP-MS is being increasingly applied for the precise and accurate determination of $^{235}$U/$^{238}$U isotope ratios at the trace and ultratrace level in medical samples, mostly in urine [3], in order to demonstrate possible contamination with uranium. An analytical procedure has also been developed for the determination of Pu in urine at the low attogram per ml. concentration level by double-focusing sector field ICP-MS (ICP-SFMS) [4]. One litre of urine doped with pg $^{242}$Pu was analysed after co-precipitation with Ca$_3$(PO$_4$)$_2$ followed by extraction chromatography on TEVA resin in order to enrich the Pu and remove uranium and matrix elements. Figures of merit of ICP-SFMS for the determination of Pu were studied using two nebulizers, PFA-100 and DIHEN (Direct Injection High Efficiency Nebulizer), for solution introduction with uptake rates of 0.06 and 0.58 ml. min$^{-1}$, respectively. Recovery using $^{232}$Pu tracer was about 70%. The limits of detection for $^{239}$Pu in one litre of urine, based on an enrichment factor of 100 for the PFA-100 nebulizer and 1000 for the DIHEN, were $9 \times 10^{-18}$ and $1.02 \times 10^{-18}$ g mL$^{-1}$, respectively. Of similar interest is the determination of $^{90}$Sr ($T_{1/2} = 29.1$ years) at the ultratrace level since it appears as a radionuclide in the decay series of nuclear fission and can therefore be found in nuclear waste or may be released by nuclear accidents. $^{90}$Sr in urine was measured after a careful separation in our laboratory under cold plasma conditions (optimum rf power: 750W) at the ultratrace level by ICP-SFMS [5]. The detection limit in separated fractions corresponds to the detection limit of 0.4 pg L$^{-1}$ in the original urine sample. The recovery of $^{90}$Sr, determined by the analytical method in spiked urine samples was in the range of 82-86%.
Recently, Pu contamination of the Sea of Galilee (analysing 100 L) was detected, whereby the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio of 0.17 at a Pu concentration level of 0.1 ag mL$^{-1}$ measured by MC-ICP-MS is evidence of contamination due to global nuclear fallout after the nuclear weapons tests in the sixties.

Furthermore, plutonium isotope ratios and americium were determined by laser ablation ICP-MS (LA-ICP-MS) in moss samples collected from the eastern Italian Alps. The limits of detection of LA-ICP-MS for several actinides deposited on stainless steel plates after chemical separation are at the $10^{-15}$ g g$^{-1}$ concentration level [6].

Due to instrumental progress by the introduction of the multiple ion collector ICP-MS (MC-ICP-MS) or the collision cell in order to dissociate disturbing argon-based molecular ions or to neutralize the disturbing noble gas ions (e.g., of $^{129}\text{Xe}^+$ for the determination of $^{129}\text{I}$) the determination of isotope ratio measurements of long-lived radionuclides in ICP-MS has achieved a high scientific level and a wide application field. In this way, disturbing noble gas ions (e.g., $^{129}\text{Xe}^+$) were neutralized by collision-induced reactions in a gas-filled collision cell, which is relevant for the ultrasensitive determination of $^{129}\text{I}$. Combining an on-line hot extraction of iodine from the soil sample and the collection of volatile analyte iodine in a cooling finger before transport in the inductively coupled plasma of a ICP-CC-QMS permits a direct $^{129}\text{I}$ determination in sediments with a detection limit at 0.4 pg g$^{-1}$ and $^{129}\text{I}/^{127}\text{I}$ isotope ratios at the $10^{-6}$ level in contaminated soil samples [7].

Nowadays, LA- ICP-MS is used for analysing long-lived radionuclides in proteins separated by two-dimensional gel electrophoresis.

The lecture describes the state of the art and the progress in mass spectrometry for the determination of long-lived radionuclides in quite different materials (e.g., in environmental, biological and medical samples).

SEPARATION OF PLUTONIUM AND NEPTUNIUM SPECIES
BY CE-ICP-MS AND APPLICATION TO NATURAL
GROUNDWATER SAMPLES

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Plutonium and neptunium represent the major contributors to the radiotoxicity of spent nuclear fuel after storage times of more than 100 years. Under environmental conditions they can occur simultaneously in different oxidation states. The oxidation states show significant differences in their chemical behaviour with respect to hydrolysis and complex formation with various ligands. Therefore, the determination of the co-existing oxidation states is mandatory for the understanding of the migration behaviour of these elements in the environment.

The different oxidation states of plutonium and neptunium are normally analysed by absorption spectroscopy, liquid-liquid extraction, or ion chromatography. The spectroscopic methods need rather high concentrations (>10^4 mol/l) of these elements, and the chromatographic and extraction methods can influence the redox system, so that the data obtained may not be reliable.

To use the separation performance of capillary electrophoresis (CE), it was necessary to find a sensitive detection unit for plutonium and neptunium. For trace analysis, the coupling of CE with ICP-MS is well suited [1]. In a first step, the running times for the different species of plutonium and neptunium were determined by using electrochemically prepared solutions containing the actinide ions in one oxidation state. Then, mixtures of the various species were separated and the electropherograms are shown in Fig. 1.

![Figure 1: Separation of different neptunium and plutonium oxidation states by CE-ICP-MS](image-url)
The reproducibility of CE-ICP-MS was investigated with a solution containing Pu(III), Pu(V) and Pu(V) resulting in a peak precision for plutonium of approximately 4.5% RSD (n=5) as illustrated in Table 1.

Table 1: Reproducibility of the separation of plutonium oxidation states by CE-ICP-MS.
% RSD (n=5)

<table>
<thead>
<tr>
<th>Pu species</th>
<th>Pu(III)</th>
<th>Pu(V) + unknown Pu species</th>
<th>Pu(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative amount [%]</td>
<td>31.34</td>
<td>60.27</td>
<td>8.40</td>
</tr>
<tr>
<td>Peak data [%] RSD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Migration time</td>
<td>0.22</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td>Peak area</td>
<td>4.07</td>
<td>4.50</td>
<td>4.74</td>
</tr>
<tr>
<td>Peak height</td>
<td>4.87</td>
<td>2.30</td>
<td>8.94</td>
</tr>
</tbody>
</table>

The CE-ICP-MS results were compared with UV/VIS absorption spectroscopic measurements to demonstrate their complementarity. Fig. 2 shows the absorption spectra and the electropherogram of a sample containing different oxidation states of plutonium. A good agreement of both techniques was found (Table 2).

Figure 2: UV/VIS absorption spectrum (upper part) and electropherogram (lower part) of a sample containing plutonium in different oxidation states
Table 2: Contents of Pu(III), Pu(IV), and Pu(V) in a sample as measured by absorption spectroscopy and CE-ICP-MS

<table>
<thead>
<tr>
<th>Pu species</th>
<th>Pu(III)</th>
<th>Pu(V)</th>
<th>Pu(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Spectroscopy</td>
<td>49.0 %</td>
<td>51.0 %</td>
<td>n.d.</td>
</tr>
<tr>
<td>CE-ICP-MS</td>
<td>47.5 %</td>
<td>51.9 %</td>
<td>0.6 %</td>
</tr>
</tbody>
</table>

CE-ICP-MS was also used for studies of the redox behaviour of plutonium added to natural groundwater samples, especially from Gorleben (Germany). An electropherogram obtained with Gorleben groundwater at pH 1.7, 20 h after the addition of Pu(VI) is shown in Fig. 3. The sample could be injected without a special preparation.

![Electropherogram](image)

Figure 3: Determination of the plutonium oxidation states by CE-ICP-MS 20 h after addition of Pu(VI) to a groundwater sample from the Gorleben site.

It could be demonstrated that the CE-ICP-MS method is well suited for the analysis of the different oxidation states of plutonium and neptunium in natural water samples at low metal ion concentrations.

In the future, this method will be used for the analysis of actinide species in natural water samples at different pH values relevant for the long term safety assessment of a repository for nuclear waste. Also, we plan the adoption of a diode-array detector for investigating anionic species, like humate complexes, the transfer to a fast CE-LIF system, and the combination of CE with laser mass spectrometry (RIMS) to improve the detection limit.

**Reference**

MEASUREMENTS OF ACTINIDES ON A COMPACT ACCELERATOR MASS SPECTROMETRY SYSTEM

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Accelerator mass spectrometry is an efficient method to measure long-lived radioisotopes, found in very low concentrations in the environment. Relatively small accelerators have been developed in recent years [1]. Here it will be shown, that even the heaviest elements and isotopes can be measured with such compact accelerator mass spectrometry (AMS) systems.

AMS systems at accelerator voltages of 3 – 11 MV are already used to determine low actinide concentrations in the environment [2,3]. In contrast to other mass spectrometry techniques [4], AMS has the advantage to measure isotopes avoiding molecular interferences, thus generally having lower detection limits, namely for isotopes like $^{238}$U. A drawback is the complexity of such measuring systems and the resulting costs for a measurement. New compact AMS systems are much simpler and therefore more cost-efficient. Only such systems could make the AMS technique more widely used for the measurements of actinides.

Our compact AMS system originally designed for $^{14}$C measurements was adopted for the measurement of heavy elements. Actinides injected as $\text{AcO}^-$ were stripped in argon gas to the $3^+$-charge state at a potential of 300 kV with a yield of about 15 %. This insures that any molecules are destroyed before the ions are separated in a double focusing mass filter consisting of a magnetic and an electrostatic analyser. The final ion identification was performed in a gas ionisation chamber designed for the detection of particles at low energies. An ultra-thin silicon nitrate entrance window (50 nm) makes an energy separation of particles with an energy less than 1 MeV possible. Ions with the same $m/q$ ratio but different charge state, that may pass the high-energy mass filter, can then be separated in the detector. In Fig. 1 the peak position and shape of $^{239}$Pu$^+$ and $^{159}$Dy$^+$ with the same $m/q$ is shown. Only about 25 % of the Pu$^{2+}$ has to be cut off to eliminate any $2+ \leftrightarrow 3$ energy. The compact AMS system was tested for its potential to measure different nuclides of actinides. First tests showed that the efficiency of the measurements is comparable or better for most nuclides than on big AMS systems operating at ≥4 MV. A detection limit of about 1 fg for $^{239}$Pu, $^{240}$Pu and $^{241}$Am isotopes was achieved, with potential for improvement. Only for $^{237}$Np a relatively high detection limit of 140 fg was obtained, as it could not be separated well enough from $^{238}$U. Very encouraging looks again the background on a $\text{U}_3\text{O}_8$ sample, where a $^{235}\text{U}/^{238}\text{U}$ ratio of less than $10^{-10}$ was measured.
Fig. 1: Energy spectrum of $^{166}$Dy$^{2+}$ and $^{240}$Pu$^{3+}$. Cutting off about 25% of the Pu (left of the dotted line) eliminates the $^{166}$Dy$^{2+}$ interference.

In order to show that also real environmental samples can be measured, a method to isolate Pu for $\alpha$-spectrometry from soil was adopted to get targets for the AMS measurements [5]. $^{241}$Pu tracer in diluted HCl was added to the samples and dried. After the samples were ashed at 450°C they were leached with 8 M HNO$_3$. From the filtered solution the Pu was then co-precipitated with iron hydroxide. After redissolving the precipitate in HNO$_3$, the Pu was separated from remaining impurities on a 1-X8 anion exchange resin. Iron nitrate was then added to the eluent containing Pu, before the solution was dried down and backed at 800°C. The iron oxide containing the Pu was mixed with Al pressed into target holders for the measurement.

In Table 1 the Pu concentration of 4 soil samples measured on an AMS and an $\alpha$-spectrometry system are compared. The activity of the $^{239}$Pu and $^{240}$Pu together is given, as with $\alpha$-spectrometry only the sum can be determined. The measurements are in good agreement. The ratio of $^{240}$Pu/$^{239}$Pu can be determined with AMS as well and may give additional information. Here the samples C 1 and A 9 are showing a relatively low $^{240}$Pu/$^{239}$Pu ratio compared to global fallout Pu, indicating that the Pu originates mainly from an accident with nuclear weapons that occurred near the sampling site.
Table 1: Comparison of measured $^{239-240}$Pu concentrations

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-Spectroscopy</th>
<th>AMS</th>
<th>240Pu/$^{239}$Pu</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mBq/g</td>
<td>error</td>
<td>mBq/g</td>
<td>error</td>
</tr>
<tr>
<td>F</td>
<td>9.5</td>
<td>2.40</td>
<td>6%</td>
<td>2.07</td>
</tr>
<tr>
<td>K</td>
<td>12.5</td>
<td>1.41</td>
<td>5%</td>
<td>1.44</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0.64</td>
<td>9%</td>
<td>0.67</td>
</tr>
<tr>
<td>A</td>
<td>9</td>
<td>0.06</td>
<td>17%</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Our compact AMS system originally designed for $^{14}$C measurements was successfully used for a whole range of nuclides of actinides. We could for the first time measure Pu in soil samples using the compact AMS system. The overall efficiency is comparable to that of a large tandem accelerator. Improvements are still possible making this system an affordable tool to measure isotopes of actinides without molecular interference.

References

\( \gamma \gamma \)-PERTURBED ANGULAR CORRELATION
ONE-DETECTOR METHOD (1-PAC) FOR INVESTIGATION OF
PHYSICO-CHEMICAL PROPERTIES OF MATTER

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While the nuclear decay characteristics of radionuclides can be measured exactly, the determination of their physico-chemical states in the explored systems basing on \( \gamma \)-spectroscopy is difficult if not impossible. This problem may be solved in part with a method of perturbed angular correlations (PAC) of cascade \( \gamma \)-rays. The PAC method has been developed as a sensitive tool in condensed matter science, with applications to a wide range of tasks involving nuclear hyperfine interactions (HFI) [1]. In this work a new method of the perturbed angular \( \gamma \gamma \)-correlation (PAC) measurements was developed using one HPGe detector only (1-PAC) [2]. The PAC method is based, on the one hand, on the phenomenon of an angular correlation between outgoing directions of cascade \( \gamma \)-rays emitted from the same nucleus (it is a nuclear physics constant and a characteristic of the concrete nucleus) and, on the other hand, on the perturbation of this correlation by extranuclear fields due to the interaction of a nuclear quadrupole moment Q and/or magnetic dipole moment with an electric field gradient and/or magnetic fields which arise from all surrounding extranuclear charge distributions. The time-integrated angular correlation of cascade (TIAC) \( \gamma \)-rays is given by

\[ W(\theta, \phi) = 1 + A_{22} G_2(\infty) Q_2 P_2(\cos \theta) + \ldots \]

\( A_{22} \)-angular correlation coefficients depending on spins and multipolarities of transitions; \( P_2(\cos \theta) \) - Legendre polynomials; \( Q_2 \)-solid angle correction factors; \( G_2(\infty) \)-TIAC perturbation factor. The TIAC \( W(\theta, \phi) \) of the \( ^{111}\)In cascade \( \gamma \)-ray (Fig.1) coincidences are given in Fig. 2. As for this nuclide \( A_{22} \approx A_{32} \), only \( A_{22} \) has been considered in further calculations. The solid line represents the unperturbed angular correlation (\( G_2(\infty) = 1 \)); the dotted line represents the perturbed angular correlation (\( G_2(\infty) = 0.2 \)). Experimentally, \( G_2(\infty) \approx 1 \) corresponds to solutions of \( ^{111}\)In in inorganic acids ("liquid"), while \( G_2(\infty) = 0.2 \) corresponds to the hydroxide ("solid" sample) as formed in alkaline solutions [2].

![Decay schemes of \( ^{111}\)In and \( ^{111m}\)Cd.](image1)

![Fig. 2. \( ^{111}\)In time integrated angular correlation dependencies for "solid" state and "liquid" states.](image2)
This leads to a considerable difference of 15% in the TIAC for $^{111}$In at $\theta = 0^\circ$ for "solid" and "liquid" states. The $\gamma$-spectrum of $^{111}$In (Fig. 3) has been obtained using an HPGe-detector with a beryllium window. The spectrum consists of "mono peaks" (MP) corresponding to $\gamma$- and X-ray full-energy peaks and "summing peaks" (SP) corresponding to the summing energy of these radiations in different combinations. The "summing peak" is named the "true summing peak" (TSP) in the case of the genetically related radiation (corresponding to the decay of one nucleus). It is assumed that the relative probability of recording of cascade $\gamma$-rays ($R_{\gamma_1,\gamma_2}$) in TSP at the individual values of $A_{m}, G_{o}(\omega)$ and $Q_i$ is equal to TIAC $W(\theta=0')$ with $R_{\gamma_1,\gamma_2} = W_{\gamma_1,\gamma_2}(\theta = 0', \infty)$.

Fig. 3. The $\gamma$-spectrum of $^{111}$In obtained using an HPGe-detector. 1 - X-ray peaks ($K_{o}$); 2,4 - cascade $\gamma$-ray full-energy peaks (171.3 keV and 245.4 keV); 3,5 - summing of an X-ray and a cascade $\gamma$-ray full-energy peak; 6,9 - accidental coincidence peaks (171.3 keV + 171.3 keV and 245.4 keV + 245.4 keV); 7 - summing of cascade $\gamma$-ray peaks (171.3 keV + 245.4 keV); 8 - triple summing peaks (171.3 keV + 245.4 keV + $K_{o}$).

The first observations of a change in the sum peak intensity due to changes in the chemical environment were reported for $^{181}$Hf compounds by De Bruin et al. [3] and for $^{111}$In compounds by Yoshihara et al. [4]. However, proposed methods had not received practical applications. In our approach for quantifying the perturbation factor [2], the ratio $R_{\gamma_1,\gamma_2}$ of the summing peak composed of two $\gamma$-rays (the perturbation-affected parameter) to the summing peak composed of one $\gamma$-ray and X-ray (the perturbation non-affected parameter) was used. For $^{111}$In the following calculations were applied:

$$R_{\gamma_1,\gamma_2} = \frac{N_{m} S_{m,\gamma_1}\cdot S_{m,\gamma_2}}{S_{\gamma_1}\cdot S_{\gamma_2}\cdot S_{m,\gamma_1\gamma_2}}$$

where $S_{m}$ - MP area, $S_{m,\gamma_1\gamma_2}$ - SP area and $N_{m,\gamma_1\gamma_2}$ - constants. Analogue calculation procedures were developed for $^{111}$In Cd ($A_{22} = +0.16$) and $^{154}$Eu ($A_{22} = +0.23$).

**Experimental:** Chemically inert electrolytes of type HCl / NaClO4 / NaOH (for hydrolysis reactions) and identical systems containing DTPA in addition (for complex formation reactions) were prepared from high-grade pure chemicals. The volume of the samples was 500 $\mu$L using polyethylene Eppendorf vials. The measurements were carried out at room temperature. Measurements have been carried out with a coaxial HPGe detector.
For $^{111}$In the experimental data are summarized in Fig. 4. The $R_{H^+Z^2}$-values reflect the transition of the species of In(III) in the systems explored: $[\text{In(H}_2\text{O})_6]^{3+} \rightarrow \text{In(OH)}_3(c)$ (without DTPA) and $[\text{In(H}_2\text{O})_6]^{3+} \rightarrow \text{InDTPA} \rightarrow \text{In(OH)}_3(c) \rightarrow \text{In(OH)}_4^-$ (with DTPA). 1-PAC measurements were also performed for $^{154}$Eu and $^{111m}$Cd (Table 1). Each individual chemical form is represented by its species-specific $R_{H^+Z^2}$-value.

![Fig. 4](image)

Fig. 4.
The $R_{H^+Z^2}$ dependencies for $^{111}$In in aqueous solutions of different pH as measured by means of 1-PAC method.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Electrolytes / Compounds</th>
<th>$R_{H^+Z^2}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{154}$Eu</td>
<td>1 M HClO$_4$</td>
<td>1.1945</td>
<td>0.0043</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>0.01 M HClO$_4$</td>
<td>1.1946</td>
<td>0.0043</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>EuDTPA</td>
<td>1.1519</td>
<td>0.0040</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>Eu(OH)$_3$(c)</td>
<td>1.1176</td>
<td>0.0041</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>EuF$_3$(c)</td>
<td>1.0964</td>
<td>0.0040</td>
</tr>
<tr>
<td>$^{111m}$Cd</td>
<td>0.01 M HClO$_4$</td>
<td>1.095</td>
<td>0.007</td>
</tr>
<tr>
<td>$^{111m}$Cd</td>
<td>Cd(OH)$_2$</td>
<td>0.972</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Conclusion:** It was shown, that reproducible and reliable values of $R_{H^+Z^2}$ can be obtained by the proposed 1-PAC method. Each individual chemical form of the radionuclide considered is represented by its species-specific $R_{H^+Z^2}$-value. Besides the above-mentioned nuclides it might be possible to use other radionuclides such as $^{199}$Hg, $^{133}$Ba, $^{204}$Pb and $^{118m}$Sb in the 1-PAC method as well.

**Acknowledgements:** This work was supported by grants RFFI 03-03-32120a and DFG RUS-113/24. Acknowledgement is made to the crew of the research reactor BER II at the Hahn-Meitner-Institute Berlin for the radiation.

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COMPLEX FORMATION OF In(III) WITH D-Gluconate AND Glycolate IN NEUTRAL AQUEOUS PERCHLORATE SOLUTIONS IN WIDE RANGE OF pH


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The mechanism of complexation of In(III) with D-gluconate and glycolate (Fig.1) was investigated in chemically inert aqueous perchlorate solutions with an overall ionic strength \( \mu = 0.1 \) at \( \text{pH} = \text{7.0(3)} \) and \( \text{pH} = 12.50(2) \) both by the method of perturbed angular \( \gamma-\gamma \) correlation measurements using one HPGe detector only (1-PAC) and by an electromigration technique.

![Molecular structure of glycolic acid (a) and D-glyconic acid (b)](image)

Figure 1. Molecular structure of glycolic acid (a) and D-glyconic acid (b)

Hydroxycarboxylate ligands, such as D-gluconic acid, have found industrial applications as sequestering agents for metal ions. The complexation reactions are not understood in detail, but under alkaline condition higher stability of complexes was found [1]. At high pH hydroxyl group seems to be involved in the coordination. Furthermore, under highly alkaline condition, hydrolysis of metals and complex formation overlap. All of this complicates interpretation of the experimental data and diminishes the spectrum of applicable analytical methods.

The underlying physical phenomena of \( \gamma\gamma\text{PAC} \) methods are (i) an angular correlation between outgoing directions of cascade \( \gamma \)-rays emitted from the same nucleus, (ii) the perturbation of this correlation by extra-nuclear fields due to the interactions of a nuclear quadrupole moment \( Q \) and/or a magnetic dipole moment with an electric field gradient and/or a magnetic field caused by interaction of the nucleus (lifetime of the intermediate level: > ns) with its chemical environment (hyperfine interaction). Perturbed angular \( \gamma-\gamma \)-correlation (PAC) measurements using one HPGe detector only (1-PAC) were described in detail elsewhere [2]. In the case of \( ^{111}\text{In} \), two consecutive \( \gamma \)-quanta (\( E_1 = 171.4 \) and \( 245.3 \) keV) are emitted following the EC-decay with a lifetime of the intermediate level of 85 ns. The relative probability of recording the cascade \( \gamma \)-rays \( \gamma_1, \gamma_2 \) in the true summing peak \( R_{\gamma1\gamma2} \) (the
perturbation-affected parameter) reflects information about the chemical environment. The reliable, reproducible values of \( R_{\gamma_{1},\gamma_{2}} \) can be obtained using the true summing peak composed of two cascade \( \gamma \)-rays (the perturbation-affected parameter) and the summing peak composed of one \( \gamma \)-ray and one \( K_{x} \) (the perturbation non-affected parameter). For \( ^{111} \text{In} \) in the \( R_{\gamma_{1},\gamma_{2}} \) value increases with increasing molecular mass of the species and is maximum for the solid state.

The free-electrolyte continuous electromigration technique and the analytical procedure for the on-line determination of absolute migration velocities of radio-ions are well known and described in detail elsewhere [3].

No-carrier-added \( ^{111} \text{In} \) (T1/2 = 2.81 d) was purchased from Mallinkrecht, in 0.1 M HCl stock solution with a specific activity of 370 MBq/ml. Aqueous solutions of type NaL / NaClO4 / NaOH were prepared for the investigations, where NaL represents sodium glycolate or D-gluconate. Appropriate amounts of NaOH were added to the solutions to adjust their pH to 7.0(3) and 12.50(3), while maintaining a constant overall ionic strength of \( \mu = 0.1 \). For all measurements carrier amounts of \( 10^{-5} \) M indium (III) perchlorate were added.

1-PAC measurements were performed using polyethylene vials ("Eppendorf") of 2 ml volume. The activity of the samples was 40-50 kBq. The volume of each sample was 0.5 ml. The measurements were carried out with a coaxial HPGe detector of 250 cm² volume, 64.8% relative efficiency (1332 keV) at room temperature.

The overII ion mobilities were measured at \( T = 298.1(1) K \) at an electric field intensity of 10 V/cm. About 1-2 \( \mu L \) of the \( ^{111} \text{In} \) solutions (100-200 kBq) were injected into the electromigration tube, which contains the electrolyte.

In the region of \( pH \approx 6-12.7 \) \( \text{In(III)} \) forms an insoluble hydroxide \( \text{In(OH)}_{3}(c) \). The individual \( R_{\gamma_{1},\gamma_{2}} \) -value for this species is \( R_{\gamma_{1},\gamma_{2}} = 0.963(14) \) and is close to the literature value [2]. In order to investigate the influence of the \( pH \) on the mechanism of complexation of D-gluconate and glycolate, the dependencies of \( R_{\gamma_{1},\gamma_{2}} \) -values on the concentration of the ligands were measured at \( \text{pH} = 7.0(3) \) and \( \text{pH} = 12.50(2) \) (Fig. 2a). For D-gluconate concentrations of \( < 7 \times 10^{-3} M \), at \( \text{pH} = 7.0(3) \) the \( R_{\gamma_{1},\gamma_{2}} \) -values correspond to those of \( \text{In(OH)}_{3}(c) \). With increasing ligand concentration the \( R_{\gamma_{1},\gamma_{2}} \) -values decrease, reflecting dissolution of the hydroxide. At \( \text{pH} = 12.50(3) \), formation of \( \text{In-D-gluconate complexes} \) was obtained at lesser concentration of the ligand, i.e. already at \( > 10^{-4} M \) (Fig. 2a). For glycolate, the dissolution of the hydroxide occurred at \( [L] > 4 \times 10^{-2} \) M independent of the \( \text{pH} \) of the medium. Glycolate has a lower tendency for complex formation compared with D-gluconate.

To determine whether the hydroxyl groups are involved in the complexation, the overall ion mobilities of the \( \text{In(III)}/\text{D-gluconate complexes} \) were measured at \( \text{pH} = 7.0(3) \) and \( \text{pH} = 12.50(2) \) in the range of the ligand concentration \( 10^{-3} \) - \( 10^{-1} M \) (Fig. 2b). At \( \text{pH} = 7.0(3) \) the \( \text{In} \) species migrate as cations. The corresponding stoichiometry may be represented by the following equilibrium: \( \text{InL}^{2+} \rightarrow \text{InL}^{3+} \rightarrow \text{InL}^{5+} \). Estimations of the direction and velocity of the migration thus lead to the conclusion, that at \( \text{pH} = 7.0(3) \) the ligand has a charge of 1- (monodentate coordination), corresponding to the dissociation of carboxylic groups. At \( \text{pH} = 12.50(2) \) the ligand is 2- charged (bidentate coordination), corresponding to an additional dissociation of one of the hydroxyl groups.

Changes of the mechanism of complexation from mono to bidentate coordination for D-gluconate were found to occur at \( \text{pH} > 11 \).
Figure 2. (a) $R_{\text{eff}}$ value versus D-glycogen concentration. NaL / NaOH / NaClO$_4$ electrolytes, $\mu = 0.1$, room temperature, $C_{\text{In}[\text{II}]} = 10^{-3}$ M, at pH = 7.0(3) (circles); at pH = 12.50(3) (triangles); (b) overall ion mobility of $^{111}$In$^{3+}$ species versus D-gluconate ligand concentration. NaL / NaOH / NaClO$_4$ electrolytes, $\mu = 0.1$, $T = 298.1(1)$, $C_{\text{In}[\text{II}]} = 10^{-3}$ M, at pH = 7.0(3) (circles); at pH = 12.50(3) (triangles).

References
FREE-ION SELECTIVE RADIOTRACER EXTRACTION (FISRE) - A NEW TECHNIQUE TO STUDY THE LABILITY OF METAL COMPLEXES IN RADIOPHARMACY

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Introduction
Metal complexes play an important role in many different parts of our lives. Depending on their application the stability of these complexes in the corresponding systems is mandatory. In literature the stability of these complexes is commonly expressed by the stability constant K. However, these constants are usually determined assuming thermodynamic equilibrium of the system. If we consider only two typical situations where metal complexes are usually studied, namely the application of such compounds in radiopharmacy and nuclear medicine, and the investigation of humic or fulvic acid complexes in the environment, it becomes clear, that thermodynamic equilibrium is not always given. Instead we have to consider the lability of a complex, which is a kinetic parameter and is defined as the ability of a metal complex to dissociate into a free metal ion and the ligand it was originally bound to. This lability can be expressed by the association rate constant $k_a$ and the dissociation rate constant $k_d$. For a first order reaction they are given by

$$M^m + L^n \xrightleftharpoons[k_d]{k_a} (M-L)^{m+n}$$

where $M^m$ is the free metal ion with charge m, $L^n$ is the free ligand with charge n and $(M-L)^{m+n}$ is the metal complex with charge m+n, respectively.

Free-Ion Selective Radiotracer Extraction (FISRE) is a technique based on the use of radionuclides of high specific activity, which allows us to distinguish between the two metal species $M^m$ and $(M-L)^{m+n}$. By performing these ion selective extraction experiments as a function of time we can obtain $k_a$ and $k_d$ for the metal complex under investigation. Several experiments were performed with simple cobalt complexes to generally improve the technique then first experiments were performed to measure the lability of Lu-DOTA, which is investigated in nuclear medicine for applications in radiotherapy.

Experimental set-up
FISRE can be operated in two different modes: for determination of dissociation rate constants the continuous mode is used, association rate constants are measured in batch mode. For both methods a Chelex column is saturated with the (non-radioactive) metal of interest, the eluent consists of a solution of the free (non-radioactive) metal ion. The
radionuclides used were $^{60}$Co, which was obtained commercially and $^{177}$Lu, which was produced through $^{176}$Lu(n,γ)$^{177}$Lu or $^{176}$Yb(n,γ)$^{177}$Yb(β)$^{177}$Lu, respectively. 

Dissociation constants are determined by injecting a small volume of a solution, containing the metal complex of interest in thermodynamic equilibrium, to which a small amount of radioactive metal has been added. After injection the complex passes the column, where (radioactive and non-radioactive) metal ions which have just been released from the complex can associate again with (non-radioactive) metal ions present on the column. The experiment is repeated using different flow rates (=contact time with the column). The ratio of radionuclide in the original sample and after extraction is plotted against the contact time and $k_d$ can be obtained from the graph according to equation 1.

$$\left\{\text{(radioactive } M - L \text{)}^{m+n}\right\}_t = \left\{\text{(radioactive } M - L \text{)}^{m+n}\right\}_{t_0} \cdot e^{-k_d \cdot t} \tag{1}$$

Association constants are obtained by injecting small volumes of the sample containing the metal complex at certain times after addition of the radionuclide. In this way the incorporation of the radionuclide into the system can be followed for constant contact times until thermodynamic equilibrium is reached. Mathematical analysis of the data yields $k_a$:

$$\left\{\frac{\text{(radioactive } M - L \text{)}^{m+n}}{\text{(radioactive } M^p L^q)}\right\}_t = \frac{k_a \cdot \left\{L^q\right\}_t}{k_d + k_a \cdot \left\{L^q\right\}_t} \cdot \left(1 - e^{-(k_d + k_a) \cdot (L^q) \cdot t}\right) \tag{2}$$

Results and discussion

Influence of several salts on the $k_d$ of Co-NTA

Four different salts (NaCl, NaNO₃, CaCl₂, Na₂SO₄) were added to the system for ionic strength and their influence on the $k_d$ was measured (Table 1). The concentration of the salts was 1 mM.

Table 1: $k_d$ values for Co-NTA using different salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>$k_d$ s.d. (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.139 0.01</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.104 0.02</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.114 0.01</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.130 0.01</td>
</tr>
<tr>
<td></td>
<td>0.520 0.07</td>
</tr>
</tbody>
</table>

The fit for all experimental data was very good except when CaCl₂ was added. In this case it was assumed that the complexation of Co-NTA yields two complexes with different $k_d$'s. The results were re-fitted using the following equation:

$$\left\{\frac{\text{radioactive } M - L}{\text{radioactive } M - L_1}\right\}_t = \left\{\frac{\text{radioactive } M - L_1}{\text{radioactive } M - L_2}\right\}_{t_0} \cdot e^{-k_d \cdot t} + \left\{\frac{\text{radioactive } M - L_2}{\text{radioactive } M - L_2}\right\}_{t_0} \cdot e^{-k_d_1 \cdot t} \tag{3}$$

The resulting fit is shown in figure 1. For comparison the fit for only one $k_d$ is also shown.
Figure 1: Fitting functions for one and two different $k_d$ values when CaCl$_2$ was used as salt

Determination of $k_d$ for Lu-DOTA

Table 2 shows the $k_a$'s and $k_d$'s obtained for three measurements of Lu-DOTA at pH=4.3.

Table 2: $k_a$, $k_d$ and log K values for Lu-DOTA at pH=4.3

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$k_a$ (min$^{-1}$)</th>
<th>$k_d$ (min$^{-1}$)</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9.4·10$^3$</td>
<td>8.3·10$^3$</td>
<td>6.0</td>
</tr>
<tr>
<td>II</td>
<td>3.8·10$^3$</td>
<td>8.2·10$^3$</td>
<td>5.7</td>
</tr>
<tr>
<td>III</td>
<td>6.4·10$^3$</td>
<td>8.8·10$^3$</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The table shows that different values were found for $k_a$ for the three measurements. However, the $k_d$ and log K values are identical. The variation in the $k_a$ values is probably caused by the fact that due to the decay of $^{177}$Lu a larger volume of the $^{177}$Lu solution had to be added to the original sample for the later experiments. The $^{177}$Lu was kept in nitric acid and addition of higher volumes automatically caused a decrease of the pH value. Since the complex association of Lu-DOTA is strongly depending on the pH value, the lower pH value had a direct influence on the $k_a$ value. The calculated log K values can not be directly compared to the literature values for Lu-DOTA, since a simplified complexation model has been used for the analysis our results. For a detailed calculation all possible species of Lu and DOTA ($H_4$DOTA, $H_3$DOTA$^-$, $H_2$DOTA$^{2-}$, HDOTA$^{3-}$, DOTA$^{4-}$) have to be taken into account.

Future work

In several preliminary experiments FISRE has been shown to be a powerful technique for determining the association and dissociation rate constants for metal complexes. However, several improvements of the technique are necessary: different materials for separating the metal species involved should be investigated. Also, column preparation and filling is so far performed manually and should be automated. Experiments with medically interesting compounds should be performed using different buffers and under physiological conditions. Another application of FISRE is the investigation of lanthanide and actinide complexes with humic and fulvic acid. Such experiments could contribute to the basic understanding of the kinetic behaviour of these elements after release into the environment.
ANALYTICAL CAPABILITIES OF THE NEW THERMAL NEUTRON PROMPT GAMMA-RAY ACTIVATION ANALYSIS INSTRUMENT AT THE NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY CENTER FOR NEUTRON RESEARCH

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A new thermal neutron prompt gamma-ray activation analysis (PGAA) instrument was designed and built to replace the original PGAA system [1] at the National Institute of Standards and Technology’s Center for Neutron Research. The new PGAA instrument was constructed to achieve a reduction of the fast neutron beam component, a reduction of background gamma-radiation (including gamma-ray lines that directly interfere with element analyses, low-energy scattered gamma rays, and Compton scattered gamma rays), improvement in element sensitivities and limits of detection (LODs), and a simplified instrument set-up procedure.

By placing a sapphire filter in the neutron beam shutter assembly, the fast neutron fluence rate was reduced by a factor of five and low-energy (50 keV to 200 keV) gamma-ray intensities were reduced by factors of 5 to 10 (see Figure 1). The thermal neutron fluence rate was reduced by only a factor of 1.13. A new external beam tube, sample chamber, beam stop, and support structure were built and a new detection system installed. The new beam tube is made of two cylindrical aluminum sections lined with a lithiated polymer. Both sections are kept under vacuum to reduce the number of neutrons scattered by air into the beam tube walls. The sample chamber is also fabricated from aluminum and lined with lithiated polymer, and may be evacuated to minimize the number of neutrons scattered and absorbed by air. The beam tube and sample chamber assembly is suspended from the aluminum support structure.

The detection system consists of a 40% efficient (relative) germanium detector (resolution 2.0 keV at 1332.5 keV) and a bismuth germanate Compton suppressor. The detection system is shielded by lead, surrounded by borated and lithiated polyethylene, and clamped onto a table which is attached to the support structure. The new, more compact beam stop is welded to the support structure. Capture gamma-ray photopeaks from hydrogen, boron, carbon, nitrogen, sodium, aluminum, iron, germanium, iodine, and lead in the background spectrum were either of lower intensity or eliminated with the new PGAA instrument.

Element sensitivities for the new system were determined by PGAA of several standards that have been used previously and of some newly prepared standards. In general, the new instrument provides element sensitivities that are 5% to 50% higher than those...
obtained using the older instrument. Limits of detection have been greatly reduced compared with those of the original instrument due to reduced Compton and scattered gamma-ray backgrounds (especially in the low energy region), increased sensitivities, and reduction of background gamma-ray photopeak intensities. Recent applications include the determination of boron, chlorine, and potassium in Standard Reference Material (SRM) 1575a Pine Needles, hydrogen, boron, sulfur, chlorine, and zinc in SRM 1848 Lubricating Oil Additive Package, and cadmium in SRM 2702 Inorganic Sediment. Research is in progress to determine nitrogen in residual fuel oil.

![Graph](image)

Figure 1. Low energy region of PGAA spectra of a 0.74-g portion of SRM 1632c Trace Elements in Coal acquired using the original PGAA instrument before (gray, upper trace) and after (black, lower trace) installation of the sapphire beam filter.

Reference

REMOVAL OF ACTINIUM FROM EUROPIUM
FOR THE DETERMINATION OF SPECIFIC RADIOACTIVITY
OF ULTRA LOW-LEVEL Eu-152 IN A SAMPLE EXPOSED TO
ATOMIC-BOMB NEUTRONS IN NAGASAKI

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1. Introduction
Measurements of specific radioactivities of residual neutron-induced radionuclides such as
\(^{152}\text{Eu}\) and \(^{54}\text{Co}\) have been carried out to check the validity of a series of computer calculations
employed for the atomic-bomb neutron dosimetry in Hiroshima (exposed to uranium bomb) and
Nagasaki (exposed to plutonium bomb)[1]. The use of these nuclides for atomic-bomb
neutron dosimetry, however, has been limited by the following difficulties: (1) today, these
radionuclides are found only at extremely low concentrations in materials exposed to the
atomic-bomb and (2) the neutrons that induced these radionuclides were thermal and
epithermal, while the neutron dose received in Hiroshima and Nagasaki is attributable to fast
neutrons. In order to overcome the first difficulty, we established a chemical procedure to
extract Eu and Co from materials exposed to the atomic-bomb, and the chemical procedure
has been successful for the materials exposed to atomic-bomb within 1400 m in slant distance
from the explosion point [2, 3]. As for Nagasaki, materials exposed in the distances farther
than 1200 m have never been subjected to the measurement of residual neutron-induced
radionuclides. In this work, determination of specific radioactivity of \(^{152}\text{Eu}\) (half-life: 13.542
y) in a sample exposed to Nagasaki atomic-bomb at a distant place from the explosion point
was undertaken. But, because of radioactive decay during this ~60 years since 1945 and long
distance from the explosion point, the present specific radioactivity of \(^{152}\text{Eu}\) in the sample is
extremely low (estimated to be ~3 \times 10^{−4} \text{ Bq/152Eu/mg-Eu}), and a serious problem is
interferences from daughters of \(^{227}\text{Ac}\) (half-life: 21.8 y) in the measurement of ultra low-level
radioactivity of \(^{152}\text{Eu}\). Hence, our chemical procedure to obtain Eu-enriched counting source
should be improved, and much attention is being denoted to removal of Ac from Eu.

2. Experimental
About 19 kg of concrete sample was obtained from the outer surface of a building exposed to
Nagasaki atomic-bomb at a distance 1596 m from the explosion point. From the concrete
sample ~9.6 kg of andesite (used as osteodentin) and ~7.7 kg of mortar were separated.
Because preliminary neutron activation analysis demonstrated that Eu concentration in the
andesite fraction (0.96 ppm) was higher than that in the mortar fraction (0.41 ppm), ~7.8 kg
aliquots of andesite were subjected to chemical procedure to separate rare-earth elements
(REEs) including Eu. After total decomposition of pulverized andesite by fusion with
sodium hydroxide, removal of major elements (such as Si, Al, Fe, Ca, Na, K, and Mg) was
carried out by precipitation, solvent extraction and ion-exchange column methods. A crude
specimen thus obtained was subjected to preliminary measurement of Eu and radionuclides.
The crude specimen enriched in REEs from total decomposition and chemical procedures to obtain purified specimen almost free from major elements and Ac. For
the purpose to remove Ac from REEs, after the removal of major elements, solvent extraction using 1M HDEHP-benzene was applied to the fraction of REEs in dilute nitric acid medium.

3. Results and discussion
Preliminary measurements of Eu and radionuclides in the crude specimen revealed that the content of $^{227}$Ac daughters in the specimen was too much to determine low-level radioactivity of $^{152}$Eu. By a series of tracer experiments using $^{152}$Eu and $^{228}$Ac, it was confirmed that solvent extraction in 1M HDEHP-benzene/dilute HNO$_3$ system is efficient to remove Ac from Eu (Figs. 1 & 2). For the actual crude specimen enriched in REEs, Eu and Ac were first extracted into 300 mL of 1M HDEHP-benzene from 300 mL of 0.1 M HNO$_3$ solution, and the organic phase was then washed with five 300 mL portions of 0.2 M HNO$_3$. Some results of enrichment and purification of Eu from the atomic-bombed sample are given in Table 1. Although the overall recovery of Eu in the purified specimen is only ~26 %, by removing Ac from Eu, it has finally become feasible to detect radioactivity of $^{152}$Eu. The measurement of $^{152}$Eu radioactivity in the purified specimen should be continued at least ~3 months.

![Fig. 1](image1.png)  ![Fig. 2](image2.png)

**Fig. 1.** Extraction of Eu and Ac from HNO$_3$ solution into 1M HDEHP in benzene.  **Fig. 2.** Separation of Eu and Ac extracted in 1M HDEHP in benzene by washing the organic phase with 0.2 M HNO$_3$.

**Table 1.** Results of Eu enrichment and removal of Ac by the present chemical procedure.

<table>
<thead>
<tr>
<th>Sample, Specimen</th>
<th>Mass/g</th>
<th>Eu content/mg (Recovery)</th>
<th>La content/mg (Recovery)</th>
<th>$^{227}$Ac content/Bq (Recovery)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesite</td>
<td>7755</td>
<td>7.44 (~100 %)</td>
<td>109 (~100 %)</td>
<td>5.41 (~100 %)</td>
</tr>
<tr>
<td>Crude specimen</td>
<td>53.76</td>
<td>4.93 (~66 %)</td>
<td>74.9 (~69 %)</td>
<td>3.87 (~72 %)</td>
</tr>
<tr>
<td>Purified specimen</td>
<td>0.573</td>
<td>1.91 (~26 %)</td>
<td>not detected</td>
<td>not detected</td>
</tr>
</tbody>
</table>

**References**
DESTRUCTIVE RADIOCHEMICAL ANALYSIS OF URANIUM SILICIDE FUEL FOR BURNUP DETERMINATION

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During the design phase of the French research reactor Jules Horowitz (RJH) several types of low enriched uranium fuels (LEU), i.e. < 20% 235U enrichment, are studied as possible candidate fuel elements for the reactor core. One of the LEU fuels that is taken into consideration is an uraniamisilicide based fuel with U3Si2 dispersed in an aluminium matrix. The development and evaluation of such a new fuel for a research reactor requires an extensive testing and qualification program, which includes destructive radiochemical analysis to determine the burnup of irradiated fuel with a high accuracy. In radiochemistry burnup is expressed as atom percent burnup and is a measure for the number of fissions that have occurred per initial 100 heavy element atoms (%FIMA). It is determined by measuring the number of heavy element atoms in the fuel and the number of atoms of selected key fission products that are proportional to the number of fissions that occurred during irradiation. From the few fission products that are suitable as fission product monitor, the stable Nd-isotopes 144Nd, 146Nd, 148Nd, 150Nd and the gamma-emitters 137Cs and 137mCe are selected for analysis. Samples from two curved U3Si2 plates, with a fuel core density of 5.1 and 6.1 g/cm3 (35% 235U) and being irradiated in the BR2 reactor of SCK•CEN, were analyzed.

A first requirement for a successful radiochemical burnup analysis is a quantitative dissolution of the heavy atoms U, Pu and minor actinides and of the selected burnup monitors. For commercial UO2 and MOX fuels with homogeneous fuel pellets that are packed in a cylindrical zircaloy cladding, the fuel can be selectively dissolved from the cladding material in 8 M HNO3. However this is not the case for the uraniamisilicide fuel plate samples (~1.3 mm thick) where the U3Si2 fuel is mixed with Al-powder and is confined as a thin wafer (~0.5 mm thick fuel metal) between aluminium plates (~0.4 mm thick each). The specific design of the fuel plates imposes the necessity of dissolving the U3Si2 fuel as well as the Al material. Therefore a suitable dissolution method, which can be applied in a stainless steel alpha-box shielded with 15 cm of lead, has been developed using unirradiated samples. The resulting chemical dissolution procedure includes 2 steps. In the first step the external Al plates and the Al-matrix of the fuel meat are dissolved in HNO3 in presence of Hg(II)-catalyst to aid the dissolution of Al. During this phase also part of the fuel itself goes into solution. The residue that is left is filtered off. In the second step emphasis is put on the complete dissolution of the actinides and the fission products and the residue is treated with 10 M HNO3 and 0.1 M HF. The described procedure has been applied with success on the 2 irradiated samples.

The heavy atoms and fission product monitors in the resulting fuel solution are analyzed using mass-spectrometry and radioanalytical techniques. For the determination of the isotope vector and concentration of U, Pu and Nd, isotope addition and isotope dilution analysis using thermal ionization mass-spectrometry (TIMS) is the method of choice. For
isotope dilution analysis approximately 0.5 mg of dissolved fuel is spiked with $^{144}$Nd, $^{233}$U and $^{242}$Pu standards. After careful separation using a combination of anion exchange and extraction chromatography columns $^{22}$ U, Pu and Nd are analyzed with uncertainties ranging up to 0.1% to 5% (2σ) depending on the abundance level of the isotopes and the element concentration. The minor actinides $^{242}$Cm and $^{244}$Cm are measured with α-spectrometry, while the γ-emitters $^{241}$Am and $^{144}$Ce and $^{137}$Cs are analyzed with γ-spectrometry. $^{237}$Np is analyzed with inductively coupled plasma mass-spectrometry (ICP-MS) fitted in a glove box.

Material balance calculations are performed to assess the overall quality of the destructive burnup measurements. In commercial fuels this is fairly straightforward and only the weight of the fuel that was dissolved for analysis, the determined number of heavy atoms and calculated number of fissions have to be considered. However in case of the $\text{U}_2\text{Si}_2$ plate samples also the Al matrix was dissolved and has to be taken into account. For material balance calculations Al is analyzed with ICP-MS.

For final burnup calculations the experimental data are recalculated from the date of analysis to the end of irradiation date and burnup values are derived from the different selected fission product monitors. As cross-sections for $\text{n},\gamma$ capture of the Nd-isotopes $^{141}$Nd and $^{143}$Nd are relatively high, the results of $^{142}$Nd + $^{144}$Nd and of $^{145}$Nd + $^{146}$Nd were summed for final calculation of %FIMA. As the plates were subjected to a high neutron flux during irradiation in the BR2 reactor corrections for the buildup of $^{148}$Nd due to the $^{147}$Nd(n,γ)$^{148}$Nd reaction on short-lived $^{147}$Nd are carried out. The radioactive fission product monitors $^{137}$Cs and $^{144}$Ce are corrected for in-pile decay during irradiation.

The averaged results for %FIMA from 6 separate burnup determinations, i.e. $^{143+144}$Nd, $^{145+146}$Nd, $^{148}$Nd, $^{150}$Nd, $^{137}$Cs and $^{144}$Ce, are (8.34 ± 0.24)% for sample RJH4 from the fuel plate with 5.1 g U/cm² loading and (7.74 ± 0.16)% for sample RJH5 from the fuel plate with 6.1 g U/cm² loading. The relative uncertainty on the averaged value of %FIMA of 3% and 2% is in good agreement with the overall uncertainty budget of 4% attributed to the destructive burnup analysis. For $^{148}$Nd, which is the recommended fission product monitor in the ASTM procedure ASTM E321-96 $^{13}$ %FIMA was 8.37% and 7.80% respectively. Material balance calculations were found to be 98.5% for RJH4 and 98.6% for RJH5 demonstrating a good overall quality of the analysis performed.


SCINTILLATING POLYMER INCLUSION MEMBRANE FOR
PRECONCENTRATION AND DETERMINATION OF RADIONUCLIDES:
EFFECT OF PLASTICIZER


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Extractive scintillators enable the preconcentration of a radionuclide of interest from an
aqueous sample directly into the scintillator organic phase and its detection by scintillation
counting. Many schemes for selective preconcentration and measurement of α and β emitting
nuclides have been developed using extractive scintillator liquids and resins [1-4]. The
extractive scintillating resins are prepared by impregnating polymer beads with an organic
phase containing extractant, primary scintillator and a wavelength shifter. The extractive
scintillating resins have the advantage over the extractive scintillating liquids, as they are
amenable for on-line use with a high preconcentration factor. However, the stability of the
organic phase held inside the resin matrix is a key issue for their application. As an
alternative to extractive scintillating resins, we have developed a scintillating polymer
inclusion membrane (S-PIM) for the preconcentration and determination of α - emitting
radionuclides [5]. The S-PIM was prepared by physical immobilization of an extractant bis(2-
ethylhexyl)phosphoric acid (HEHP) and, 2,5-diphenyloxazole (PPO) and 1,4-bis(2-
methylstyryl)benzene (MSB) as primary and secondary fluors respectively in a diocetyl
phthalate (DOP) plasticized cellulose triacetate (CTA) matrix. The S-PIM has been found to be
effective for quantitative sorption of trivalent lanthanides and actinides. The α emitting
radionuclides held in the sample of S-PIM could be directly measured by scintillation
counting. It was observed that β-scintillation pulses could be discriminated from α pulses
based on their pulse height, thereby achieving α/β discrimination. In this work we have tested
different plasticizers for preparing the S-PIM, in terms of maximum extraction and
scintillation efficiency.

The S-PIM was prepared in the following manner. Solution of cellulose triacetate (CTA) was
prepared by dissolving appropriate amount of CTA (200mg) in 10 mL of chloroform. Separate
solution in chloroform (5 mL) containing known amounts of a plasticizer (400mg)
and additives (HEHP = 110±10 mg, PPO = 65±1 mg, and MSB = 5±1 mg) were prepared.
Five different plasticizers were used to prepare the S-PIM. They are 2-nitrophenyl octyl ether
(NPOE), bis(2ethylhexyl sebacate) (DOS), tris(2-ethyl-hexyl) phosphate (T2EHP), dioctyl
phthalate (DOP) and bis(2ethylhexyl) terephthalate (DOTP). The casting solution of the S-
PIM was prepared by mixing solutions of CTA and other components in chloroform. This
casting solution was then spread on a 9cm-diameter flat bottom glass petri dish kept on a
leveled surface. The petri dish was covered in such a way to allow aeration, but avoiding any
cross contamination. Chloroform was allowed to evaporate slowly overnight. It was observed
that the addition of small amount of xylene (0.5 mL) in casting solution prevented the phase
separation of MSB on chloroform evaporation. After the evaporation of chloroform, a

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transparent homogeneous membrane was formed. The membrane was annealed at 50°C for 3 h to remove residual solvent, and then water was added into petri dish to peel off the membrane from it. The initial composition in weight percent of the S-PI M was kept as follows CTA = 25.2%, Plasticizer = 51.3%, HDEHP = 14.3%, PPO = 8.2% and MSB = 0.6%. The amounts of PPO and MSB were fixed so as to keep their amounts in a 1x3cm² S-PI M comparable to that used in a standard 5ml liquid scintillation cocktail.

The uptake and kinetics for quantitative sorption of 241Am using this S-PI M were measured by immersing a 1x3 cm² S-PI M sample into 15 mL stirred aqueous solution containing 241 Am (> 23 Bq/mL) having a pH = 2.5. The acidity of the equilibrating solution was adjusted with dilute HNO3. The % extraction of 241Am by the S-PI M was estimated from radioactivity balance of equilibrating aqueous solution. The 59.6 keV gamma ray of 241Am was monitored for the uptake studies using a NaI(TI) detector coupled to an SCA to determine the extraction efficiency. The kinetics of up-take were monitored in similar experiments, but by periodically removing the SPIM from the aqueous equilibrating solution and measuring its activity using a NaI(TI) detector. A time period of 200 min was found to be sufficient for quantitative uptake of 241Am by the S-PI M. The desorption studies were carried out by equilibrating 241Am loaded samples of S-PI M with 0.25 mol/L HNO3.

CTA can be plasticized with a variety of plasticizers having different extent of lipophilicity and dielectric constant. The role of the plasticizer is not only to reduce the glass transition temperature of the polymer and solubilise the additives in the membrane matrix, it should also be hydrophobic enough to prevent water from entering the membrane phase. For its application in extractive scintillators, the plasticizer should also linearly transfer the energy from the incident particles (α,β) to the fluor. For this purpose a variety of plasticizers as mentioned above were used to prepare the SPIM. The SPIM samples made of different plasticizers, were loaded with a constant amount of 241Am as mentioned earlier. After quantitative sorption of 241Am in the S-PI M, they were washed with excess of deionized water, and dried between folds of tissue paper. The radionuclide loaded SPIM samples (1x3 cm²) were then mounted on to the inside wall of a 1x1x5 cm³ quartz cell, and assayed by scintillation counting for appropriate time. The quartz cell containing SPIM sample was kept in a chamber optically coupled to a photo multiplier tube (EMI 9514) of the scintillation counter. An appropriate lower discriminator level was used for reducing the background noise to 0.8 counts/sec. For pulse height analysis, the amplified signal from scintillator counter was fed to a PC based multichannel analyzer. The composition and the properties of the films prepared using different plasticizers are listed in Table1. It can be seen from Table 1, that the extraction efficiency of all the plasticizers is practically the same except for T2EHP which shows only 94 % extraction. The pulse height spectra of the SPIM made of different plasticizers and a non-plasticized SPIM, loaded with a constant amount of 241Am is shown in Fig1. Comparison of pulse height spectra of α-scintillation of the non-plasticized and plasticized SPIM indicates that the plasticizer plays an important role in the energy absorption from the α particles. The pulse height increased on plasticizing the S-PI M with all plasticizers except NPOE and is maximum for the T2EHP plasticized S-PI M. The scintillation efficiency is minimum in NPOE plasticized SPIM (Table 1), due to quenching by the -NO2 group present in it. The S-PI M composed of T2EHP plasticizer gave the maximum scintillation efficiency when compared to the liquid scintillator (Table 1).
The reusability/hysteresis studies of this S-PIM were carried out by repeating $^{241}$Am sorption and desorption cycle twice using the same sample in the aqueous solutions at pH=2.5 and 0.25 mol/L HNO$_3$, respectively. The sorption and desorption of $^{241}$Am in S-PIM sample were found to be reproducible (±2%) for 2 cycles (Fig 2). The reusability of the S-PIM for the third cycle was not tested.

The work carried out in this study indicates that both the extraction and scintillation efficiency of the S-PIM depend upon the plasticizer used. The plasticizers, T2EHP and DOP were found to be the best suited for maximum scintillation and extraction efficiency amongst those studied in the present work. The S-PIM developed in this study was found to be reusuable for two cycles. The present work demonstrates that the T2EHP/ DOP plasticized S-PIM can be used for the simultaneous preconcentration and detection of radionuclides from aqueous samples.

REFERENCES

Table 1. Composition and analysis of various thin film scintillators

<table>
<thead>
<tr>
<th>ID</th>
<th>CTA</th>
<th>Plasticizer</th>
<th>PPO</th>
<th>MSB</th>
<th>HDEHP</th>
<th>Extraction Efficiency (%)</th>
<th>Counting efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOP</td>
<td>0.2028</td>
<td>0.4063</td>
<td>0.065</td>
<td>0.00517</td>
<td>0.1119</td>
<td>97.03</td>
<td>87.21</td>
</tr>
<tr>
<td>T2EHP</td>
<td>0.2022</td>
<td>0.3997</td>
<td>0.065</td>
<td>0.00517</td>
<td>0.1181</td>
<td>94.08</td>
<td>97.66</td>
</tr>
<tr>
<td>DOP</td>
<td>0.2002</td>
<td>0.4073</td>
<td>0.065</td>
<td>0.00517</td>
<td>0.1151</td>
<td>98.57</td>
<td>94.61</td>
</tr>
<tr>
<td>DOS</td>
<td>0.2016</td>
<td>0.4020</td>
<td>0.065</td>
<td>0.00517</td>
<td>0.1152</td>
<td>97.38</td>
<td>91.35</td>
</tr>
<tr>
<td>NPOE</td>
<td>0.2000</td>
<td>0.4027</td>
<td>0.065</td>
<td>0.00517</td>
<td>0.1151</td>
<td>96.70</td>
<td>1.24</td>
</tr>
</tbody>
</table>

a) counting efficiency with respect to Liquid Scintillating counting

![Fig 1](image1.png) Pulse height spectra of a scintillating S-PIM made of different plasticizers

![Fig 2](image2.png) Reusability study
COMPARING PERFORMANCE OF K-ZERO NEUTRON ACTIVATION: FRESH AND FREEZE-DRIED ANIMAL TISSUE ANALYSIS

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Introduction: The success attainable in K-zero Neutron Activation Analysis using a Triga Mark-I reactor, IPR-R1 CDTN/CNEN, Belo Horizonte – Brazil, operating at 100 MW and thermal neutron flux of $6.6 \times 10^{11}$ neutron cm$^{-2}$ s$^{-1}$ is to a large degree dependent on the sample composition and the upper limit of each element considered. In practice, carrying out investigations on essential and non-essential elements in fresh cattle muscle tissues, only concentrations of major elements which often dominate the gamma-ray spectrum are obtained by virtue of their relative high values. In order to evidence additional elements when their concentrations have values under the upper limits, the pre-concentration of biological matrices before applying K-zero Neutron Activation Analysis will probably be an appropriate alternative. For this purpose, a nondestructive freeze-drying process - lyophilization [1] was carried out in this study due to small losses of chemical elements as reviewed in previous studies [2].

Experimental procedures: Sample preparation: Performing the compositional analysis of cattle tissues, data were collected under strict repeatability conditions: single laboratory, single equipment, one analyst, all samples were prepared following the same freeze-drying procedure. Approximately two amounts of 200 g of each specimen were separated: the first one to be analyzed in fresh condition. Material for a second group were frozen at $-70^\circ$C and lyophilized. Each freeze-dried sample was powdered and homogenized and around 300 mg was weighed into polyethylene irradiation vials. The same mass of correspondent fresh sample was weighed into same kind of vials. Quality control: Samples were replicate for quality control. Biological reference materials were analyzed in order to verify the efficiency of the method and the traceability of element level determinations. The reference materials used were bovine muscle powder - NIST-SRM 8414 [3] and bovine liver powder - NIST-SRM 1577b [3] from National Institute of Standards and Technology, USA. These reference materials were also weighed, around 300 mg, into polyethylene irradiation vials.

Analytical technique applied on elemental determination: K-zero Instrumental Neutron Activation Analysis [4] is a variation of Neutron Activation in which the sample is irradiated without previous chemical preparation. This specific method is based on nuclear constants - the K-zero factors and reactor parameters. For 91 isotopes the K-zero values have been determined in several laboratories throughout the world, and these constants are available in the literature with about 2% of uncertainty. Complementary, for 21 different elements the uncertainty values are about 5%. Irradiations were carried out in the reactor TRIGA MARK I IPR-R1 at 100 kW and the thermal neutron flux was $6.6 \times 10^{11}$ neutrons cm$^{-2}$ s$^{-1}$.

The samples, gold foils (monitor) and the reference materials were exposed to the same three schemes of irradiation: 5 minutes placed in a position of the rotatory specimen rack to detect the short half-life radionuclides; 4 hours placed in a specimen rack that rotates around the core to detect the medium, and 20 hours placed in a specimen rack that rotates around the core to detect the long half-life radionuclides.

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Results and discussion: Freeze Dry Rate After freeze-drying process, the concentration of elements in the cattle tissues gave rise about 300% from their fresh tissue concentrations. K-zero Neutron Activation Analysis: (i) Quality Control: A good agreement was found between the experimental and certified values for concentrations in both bovine muscle powder (NIST-SRM 8414) and bovine liver powder (NIST-SRM 1577b) from National Institute of Standards and Technology [3]. Aluminum was an exception varying more than 10%.(ii) Comparing fresh and freeze-dried tissue analysis: Instead of seven elements (Na, Cl, K, Fe, Zn, Cu and Rb) determined in fresh tissue analysis, twelve elements (Na, Cl, K, Fe, Zn, Cu, Rb, Al, Se, Mg, Cd and Mn) were determined in freeze-dried material analysis. Differences between freeze-dried and fresh tissue concentrations were less than 5%, practically on the same level of the method accuracy.

![Diagram](image)

Fig. 1: Elements in just-fresh and freeze-dried tissue analysis

[Element Mass. 100% / \sum Element Mass] (n=14; uncertainty 4%)

Conclusion: In this study, 12 elements in freeze-dried tissue were reliably determined. Indubitably, there is an improvement using freeze-dried biological tissues in K-zero Neutron Activation Analysis, allowing the quantification of a greater number of elements some not determined in fresh tissue analysis.

References


PEAK TREATMENT OF \( \alpha \) LIQUID SCINTILLATION SPECTRA FOR THE DETERMINATION OF ACTINIDES IN WATER SAMPLES

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Introduction

Alpha liquid scintillation with alpha/beta discrimination is a promising technique for the determination of actinide elements in environmental samples, due to high sensitivity, fast sample preparation and cheaper analytical costs. However, this technique suffers from a lack of resolution leading in some cases to the impossibility to resolve two adjacent peaks, as for \(^{241}\)Am\(^{243}\)Am and \(^{210}\)Po\(^{210}\)Po. In most cases, though, the resolution is sufficient to separate thorium isotopes (\(^{232}\)Th, \(^{228}\)Th, \(^{226}\)Th), uranium isotopes (\(^{238}\)U, \(^{234}\)U, \(^{232}\)U), plutonium isotopes (\(^{239-241}\)Pu, \(^{240}\)Pu) and curium isotopes (\(^{252}\)Cm, \(^{244}\)Cm, \(^{246}\)Cm, \(^{248}\)Cm). The individual quantification of any isotope from another requires a deconvolution process since all peaks partially overlap. Therefore, before attempting any actinide quantification by applying a fitting procedure, the physical process involved to explain the peak shape must be well understood in order to apply the proper mathematical function. We remind that the internal conversion is a very fast physical deexcitation process (\(t < 1\) ns) occurring systematically for the actinide isotopes and gives \(\beta\) scintillation of monoenergetic electron piling up with the \(\alpha\) event [1]. Therefore, we propose a practical database whose purpose is to provide all necessary parameters for the quantitative determination of actinides by \(\alpha\) liquid scintillation with \(\beta/\gamma\) discrimination.

Theoretical part and deconvolution methodology

The data used to deconvolute alpha liquid scintillation spectra of actinides are given in Table 1. We have only taken into account the internal conversion on L-Shell and the sum of all other internal conversions on M-shell, N-shell, etc. Indeed, the electron binding energies on N-shell are above are very small and give additional peaks positioned near the peak corresponding to the M-shell. Since the resolution in alpha liquid scintillation is a few hundred keV, we have considered that those peaks are all standing in a single one. Calculations for the absolute intensities have been carried out according to the following equations and using our data in [1]

\[
I_{\alpha}^{\text{int}} = I_{\alpha0} + (1 - I_{\text{IC}}) \times I_{\alpha1},
\]

with \(I_{\alpha0}\) the intensity of the main \(\alpha\) ray, \(I_{\text{IC}}\) the intensity of the total internal conversion (including all shells) and \(I_{\alpha1}\) the intensity of the additional \(\alpha\) ray.

\[
I_{L}^{\text{int}} = I_{L,c} \times \frac{\alpha_{L}}{\alpha_{T}} \times I_{\alpha1},
\]

with \(\alpha_{L}\) the total internal conversion coefficient and \(\alpha_{L}\) the conversion coefficient for the L-shell,
Other shells: $I_{a\alpha}^{IC} = I_{a\alpha} \times \left(1 - \frac{\alpha_{IC}}{\alpha_{\gamma}}\right) \times I_{a\alpha}$.

The following linear constraints have been applied in the fitting procedure: a) the peak shape of all $\alpha$ and IC peaks is assumed to be Gaussian, b) the relative intensity ratio $I_{IC}/I_{a\alpha}^{IC}$ according to the data in Table 1 is kept constant, c) the fwhm (full width at half maximum) of both IC peaks for each isotope is identical, d) in addition, linear constraints are applied on the IC peak position in order to avoid discrepancy in the determination of the isotopic ratio and therefore in the quantification of the element. A typical spectrum is shown in Figure 1.

Table 1: Absolute and relative intensities of $\alpha$ ray and the $\alpha +$ internal conversion peak [2].

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>$E_{\alpha}$ (keV)</th>
<th>Relative intensity (%)</th>
<th>Absolute intensity $I_{a\alpha}^{IC}$ (%)</th>
<th>Nuclide</th>
<th>$E_{\alpha}$ (keV)</th>
<th>Relative intensity (%)</th>
<th>Absolute intensity $I_{a\alpha}^{IC}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U</td>
<td>4196</td>
<td>100</td>
<td>79.16</td>
<td>$^{232}$Th</td>
<td>582</td>
<td>100</td>
<td>74.00</td>
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<td>IC L-shell</td>
<td>4366</td>
<td>7.16</td>
<td>15.17</td>
<td>IC M-shell</td>
<td>5865</td>
<td>25.65</td>
<td>18.08</td>
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<td>IC M-shell</td>
<td>4512</td>
<td>5.67</td>
<td></td>
<td>IC M-shell</td>
<td>5982</td>
<td>9.49</td>
<td>7.02</td>
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<td>$^{238}$U</td>
<td>4375</td>
<td>100</td>
<td>71.70</td>
<td>$^{238}$Pu</td>
<td>5157</td>
<td>100</td>
<td>88.54</td>
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<tr>
<td>IC L-shell</td>
<td>4988</td>
<td>28.37</td>
<td>20.60</td>
<td>IC L-shell</td>
<td>5349</td>
<td>9.40</td>
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<tr>
<td>IC M-shell</td>
<td>5112</td>
<td>7.70</td>
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<td>IC M-shell</td>
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<td>3.55</td>
<td>3.44</td>
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<td>$^{232}$Th</td>
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<td>IC M-shell</td>
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<td>$^{232}$Th</td>
<td>4010</td>
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<td>$^{232}$Pu</td>
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<td>4307</td>
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<td>IC L-shell</td>
<td>5933</td>
<td>34.24</td>
<td>33.41</td>
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<td>IC M-shell</td>
<td>4386</td>
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<td>IC M-shell</td>
<td>5698</td>
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<td>14.44</td>
</tr>
</tbody>
</table>

* The location of the IC peaks is calculated according to the relation $E_{\alpha} = E_{\alpha} + \Delta E_{\alpha}$, and assuming that $k = 8$.

![Figure 1: Uranium isotopes spectrum. Histograms show the expected location of all peaks and their relative intensities normalized to the main $\alpha$ rays of each nuclide.](image)
Application to actinide measurements

The procedures for actinide extraction into the scintillating phase is detailed in [2]. The results gathered in Table 2 show a good agreement with the target values for a large range of radioactivity.

Table 2: Quantitative determination of actinides in water sample at 67 % confidence level.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Nuclide</th>
<th>Activity (Bq/g)</th>
<th>Reference activity (Bq/g)</th>
<th>u-test</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 4509/99</td>
<td>$^{229}$Th</td>
<td>10.40 ± 0.20</td>
<td>10.72 ± 0.10</td>
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<tr>
<td></td>
<td>$^{230}$Th</td>
<td>10.38 ± 0.35</td>
<td>9.82 ± 0.20</td>
<td>0.92</td>
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<tr>
<td>B 303/99</td>
<td>$^{232}$Th</td>
<td>0.0143 ± 0.0008</td>
<td>0.01394 ± 0.000062</td>
<td>2.51</td>
</tr>
<tr>
<td>65 SR 300 *</td>
<td>$^{229}$Th</td>
<td>0.151 ± 0.005</td>
<td>0.167 ± 0.010</td>
<td>1.43</td>
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<tr>
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<td>$^{230}$Th</td>
<td>0.434 ± 0.014</td>
<td>0.465 ± 0.023</td>
<td>1.15</td>
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<td>$^{232}$Th</td>
<td>0.133 ± 0.008</td>
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<td>37.01 ± 0.80</td>
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<tr>
<td>SAIL</td>
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<td>0.449 ± 0.009</td>
<td>0.456 ± 0.050</td>
<td>0.25</td>
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<tr>
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<td>0.498 ± 0.009</td>
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<td>0.470 ± 0.009</td>
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<td>#4 $^{238}$U</td>
<td>0.470 ± 0.009</td>
<td>0.477 ± 0.009</td>
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<tr>
<td></td>
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<td>#5 $^{238}$U</td>
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<td>(4.5 ± 1.3)10^{-3}</td>
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<td></td>
<td>$^{234}$U</td>
<td>(8.4 ± 0.3)10^{-3}</td>
<td>(9.0 ± 0.2)10^{-3}</td>
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<td>IAEA-430</td>
<td>$^{232}$U</td>
<td>0.475 ± 0.006</td>
<td>0.486 ± 0.0015</td>
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<tr>
<td></td>
<td>$^{234}$U</td>
<td>0.465 ± 0.006</td>
<td>0.468 ± 0.0023</td>
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<tr>
<td>PT1A89 C</td>
<td>#1 $^{230}$Pu</td>
<td>(5.71 ± 0.20)10^{-3}</td>
<td>(5.83 ± 0.22)10^{-3}</td>
<td>0.40</td>
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<tr>
<td></td>
<td>#2 $^{230}$Pu</td>
<td>(5.08 ± 0.27)10^{-3}</td>
<td>(5.14 ± 0.55)10^{-3}</td>
<td>0.11</td>
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</tbody>
</table>

* Lake sediment dissolved in HNO$_2$-HCl mixture, (a) Direct extraction into the scintillating phase – no spike, (b) Measurement by ICPMS with $^{242}$Pu, (c) Measurement by $\alpha$ spectrometry (grd chamber) with $^{242}$Pu, (d) Reduction-oxidation cycle with $^{236}$Pu, (e) Measurement by $\alpha$ spectrometry (grid chamber) with $^{236}$Pu.

ROBUST METHODS FOR THE DETERMINATION OF RADII AND URANIUM IN WATER SAMPLES

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Introduction

Nowadays, alpha liquid scintillation with α/β discrimination for the measurement of α emitters in environmental samples has become attractive because of high sensitivity, low analytical cost and fast sample preparation. Among all α emitters, many authors have focused on $^{226}\text{Ra}$ and $^{238,234}\text{U}$ isotopes, to which is attributed the highest part of the internal exposure to the population. In France, the translation in the French Law of the directive of the European Union on the quality of water dedicated to human consumption results in a maximum admissible exposure of 0.1 mSv and maximum α and β activities of 0.1 Bq/L and 1 Bq/L, respectively. As a consequence, detection limits of 40 mBq/L for $^{226}\text{Ra}$ and 1 µg/L for uranium are imposed. Under these conditions where the regular control of water quality leads to the analyses of numerous samples, fast sample preparation, low analytical cost and relative high sensitivity are required. The α liquid scintillation with α/β discrimination presents these advantages notwithstanding a poor energy resolution. Most of the authors using alpha liquid scintillation have focused on sensitivity which is time-consuming rather than on rapidity. We propose to test robust and fast procedures for the measurement of $^{226}\text{Ra}$ and $^{238,234}\text{U}$ in any kind of water samples in terms of accuracy, precision, reliability and repeatability. Our methodology has been tested on natural and synthetic certified solutions at low and high salinity furnished by the International Atomic Energy Agency (IAEA). The repeatability has been determined with several natural waters during a Round-Robin exercise which gathered five international laboratories.

Chemical procedures

Schematic procedures are given in Figures 1 and 2. The methodology has been developed in order to avoid time-consuming chemical treatments like evaporation and coprecipitation. **Uranium**: in the experiments, the final concentration of DTPa is of 0.1 M. Then, pH is adjusted to 3.5 by 10 M NH$_4$OH and the extractive-scintillator cocktail Alphaex$^{TM}$ is used to extract U. The overall procedure is carried out within 2 hours. For a few samples for which the apparent chemical yields were largely above 100 %, one additional step has been added to remove Po by spontaneous reduction onto silver powder. **Radium**: three 15-mL tubes equipped with screw-cap are used: the first one contains 5-g or 5-mL sample, the second one 5-mL sample doped with a large activity of $^{226}\text{Ra}$ exceeding at least 100 times the initial $^{226}\text{Ra}$ activity in the sample, the last one is a 5-mL deionized water solution adjusted by 1 M HNO$_3$ to pH ≈ 2.0 (e.g. a blank sample). A 0.1 M HIBA solution is obtained by adding 250 µL of 2 M HIBA in all tubes. Then, radium is quantitatively extracted by Radaex at pH ≥ 10. In order to ensure the same chemical yield, the pH adjustment is controlled by pH-meter. The difference between both aliquots (doped and undoped samples) can not arbitrarily exceed ± 0.05 unit pH.
Figure 1: Chemical separation steps for radium determination in water. Sample preparation is carried out in less than one hour.

**Results**

Activity ranges between 1 mBq/kg and 25 Bq/kg for radium whereas the concentration of uranium varies from 0.04 to 20 μg/kg. Salinity varies from 0.5 to 130 g of dissolved solids/kg. Results have been gathered in Figures 3 and 4 as a t-test figure which allows a rapid comparison with the target values. A very high number of results are in good agreement with the target values.

**Uranium:** in terms of accuracy, a good agreement with the target values is noted. For $^{238}$U and $^{235}$U, we do not observe variations exceeding 10 – 15 % for activities higher than 0.01 Bq/kg. Our determination of $^{238}$U in sample IAEA-425 is about 20 % lower than that of the target value. This variation is explained by the very low statistics of counting, since the $^{238}$U activity found is only 2.5 times above the limit of detection. Nevertheless, all determinations remain compatible with the reference values with respect to experimental uncertainties. In conclusion, we generally observe accuracy better than 5 %. The detection limit is about 0.003 Bq/kg, i.e. 0.2 μg/kg. The reproducibility of the method is lower than 5 %.

**Radium:** All determinations are in good agreement with the target values. No problem has been observed. Precision is about 4 % and the detection limit is equal to 40 mBq/kg. Results show a repeatability of about 7 %.
Figure 3: $^{238}$U, $^{234}$U and U total concentration of various water samples.

Figure 4: $^{226}$Ra determination in various water samples.
AVALANCHE PHOTODIODES FOR ALPHA LIQUID SCINTILLATION DETECTION

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Introduction

For many years, scintillation detection has been based almost exclusively on photomultiplier tubes (PMT). Photomultipliers have low noise and high gain but suffer from low quantum efficiency for the emission range of many scintillators. On the contrary, solid state photodetectors, like PIN photodiodes, show higher quantum efficiency. Indeed, they have no internal gain as well as large area detectors leading to substantial leakage currents which contribute to noise. Avalanche photodiodes (APD) combine benefits of both PIN photodiodes and PMT: high quantum efficiency and internal gain. Recent advances in APD device performances and in photosensitive area (up to 2 cm²) allow APD to replace PMT for scintillation spectrometry. Moreover, APD detector is found to yield a better resolution than PMT detector with high light output crystal scintillators [1]. High quantum efficiency allows to get better statistical accuracy for light detection whereas internal gain contributes to low noise.

Theoretical part

Energy resolution of an APD-scintillator system can be written as [2]:

$$\frac{\Delta E}{E} = 2.355 \left( \frac{N_e}{N_0 M} \right)^2 + \frac{F - 1}{N_0} + \delta^2,$$  

(1)

where $N_e$ is the electronic noise (expressed in electrons r.m.s.), $N_0$ is the number of primary photoelectrons generated in the APD, $M$ is the mean gain, $\delta$ is the intrinsic resolution of the scintillator and $F$ is the excess noise factor which takes into account the random character of the multiplication process.

1. The first term is the electronic noise contribution,
2. the second term is the statistical contribution for the signal due to avalanche multiplication,
3. the third one includes all fluctuations associated with scintillation and light collection.

Results and discussion

For low gains, the resolution is dominated by the electronic noise ($N_e$) but for high gains, the resolution becomes worse as the excess noise factor ($F$) increases with the gain (Fig.1). Therefore, resolution as a function of APD gain ($M$) shows a minimum:
Fig. 1: Resolution components (calculated for \( N_p = 1050 \) e\(^+\)) as a function of the APD gain at 0°C. APD Advanced Photonix n°127-12-15, 10 mm diameter.

Because APD noise decreases with respect to temperatures, cooling the detector appears as an obvious way to improve resolution. Fig. 2 shows electronic noise as a function of APD gain for several temperatures. The noise is approximately constant for gains between 10 and 300 and temperatures below -20°C. There is no need to cool at lower temperature than -20°C to achieve the lowest electronic noise.

Fig. 2: Dependence of electronic noise on APD gain and temperature. APD Advanced Photonix n°127-12-06, 10 mm diameter.
Energy resolution measurements

Performance of avalanche photodiode in alpha liquid scintillation was studied by optically coupling a 10 mm diameter APD to a cylindrical sample vial covered with reflective material. As the temperature decreases, the resolution improves (see Fig.3).

![Graph showing energy resolution and separation factor between $^{235}$U and $^{239}$Pu](attachment:image.png)

**Fig.3**: $^{235}$U and $^{239}$Pu spectrum taken with the same APD gain ($M=100$) at several temperatures. Energy resolution is approximately 10%. Separation factor $R_s$ between $^{235}$U and $^{239}$Pu is calculated according to the relation:

$$R_s = 1 - \frac{E_{U/235} - E_{Pu/239}}{\frac{1}{2}(FWHM_{U/235} + FWHM_{Pu/239})}.$$ 

Down to -20°C, resolution decreases because of the electronic noise. Subsequently, the resolution observed at -40°C is better than one observed at -20°C because light yield of liquid scintillator increases. The number of primary electron-hole pairs per α-particle, $N_0$, is found to be:

<table>
<thead>
<tr>
<th>$N_0$</th>
<th>$^{235}$U</th>
<th>$^{239}$Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4°C</td>
<td>$921 \pm 10$</td>
<td>$1176 \pm 15$</td>
</tr>
<tr>
<td>-20°C</td>
<td>$955 \pm 12$</td>
<td>$1215 \pm 14$</td>
</tr>
<tr>
<td>-40°C</td>
<td>$1076 \pm 12$</td>
<td>$1366 \pm 14$</td>
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Conclusion and improvements

Avalanche photodiodes can be used to detect scintillation photons. The APD gain have been determined to obtain optimal resolution. Temperature plays an important role on APD properties and on light yield of liquid scintillator. Better resolution is expected in lowering temperature below -40°C.


EFFECT OF CROWN ETHERS ON THE Sr\(^{2+}\), Ba\(^{2+}\) AND Ra\(^{2+}\) UPTAKE ON TUNNEL STRUCTURE ION EXCHANGERS

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Radium is an important member of the natural uranium decay series. \(^{226,228}\)Ra released with water from uranium and coal mines causes significant radioisotope pollution in many regions. Because of the low levels of radium usually encountered in environmental samples, radium determination requires one or more preliminary separation and preconcentration steps, both to free the sample from interfering radioisotopes and to isolate it from relatively large quantities of inactive substances. Typically this separation and preconcentration includes multiple coprecipitation of Ra\(^{2+}\) with BaSO\(_4\), subsequent dissolution in EDTA solution and separation on ion exchange resin. Moreover, the radium levels in many barium reagents are not negligible, sometimes preliminary purification of the reagents is necessary.

The objective of the present work was to separate Ra\(^{2+}\) from other Group II cations in a single step utilizing synergistic effect between crown ethers complexation and ion exchange in \(\alpha\)-crystalline polyantimonic acid (PAA) and cryptomelane manganese dioxide (CMD). The inorganic ion exchangers with tunnel structure like PAA and CMD exhibit high affinity for heavy alkaline earth cations [1]. Unfortunately, the Ra-Ba separation on these sorbents is rather poor. On the other hand, it is known that crown ethers are selective ligands that form stable complexes with alkaline earth cations based on the ionic radius - cavity size compatibility concept [2].

Using \(^{85}\)Sr, \(^{133}\)Ba and \(^{224}\)Ra radiotracers distribution coefficients of heavy alkaline earth cations in acidic solutions of crown-5 and crown-6 on the PAA and CMD sorbents were determined. In the case of PAA, selectivity series of Sr\(^{2+}\)>Ra\(^{2+}\)>Ba\(^{2+}\) was found. Crown-5 and crown-6 complexation causes decreasing Ra-Sr selectivity and increasing selectivity for Ra-Ba. CMD has been demonstrated to show excellent ion-exchange selectivity for cations with a crystal ionic radius of 130-150 pm, e.g. Ba and Ra, but selectivity of Ra-Ba is low. As shown in Fig.1. Ra/Ba selectivity coefficient sharply increases with crown ether concentration,
especially with crown-5 which forms much stronger complexes with Ba$^{2+}$ than with Ra$^{2+}$.

Application of tunnel inorganic sorbents with crown ether eluent gives unique possibility to separate Ra$^{2+}$ from other Group II cations in a simple single step procedure.

Fig.1. Influence of crown ether concentration on Ra/Ba selectivity coefficient on HMD.

References

EXTRACTION AND SUBSTOICHIOMETRIC SEPARATION OF Co(II) WITH ORGANIC REAGENT EMPLOYING TRACER TECHNIQUE

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2Nuclear Chemistry Division, The Institute of Science, Bombay-400032, India

Solvent extraction also known as liquid-liquid extraction is considered to be the most versatile and popular among various methods of separation, of its ease, simplicity, speed and wide scope. Utilizing a simple separatory funnel, requiring several minutes a: the most to perform, and applicable both to macro and trace levels of metals, this extraction technique offers much to the analytical chemist. $^{60}$Co is useful in industry, medicine and science. $^{60}$Co has advantages over X-rays and radium because of its lower cost, more homogeneous gamma-radiation and softer beta-radiation, no radiation contamination from radon gas and ability to be shaped in any form before irradiation to fit special requirements. The ever expanding applications of cobalt have generated a great demand for more accurate and reliable techniques for separating it form a variety of complex matrices. Liquid-liquid extraction of divalent Co and other metal-ions using various reagents into organic solvents have been carried out[1-4].

The present investigation deals with the rapid and selective separation of Co(II) from other elements by solvent extraction with 2-mercapto-benzimidazole into nitrobenzene. Ideal conditions for the extraction and substoichiometric separation of Co(II) from other elements have been established. $^{60}$Co was used as tracer. 1.0 mg of Co(II) labeled with $^{60}$Co was taken in a separating funnel. 5.0 mg of 1.0% ethanolic solution of 2-mercaptobenzimidazole was added. The pH of the solution was adjusted to 10.0 with ammonia solution (volume = 20 ml). The aqueous phase was equilibrated with 20 ml of nitrobenzene for 5.0 minutes. The phases were allowed to separate and the volume of each phase was found to be equal. The activity of $^{60}$Co in 2-ml aliquot of each phase, after the separation was counted on a gamma-ray spectrometer at a channel corresponding to 1.332 MeV photopake of $^{60}$Co. The extraction coefficient (E) and percent extraction (%E) were calculated in the usual way. The effect of pH on the extraction coefficient value of Co(II) with 2-mercaptobenzimidazole indicated a maximum at a pH of 10.0 (Table 1). The value was found to decrease in the more acidic range. The extraction coefficient value reached a maximum value of 107 (mean) for an equilibration time of 5.0 minutes with a reproducibility of 107 ± 5. Determination of time of equilibration revealed that the percentage extraction was better than 98% for an equilibration time of 1.0 to 6.0 minute.

The effect of various solvents on the E value of Co(II) indicated that nitrobenzene was the best solvent for the extraction. The stoichiometry of the extracted species was determined by the method of substoichiometric extraction. The stoichiometry of metal to reagent was found to be 1:2. The effect of sodium, potassium or ammonium salts on the extraction coefficient value of Co(II) has been determined. The effect of
various elements on the extraction coefficient value (E) of Co(II) was studied with or without carrier. The interfering elements have been suppressed with appropriate masking agents, making the separation method highly selective.

**Table 1.** Effect of pH on the E value of Co(II) with 2-mercaptobenzimidazole into nitrobenzene. Aqueous phase: 1.0 mg of Co(II) + $^{60}$Co + 5.0 ml of 1.0% ethanolic solution of 2-mercaptobenzimidazole + ammonia + distilled water; Organic phase: 20.0 ml nitrobenzene; time of equilibration: 5.0 minutes; temperature: 28 ± 2 °C.

<table>
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<th>PH</th>
<th>Extraction coefficient (E)</th>
<th>Percentage extraction (%E)</th>
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Reproducibility: 107 ± 5.0

**References**
ANALYTICAL METHOD FOR PURE BETA RADIONUCLIDES IN REACTOR GRAPHITE, CONCRETE AND OTHER MATERIALS FOR REACTOR DECOMMISSIONING

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In decommissioning of a nuclear reactor, the radioactivity of various radionuclides has to be measured for estimation of the total inventory of radioactivity and its variation with time. Due to large volume, graphite, concrete, steel and lead are the main low-medium radioactive waste. The radioactivity of the irradiated reactor graphite, concrete, steel and water comes from many nuclides such as $^3$H, $^{14}$C, $^{36}$Cl, $^{41}$Ca, $^{90}$Co, $^{59}$Fe, $^{60}$Ni, $^{90}$Sr, $^{99}$Tc, $^{129}$I, $^{137}$Ba, $^{137}$Cs, $^{137}$Cs, $^{134}$Cs, $^{134}$Cs, $^{134}$Cs, and some transuranics, in which the determination of gamma emitters is much easier. But the beta emitters have to be separated from matrix and other radionuclides using different chemical separation methods before measurement. Most of the beta activity is contributed by $^{14}$C, $^3$H, $^{59}$Fe, and $^{59}$Ni in graphite; the content of $^{41}$Ca, $^{59}$Fe, and $^{59}$Ni in concrete is relatively high, while $^{59}$Fe and $^{60}$Ni are main beta radionuclides in steel, aluminium alloy and lead. Due to high mobility and long half-life, the determination of $^{36}$Cl, $^{129}$I and $^{99}$Tc in radioactive waste is also important for decommissioning and disposal of the waste. $^{14}$C, $^3$H, $^{90}$Sr, $^{99}$Tc and $^{129}$I are pure beta emitter; except $^{90}$Sr, others are low energy beta emitters. $^{41}$Ca and $^{59}$Fe decay by electron capture. The sample needs to be decomposed to individually separate them from other interfering nuclides and matrix element before measurement of their radioactivity by liquid scintillation counting. In our laboratory, some analytical methods have been developed for the determination of these beta radionuclides in various nuclear waste for the nuclear reactor decommissioning, they are briefly presented in this paper.

In graphite, $^{14}$C exists as carbon and $^3$H as HT or HTO. The most common method for decomposition of graphite is combustion, in which a higher temperature (>800 °C), long combustion time (2-3 hours per sample) and special catalyst such as V$_2$O$_5$ and CuO are needed to completely decompose graphite. In concrete, $^{14}$C exists as carbonate or carbon, and $^3$H as HT or HTO in pore and gaps of the concrete. The acid digestion method is normally used for decomposing it to release $^{14}$C and $^3$H. However, a special apparatus and chemicals (such as HF) are needed to completely decompose concrete and release tritium and C-14. In addition, it is also time consuming (>3 hours per sample). In this work, an oxidizing combustion method using commercial Oxidizer is investigated to decompose graphite and concrete for the determination of $^{14}$C, $^3$H and $^{129}$I. The graphite and concrete samples mixed with cellulose powder and combustion aids (an organic compound) are combusted under oxygen flow at a temperature of 1100-1200 °C. The tritium released as HTO vapour and collected in a glass vial, and C-14 released as CO$_2$ is absorbed in Carbon-sorb solution. After mixing with scintillation cocktail, the contents of C-14 and tritium are measured by liquid scintillation counter. By this method the sample preparation time can be shortened to only 2-3 minutes. The detection limit of this method for $^{14}$C and tritium are 0.96 and 0.58 Bq/g graphite and 0.11 and 0.06 Bq/g concrete respectively. The cross contamination of $^{14}$C and tritium in the preparation of samples is less than 0.2%. The interference of other radionuclides
in samples for the determination of $^{14}$C and tritium in graphite is insignificant. The analytical accuracy investigated by standard addition method using different $^{14}$C and $^3$H labelled compounds, such as Na$_2$CO$_3$, HTO, organic $^{14}$C and $^3$H compounds is better than 95%. In addition, an acid digestion method is also used to decompose graphite and concrete for comparison with the developed method. The results by two decomposition methods show a good agreement for graphite samples. Some graphite samples collected from Danish Reactors DR-2 and DR-3 have been analysed for $^3$H and $^{14}$C using the developed method. Two concrete cores drilled in Danish reactor DR-2 were also analysed for $^3$H and $^{14}$C, and the analytical results are shown in Fig. 1.

![Graph showing concentration of $^3$H and $^{14}$C against distance from the core](image)

**Fig. 1** Distribution of $^{14}$C and $^3$H in two concrete cores from Danish reactor DR-2

The behaviours of $^{35}$Cl, $^{125}$I and $^{99m}$Tc in the combustion procedure were also investigated. $^{125}$I is quantitatively released from the sample and collected in water in the tritium fraction, while, $^{35}$Cl and $^{99m}$Tc cannot be completely released from the sample in the combustion procedure. However, for the determination of $^{125}$I, it has to be further separated and purified due to high concentrations of $^3$H co-existing with $^{125}$I. The separation and measurement method for $^{125}$I is discussed. Due to incomplete recovery of $^{99m}$Tc in Oxidizer combustion procedure, the graphite and concrete samples are decomposed by digestion with a mixture of acids including H$_2$SO$_4$, HClO$_4$, and HNO$_3$, and then $^{99m}$Tc can be separated from matrix elements and purified from other radionuclides by solvent extraction and ion-exchange method. Some reactor solution, and water samples have been measured.

The reactor water, especially heavy water, contains very high activity of tritium. Due to high oxygen component in water, $^{14}$C can be also produced during neutron irradiation. In this work, a simple distillation method is developed to separate $^{14}$C from heavy water with very high concentration of tritium. The results showed that the decontamination factor for tritium reaches 10$^{11}$. The detection limit of $^{14}$C in heavy water is 0.1 Bq/ml.

$^{55}$Fe and $^{65}$Ni are neutron activation products of stable $^{56}$Fe and $^{64}$Ni. Due to relatively high radioactivity of other radionuclides in the reactor materials, such as $^{60}$Co, $^{153}$Eu, $^{60}$Zn and $^{135}$Ba, they have to be separated from these interfering radionuclides and each other. A radiochemical separation procedure based on precipitation, ion exchange chromatography and extraction chromatography is developed for the determination of $^{55}$Fe and $^{65}$Ni. The solution containing $^{55}$Fe and $^{65}$Ni is adjusted to 9 mol/l HCl and passes through an anion exchange column; Ni is collected in the effluent and 9 mol/l HCl washing, while $^{55}$Fe absorbed on the column is eluted by 0.5 mol/l HCl solution after washing with 4 mol/l HCl. The separated
$^{59}$Ni is further purified by passing the solution through an extraction chromatography column, which is made by combining dimethylglucolime on an absorver resin, after addition of complex reagent ammonium citrate and adjustment of pH 8-9. The absorbed Ni is eluted by 3 mol/l HNO$_3$ after washing the column by ammonium citrate solution to remove all isotopes of Co, Zn, Cu, Cr, Fe, rare earth elements and transuranics. The separated $^{59}$Fe is further purified by passing the Fe$^{3+}$ solution in 6 mol/l HCl through another extraction chromatography column, which is made by combining diisobutyl ketone on absorber resin, the absorbed Fe is eluted by water. The purified Ni solution is evaporated to 0.2-0.5 ml and transferred to vial for LSC measurement, while purified Fe solution is evaporated to dryness and dissolved in H$_3$PO$_4$ solution for LSC measurement. The decontamination factors of the developed method are higher than 10$^3$ for the interfering radionuclides. The chemical recoveries for both Fe and Ni are higher than 90%. For the analysis of graphite samples, the ash following acid leaching method was investigated for decomposition of sample, the results indicate that the recoveries of Fe and Ni are higher than 90% if ash temperature is lower than 850 °C and ash time lower than 2 hours. The ashed sample is dissolved in HCl for further separation and purification as described above. The developed method has been used for the analysis of graphite, concrete, steel, lead and aluminium alloy from the Danish reactors.

$^{44}$Ca is a neutron activation product by reaction $^{43}$Ca(n,$\gamma$)$^{44}$Ca. Due to high concentration of Ca in concrete, the radioactivity concentration of $^{44}$Ca in reactor concrete is relatively high. As a shielding material in reactor, heavy concrete with high BaSO$_4$ component is normally used, it makes the complete decomposition of concrete samples more difficult. In this work an alkali fusion method using NaOH and Na$_2$CO$_3$ is applied to decompose the samples. The fused cake is leached with hot water, Ba and Ca exist in the residue as hydrates and carbonate. Thern Ca and Ba are completely converted to carbonate by mixing the residue with Na$_2$CO$_3$ solution and heating the slurry 4-5 times. Ba and part of Sr are then separated from Ca, transitional metals, such as Ni and Fe, and transuranics by BaCl$_2$ and SrCl$_2$ precipitation under concentrated HCl solution. The solution containing $^{54}$Ca, $^{55}$Fe, $^{60}$Ni and transuranics is then evaporated to near dryness, and diluted with water, the transitional metals including $^{54}$Fe and $^{60}$Ni, and transuranics are precipitated as hydroxides with Fe(OH)$_3$ by adjusting pH 8-9 using diluted NaOH solution, while Ca exists in the supernatant. $^{54}$Fe and $^{60}$Ni can be determined using the above procedure after dissolve the hydroxides precipitate with HCl. For the determination of $^{44}$Ca, adding Na$_2$CrO$_4$ and ethanol to the supernatant to precipitate remaining Sr isotopes and $^{137}$Ba as SrCrO$_4$ and BaCrO$_4$, after separation of precipitate by centriguge, adding Na$_2$CO$_3$ to the supernatant to precipitate Ca as CaCO$_3$. The Fe(OH)$_3$ and BaCrO$_4$/SrCrO$_4$ precipitation are repeated to improve the decontamination of transitional metals and Ba and Sr. The purified $^{44}$Ca is measured by liquid scintillation counter via counting Auger electrons after dissolving CaCO$_3$ with HCl. The analytical results showed that the decontamination factors for $^{54}$Fe, $^{60}$Ni, $^{54}$Co, $^{60}$Zn, $^{90}$Sr, $^{90}$Y, $^{137}$Ba, $^{139}$Cs, $^{137}$Pu, and $^{239}$Pu are higher than 10$^3$, the chemical recovery of Ca is higher than 85%. The developed method has been successfully applied for the analysis of heavy concrete samples from Danish reactors for $^{44}$Ca, $^{54}$Fe and $^{60}$Ni.

$^{90}$Sr is very important nuclide in the environmental radioactivity study and nuclear waste treatment due to its high mobility and relatively high fission yield. For some nuclear waste with short term cooling time, the activity of $^{90}$Sr is also higher. However, the separation of these two isotopes is impossible. In this work, a method combining Cherenkov radiation counting and conventional LSC is presented for the determination of both $^{90}$Sr and $^{89}$Sr.
MEASUREMENT OF HYPERFINE FIELD IN MAVICYANIN
BY PERTURBED ANGULAR CORRELATION OF GAMMA-RAYS

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Introduction: Perturbed angular correlation of gamma-rays (PAC) is a powerful method to investigate hyperfine fields in a molecule in liquid state based on nuclear electric quadrupole interactions. Taking advantage of the method, it is interesting to measure the hyperfine field at a metal site of biological molecule in an aqueous solution as functioning in life.

In this study, the structure around the metal site of Mavicyanin, a protein molecule with a copper site, was investigated by using time-differential PAC of $^{117}$In. Its parent nuclide $^{117}$Cd decays by beta emission to populate the 749 keV excited state of $^{117}$In with a half-life 2.49 h, decaying to the 315 keV excited state through the 660 keV intermediate state having a spin $I = \frac{3}{2}$, $t_{1/2} = 53.6$ ns, and an electric quadrupole moment $Q = (-)0.59(1)$ b [1].

Experiments: The parent radionuclide $^{117}$Cd was obtained by irradiating enriched $^{116}$CdO (96.53%) for about 30 min in thermal neutron flux of $1.83 \times 10^{13}$ cm$^{-2}$s$^{-1}$ or $2.34 \times 10^{13}$ cm$^{-2}$s$^{-1}$ at Kyoto University Research Reactor Institute. The irradiated oxide was dissolved with M HCl solution in a 5-ml beaker and heated on a hot plate to dryness. After letting stand until cooled, the Cd ions were dissolved in 1-ml solution of 50E-6 to 300E-6 M Mavicyanin adjusted to pH 7.5 with Tris-HCl buffer and let stand for 1 hour. Here Cd ions were substituted in the metal sites of Mavicyanin, from which Cu ions were extracted beforehand. Then the solution was passed through a Sephadex G-25 column to eliminate unsubstituted Cd ions and adjust to a particular pH solution with buffer solution. The sample solution obtained in the procedure above was subjected to PAC measurements.

The time dependence of the coincidence counts $N(\chi, t)$ of the 90-344 keV cascade gamma rays for the samples containing $^{117}$Cd was taken using a measurement system consisting of standard fast-slow electronic modules and four BaF$_2$ scintillation detectors. Here, $\chi$ and $t$ denote the angle and the time interval, respectively, between the cascade gamma rays. The directional anisotropy, $A_{22}G_{22}(t)$ is derived with the formula:

$$R(t) = A_{22}G_{22}(t) = \frac{2}{N(\chi, t) + 2N(\delta, t)} \left( N(\chi, t) - N(\delta, t) \right)$$

In case of identical, static and randomly oriented molecules, the expression of $A_{22}G_{22}(t)$ is given as follows. The value of $A_{22}$ for $^{117}$In (from $^{117}$Cd), depending only on the nuclear transitions, is $-0.36$ [2]. The perturbation factor $G_{22}(t)$ for an ensemble of randomly oriented molecule in liquid but in inactive molecular motion is a function of the electric quadrupole frequency $f_Q$ if asymmetry
parameter of the electric field gradient (EFG) is assumed to be 0.45 and expressed as
\[ G_z(y) = [1 + 4 \cos(1.03 f_0 y)] / 5 \] with \( f_0 = 6 f_0 \).

**Results:** The PAC spectrum for pH = 7.5 is shown in Fig. 1 as an example. The spectrum was fitted to the equation above with the parameter \( f_0 \) as drawn in the figure with a solid line. The pH dependence of the frequency thus obtained and \( V_{zz} \) derived from \( f \) is listed in Table 1. Compared with the \( V_{zz} \) value, \( 1.71 \times 10^{12} \) Vm\(^{-2}\) reported on Stellacyanin [3], the results obtained in this work seem to be reasonable. However, more data is necessary for a detailed discussion on the structure and relevant function of the molecule.

![Graph](image)

**Fig. 1.** \(^{117}\)In-PAC spectrum for Mavicyanin with pH 7.5.

**Table 1.** Variation of frequency and EFG with pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>( f_0 ) / Mrad·s(^{-1})</th>
<th>( V_{zz} ) / ( 10^{12} ) V·m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>841</td>
<td>1.73</td>
</tr>
<tr>
<td>7.5</td>
<td>880</td>
<td>1.81</td>
</tr>
<tr>
<td>8.0</td>
<td>812</td>
<td>1.67</td>
</tr>
</tbody>
</table>

**References**

SEQUENTIAL SEPARATION OF Zn (II), Hg (II) AND Cd (II) BY
SUBSTOICHIOMETRIC SOLVENT EXTRACTION TECHNIQUE

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For radiochemical separation of elements, solvent extraction is the best method. The method is simple, clean, rapid and lends itself to radiotracer technique. In the present investigation a rapid and selective method for the sequential separation of Zn (II), Hg (II) and Cd (II) has been achieved employing substoichiometric solvent extraction technique. Tracers $^{65}$Zn (II), $^{115m}$Cd (II) and $^{203}$Hg (II) were employed for development of this method which was used to study the extent of separation.

Experimental

All the chemicals and reagents used were of A. R. grade. The standard solutions of Zn (II), Hg (II) and Cd (II) were prepared in distilled water containing a small amount of acid. The radioactivity of $^{65}$Zn (II) and $^{203}$Hg (II) was measured on a single channel $\gamma$-ray spectrometer and $^{115m}$Cd on a G. M. Counter. The reagent used was 2-mercaptopbenzimidazole[1]. A literature survey[2,3], reveals that this reagent has not been used for the extraction of Zn (II), Hg (II) and Cd (II).

Procedure

In a 100 ml beaker were taken 5.0 mg each of Zn (II), Hg (II) and Cd (II) carriers labelled with tracers of $^{65}$Zn, $^{203}$Hg and $^{115m}$Cd, respectively.

Separation of Zn (II): The mixture was warmed with 4M of sodium hydroxide and the precipitate of Hg (II) and Cd (II) was centrifuged, leaving behind Zn (II) in the centrifugate. The centrifugate was concentrated to 5ml and was made acidic. The solution was boiled and concentrated to 2ml. The solution was transferred to a separating funnel and its pH adjusted to 7.0 with dilute ammonia after adding substoichiometric amount of 2-mercaptobenzimidazole (2-HMBI). The mixture was equilibrated with CHCl$_3$ for 10.0 minutes. The phases were allowed to separate and a 2-ml aliquot of the organic phase was taken for counting on a gamma-ray spectrometer at the channel corresponding to the 1.115 MeV photopeak of $^{65}$Zn. The percentage recovery under the experimental condition was determined and is given in Table 1. The contribution of $^{203}$Hg (II) and $^{115m}$Cd (II) to the activity of $^{65}$Zn was evaluated.

Separation of Hg (II): The precipitate after washing twice with warm distilled water was dissolved in dil. HCl and stoichiometric amount of EDTA was added to suppress Cd (II). It was transferred to a separating funnel and the pH of the solution was adjusted to 3.0 with dil. ammonia after adding substoichiometric amount of 2-HMBI in ethanol. It was equilibrated with 14ml of CHCl$_3$ for 4.0 minutes. The phases were allowed to separate and 2-ml aliquot of the organic phase was taken for counting on a gamma-ray spectrometer at the channel
number corresponding to the 0.279 MeV photopeak of $^{203}\text{Hg}$. The percentage recovery under the experimental condition was determined and is given in Table 1. The contribution of $^{65}\text{Zn}$ (II) and $^{115m}\text{Cd}$ (II) to the activity of $^{203}\text{Hg}$ was evaluated.

**Separation of Cd (II):** The aqueous phase containing $^{115m}\text{Cd}$ (II) was treated with aqua-regia and the solution was concentrated by boiling. The pH of the solution was adjusted to 7.0 with dilute ammonia after adding substoichiometric amount of 2-HMBI. The mixture was equilibrated with 10ml of 1,2-dichlorobenzene for 1 minute. The phases were allowed to separate and a 2ml aliquot of the organic phase was placed on a planchet, evaporated and counted on a G. M. Counter. The percentage recovery under the experimental condition was determined and is given in Table 1. The contribution of $^{65}\text{Zn}$ (II) and $^{203}\text{Hg}$ (II) to the activity of $^{115m}\text{Cd}$ (II) was also evaluated.

<table>
<thead>
<tr>
<th>Element recovered</th>
<th>Activity (Bq)</th>
<th>Recovery (%)</th>
<th>Impurity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Taken</td>
<td>Found</td>
<td>Expected</td>
</tr>
<tr>
<td>$^{65}\text{Zn}$</td>
<td>61,056</td>
<td>47,315</td>
<td>80.0</td>
</tr>
<tr>
<td>$^{203}\text{Hg}$</td>
<td>52,471</td>
<td>39,964</td>
<td>80.0</td>
</tr>
<tr>
<td>$^{115m}\text{Cd}$</td>
<td>46,705</td>
<td>36,364</td>
<td>80.0</td>
</tr>
</tbody>
</table>

**Results and discussion**

The purity of the separated Zn (II), Hg (II) and Cd (II) fractions was confirmed by γ-ray spectra and β-Counting. The method is proposed to be used for Sequential Radiochemical Neutron Activation Analysis.

**References**


A NOVEL METHOD FOR SELECTIVE SEPARATION OF $^{111}\text{In}$ FROM IMPURITIES BY ION EXCHANGE CHROMATOGRAPHY

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$^{111}\text{In}$ is one of the most important cyclotron-produced radionuclides that is prepared from nuclear reactions like Cd $(p,xn)^{111}\text{In}$ and Cd $(d,xn)^{111}\text{In}$ [1,2]. It is used in various branches of medicine such as lymphoscintigraphy and cisternography [3]. Several methods have been reported in the literature for the separation of carrier-free $^{111}\text{In}$ from irradiated cadmium matrix [2,4-14]. But there has not been a sufficiently fast method for this purpose until recently.

![Graph showing variations of distribution coefficients of different ions on Dowex 50W-X8 resin with time in 82% (v/v) ammonia (10M) - 18% (v/v) carbonate ammonium (1M)]

Fig. 1: Variations of distribution coefficients of different ions on Dowex 50W-X8 resin with time in 82% (v/v) ammonia (10M) - 18% (v/v) carbonate ammonium (1M).

In this work, a new method has been developed for the separation of $^{111}\text{In}$ from cadmium target by using Dowex 50W-X8 as an ion exchanger. Preliminary studies have shown that all the ions investigated could be adsorbed on the resin, in a weak acidic medium. In order to find a selection of suitable eluents for In (III), distribution coefficients (Kd) of various ions were determined by batch method at different time intervals. Results have shown that the Kd values Cd(II), Cu(II), $^{65}$Zn(II) and $^{69}$Ga(II) are higher than those found for $^{111}\text{In}$. Fig.1 illustrates the major differences that exist in the Kd values of $^{111}\text{In}$ and various ions investigated at the initial two hour period. It can be concluded from the results obtained that the separation of $^{111}\text{In}$ from impurity is feasible. Column chromatographic studies have also shown that the separation of $^{111}\text{In}$ from other ions is possible. This was carried out by adsorption of a mixture of ions including $^{111}\text{In}$ on a column containing resin at a pH of approximately 10 in an ammoniacal medium. The elution of $^{111}\text{In}$ from resin was achieved by 2M ammonia – 0.8M ammonium carbonate solution. Under these conditions, Cd(II), Cu(II) and other radionuclides were retained on the resin. The radioindium solution in the final step was evaporated to dryness and the residue was dissolved in 0.01M HCl. The isotopic contamination of $^{111}\text{In}$ solution in the final step was evaluated by gamma spectrometry which showed that it is suitable for medical uses with respect to radionuclidic purity. Chemical purity of $^{111}\text{In}$
solution has also been determined by inductively coupled plasma (ICP) spectrometry. Furthermore, the effect of various eluants on the adsorption of $^{111}$In was investigated and the elution curves of separation of $^{111}$In from other ions were depicted.

References
DETERMINATION OF Cu, Ag AND Au IN ALLOY SAMPLES BY SEQUENTIAL INSTRUMENTAL THERMAL NEUTRON ACTIVATION ANALYSIS

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Cu, Ag and Au are distributed in nature and as compared to other metals, Ag and Au occur in small amounts. All the elements have excellent properties for use in industry, especially because of their high electrical and thermal conductivities. They form an important component in jewelery and laboratory wear. Various workers have developed methods for the analysis of Cu, Ag and Au in complex metals employing isotopic neutron sources using INAA [1-3]. The present work deals with the determination of Cu, Ag and Au employing sequential instrumental thermal neutron activation analysis. The induced activity was measured on a HPGe-detector and the amount of sample was determined by the comparative method. $^{252}$Cf was used as a thermal neutron source.

Experimental

All the chemicals and reagents used were of AR grade. Standard solutions of Cu, Ag and Au were prepared by a dissolving a known amount of each salt or metal and diluted with double distilled water to known volume. The alloy samples were converted to powder.

Each target for irradiation was prepared by packing a known weight of the alloy sample in a quartz ampoule and the standard was prepared by evaporating the solution containing a known amount of Cu, Ag and Au on another quartz ampoule under gentle heat of IR-lamp.

Radioassaying of Cu, Ag and Au

**Determination of Ag:** The sample of alloy and the standard were irradiated at a thermal neutron flux of $8.5 \times 10^7$ n/cm$^2$/sec from $^{252}$Cf for 15 minutes to obtain saturation activity of $^{108}$Ag. The induced activity in the sample and the standard was measured after a cooling time of 1 minute from the end of the irradiation and was counted at the channel corresponding to the 633 keV gamma energy of $^{108}$Ag on a set-up unit consisting of HPGe-detector coupled to a MCA-unit. Integral peak-area counting was employed. The sample and the standard were measured alternatively. Corrections for decay were incorporated prior to calculation. The amount of Ag present in the sample was calculated by using the standard comparative method.
Determination of Cu and Au: After the determination of Ag the activity was allowed to cool for the complete decay of $^{108}$Ag. The sample and the standard were reirradiated with thermal neutrons in close proximity to $^{252}$Cf for a duration of 72 hrs to obtain saturation activity of $^{64}$Cu. The alloy was transferred to a preweighed beaker and weighed. The standard and weighed amounts of sample were measured on a HPGe-detector coupled to a MCA-unit for the 511 keV and 411 keV $\gamma$-rays of $^{64}$Cu and the $^{198}$Au, respectively. The amount of element present in the sample was calculated by the usual comparative method.

Results and discussion

On irradiation with neutrons $^{108}$Ag is produced by the (n,γ) reaction on $^{107}$Ag and stable $^{63}$Cu and $^{197}$Au produce $^{64}$Cu and $^{198}$Au, respectively, by the (n,γ) reaction. The presence of isotope was confirmed by running the gamma spectra and by determining the half-life. The values obtained were found to be in agreement with reported values. The accuracy and the precision of the method were determined on the synthetic mixture prepared to represent the matrix. Replicate analysis revealed the accuracy and precision of the method to be 6.6 % and 4.4 %, 9.6 % and 7.14 % respectively, for the analysis.

The sensitivity limit of the method was found to be 2.5 mg for Ag, 1.06 mg for Cu when they were irradiated for saturation activity and 65 μg for Au under experimental conditions mentioned above. The activity produced was found to be double that of the background. The amount of the element present in the sample is given in Table 1. One sample and standard of Ag were processed within three minutes from the end of irradiation. Two samples and standard of Cu and Au were analyzed within 30 minutes. Thus, it can be seen that Cu, Ag and Au can be analyzed simultaneously and non-destructively with great rapidity and can be employed for the analysis of these elements in complex matrices.

<table>
<thead>
<tr>
<th>Table 1: Determination of Cu, Ag and Au by sequential instrumental thermal neutron activation analysis employing $^{252}$Cf neutron source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Ag in mg</td>
</tr>
<tr>
<td>Taken</td>
</tr>
<tr>
<td>1.05</td>
</tr>
<tr>
<td>Cu in mg</td>
</tr>
<tr>
<td>Taken</td>
</tr>
<tr>
<td>4.85</td>
</tr>
<tr>
<td>Taken</td>
</tr>
<tr>
<td>Au in μg</td>
</tr>
<tr>
<td>Taken</td>
</tr>
<tr>
<td>4.85</td>
</tr>
<tr>
<td>98.0</td>
</tr>
</tbody>
</table>

S → Sample.
References


EVALUATION OF UNCERTAINTIES IN ROUTINE DETERMINATIONS OF THERMAL TO EPITHERMAL FLUX RATIOS FOR $k_0$ BASED NEUTRON ACTIVATION ANALYSIS

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The parametric methods of neutron activation analysis historically appeared as an alternative to the relative methods, in order to gain speed, versatility and simplicity, which subsequently implied competitiveness with respect to other analytical techniques. Although they are frequently associated to non-destructive determinations, the radiochemical approach should not be excluded, especially in connection with multielement separations.

Since its introduction in 1975 [1] the $k_0$ standardisation has been consolidated as a powerful method and is nowadays applied worldwide in many activation analysis laboratories. Some refinements were gradually incorporated with the purpose to obtain better accuracy, one of them being the consideration of the departures from the ideal behaviour of the epithermal flux, through the measurement of the $\alpha$ parameter. Several methods have been proposed for $\alpha$ determination [2,3]; most of the routine measurements employ the bare triple monitor method [4] with $^{197}$Au, $^{94}$Zr and $^{96}$Zr monitors. Despite the experimental advantages of this method, the uncertainties of the results are usually high, particularly for small $\alpha$ values. The authors claimed that this was not a serious drawback, because of the large reduction factors that appeared both in the conversion formula for $k_0$ and in the use of the values for $Q_0(\alpha) = k_0(\alpha)/Q_0$ in the $k_0$ method. While this last statement is entirely right, the former seems to be slightly questionable, since a value of $\alpha$ as small as 0.025 represents percent variations, for the $^{96}$Zr and $^{92}$Zr original $Q_0$ values, respectively equal to 22.8 and 15.6.

In the present work, the uncertainties of the determination of $f$ = thermal to epithermal flux ratio, are evaluated, with emphasis on the influence of the $\alpha$ parameter and its uncertainties, for the following monitor pairs: $^{94}$Zr - $^{96}$Zr, $^{96}$Zr - $^{197}$Au, $^{59}$Co - $^{197}$Au; and $^{55}$Mn - $^{115}$In, this last monitor in connection with the production of $^{116m}$In ($t_1/2 = 54.4$ min). From irradiation of two bare flux monitors, the expression of $f$ as function of $\alpha$ is represented by the well known formula:

$$f(\alpha) = \frac{C_{\alpha(0)} e^{-\alpha (0)} - C_{\alpha(0)}}{C_{\alpha(0)} e^{-\alpha (0)} - C_{\alpha(0)}}$$

where $C_{\alpha}$ and $e$ stand for the normalised specific counting rates and the full energy peak efficiencies, respectively.

Graphic representations of the evolution of $f$ for the pairs of flux monitors studied, with $f(0)$ values that represent the actual conditions of a typical reactor core, are shown in figure 1. It can be seen that $f$ is strongly dependent of $\alpha$ for the $^{94}$Zr - $^{96}$Zr and $^{96}$Zr - $^{197}$Au pairs; this influence is notably less relevant for the $^{59}$Co - $^{197}$Au pair, whereas the $^{55}$Mn - $^{115}$In pair is almost insensitive to the variations in $\alpha$ values.
Fig. 1. Graphic representations of $f$ as function of $\alpha$, for different $f(0)$ values.

All factors forming the above formula are magnitudes subject to any kind of uncertainty. The uncertainties of temporal factors, implicitly included in the expression of the normalised counting rates, are currently negligible, as most half-lives are known with high precision, and the masses are measured with uncertainties less than $<0.1\%$. Therefore, the uncertainties of the normalised counting rates can be considered, to all practical effects, as those derived from the statistical fluctuations of the measurements. The uncertainties of tabulated $k_0$ factors and experimentally determined peak efficiencies are about $1 - 1.5\%$.

Similar influence of the uncertainties of normalised counting rates, $k_0$ factors and peak efficiencies on the overall uncertainty of $f$ can be recognised from their propagation factors. All of them are identical with respect to the individual relative uncertainties, and inversely proportional to the difference in $Q_{i}(\alpha)$ values. This fact explains the adoption of flux monitors such as $^{94}Zr$ - $^{96}Zr$ and $^{96}Zr$ - $^{197}Au$ instead of, for example, the traditionally used $^{59}Co$ - $^{197}Au$ pair. As it will be seen later, such preference should not be decided only on these grounds.

It should be pointed out that $Q_{1}(\alpha)$ and $Q_{2}(\alpha)$ are not independent variables, since both are correlated through the $\alpha$ measurement. Thus, the propagation factors have to be considered from the primary variables indirectly involved in $f$ calculation through the $Q_{i}(\alpha)$ factors, i.e. resonance integral to cross-section quotients $(Q_{o})$, mean effective resonance energies and $\alpha$ parameter. Taking into account their respective propagation factors, $\alpha$ is the variable that most affects the precision in $f$, mainly because of its experimental uncertainty.

Figure 2 shows the uncertainty of $f$ as a function of $\alpha$, for $f$ values equal to 20, 50 and 100, and $\alpha$ uncertainties of 10\%, which is of the order of the best precisions achieved for these measurements, as well as 20\% and 30\%, corresponding to those currently obtained for routine methods. For the formulation of the pertinent equations, it is assumed that $f$ and $\alpha$ are not two-fold correlated, i.e. that the measurements of the monitors are not simultaneously employed for $f$ determination and also as part of $\alpha$ calculation, as in the bare triple monitor method.

From the results, the following comments can be formulated:
For the $^{55}Mn$ - $^{115}$In pair, which was already characterised as almost insensitive to $\alpha$ variations, the uncertainty of $\alpha$ adds a nearly constant factor to the overall uncertainty in $f$.
The $^{59}Co$ - $^{197}$Au pair shows increasing uncertainties in $f$ for growing $\alpha$ values.
The influence of the uncertainty in $f$ is highly dependent on the $\alpha$ values for $^{94}Zr$ - $^{96}Zr$ and $^{96}Zr$ - $^{197}Au$ pairs. A minimum can be distinguished in the curves for both pairs at $\alpha = 0$, and a nearly symmetrical growing is observed with increasing absolute values. The slope is more pronounced for higher uncertainties of $\alpha$. 

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The relative uncertainties in \( f \) are almost independent of its magnitude for \(^{94}\text{Zr} - ^{96}\text{Zr}\) and \(^{96}\text{Zr} - ^{197}\text{Au}\) pairs; on the other hand, they strongly augment with growing values of \( f \), for the \(^{59}\text{Co} - ^{197}\text{Au}\) and \(^{55}\text{Mn} - ^{115}\text{In}\) pairs.

![Figure 2. Uncertainty in \( f \) as function of \( \alpha \), for different \( \alpha \) uncertainties.](image)

With the only exception of extreme \( \alpha \) values measured with high uncertainty, both \(^{94}\text{Zr} - ^{96}\text{Zr}\) and \(^{96}\text{Zr} - ^{197}\text{Au}\) pairs are the advisable alternative for \( f \) determination in strongly thermalised irradiation positions (high \( f \) values). This situation changes when considering positions with not too high thermalisation degree; in these cases, the \(^{59}\text{Co} - ^{197}\text{Au}\) and \(^{55}\text{Mn} - ^{115}\text{In}\) pairs render less uncertainties for most of the possibilities analysed.

From all the preceding remarks, it is apparent that the choice of the adequate pair of flux monitors for routine \( f \) determinations depends on the particular working conditions, where the magnitude of \( f \) and the uncertainties involved in its measurements are relevant factors.

References

FISSION TRACK ANALYSIS OF URANIUM-DOPED SILICA PARTICLES


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Fission track analysis is a very sensitive technique that is suitable for the detection of the trace amounts of fissile particles. This work utilized this technique to develop a screening technology for safeguard swipe samples. Uranium doped silica particles were used as a reference with various sizes and $^{235}\text{U}$ enrichment for the fission tracks analysis. The correlation of the reference uranium-doped silica particles (RUSP) size and radius, the $^{235}\text{U}$ enrichment of the RUSP and the fission track dense area were examined for the determination of the unknown uranium particle size and $^{235}\text{U}$ enrichment.

**Experiments**

For the fission tracks analysis the RUSP were used with a varied size (1–20 μm) and $^{235}\text{U}$ enrichment (0.7–50%), utilizing an aerosol generator as well as the U-absorption-aqueous technique. The silica particles were synthesized from the reaction mixtures containing water glass and water. The sedimentation method was selected for the narrow size distribution of the particles by using an optical microscope and a digital image analysis system. The RUSP were prepared by the absorption of uranium onto the silica particles in an acidic uranium solution (pH 4.0–4.3) with an agitation time of 24 hours. The RUSP were then examined using EPMA for the identification of uranium in the particles as well as the particle shape. The fission tracks for the RUSP were detected on a Lexan solid track detector. The prepared RUSP were dispersed into a dispersing agent (colloidal:EtOH=1:2) and irradiated with thermal neutrons in the HANARO reactor at the Korea Atomic Energy Research Institute for 1 minute under a neutron flux of $2.7 \times 10^{13} \text{neq}^{-2}\text{sec}^{-1}$. The chemical etching conditions of a 6.25M NaOH solution at 60°C for 10 minutes were utilized. Observation of the fission tracks was carried out using an optical microscope with a digital image analysis system.

**Results**

It can be concluded from the experimental results that the fission track size and shape depend on the particles size as well as on the uranium content in the particles. In

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addition to this, the $^{235}$U enrichment of the RUSP was also correlated with the dense fission track area. The fission tracks of the RUSP are shown in Fig. 1. Correlation of the RUSP size and fission track radius as well as the dense track area and $^{235}$U enrichment are shown in Figs. 2 and 3, respectively. The results of this correlation can be directly applied to the identification of swipe samples for safeguards purposes.

References

Fig. 1. Fission tracks of uranium-doped silica particles.
Fig. 2. Correlation of the fission track radius with the uranium-doped silica bead diameter.

Fig. 3. Correlation of the dense track area with U-235 enrichment.
STUDY OF THE ZINC EFFECT ON THE BETA-GLUCURONIDASE LEVELS OF SOME TISSUE SAMPLES USING A NUCLEAR TECHNIQUE

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No significant relation between zinc and β-glucuronidase levels has been reported in the literature. In this study, this relation has been investigated using a nuclear measurement technique for β-glucuronidase levels. 45 Male Sprague-Dawley rats (125 to 150 g weight) were used. These were randomized into three groups and fed on foods of three different zinc contents (low, normal, and excess). Following long diet periods (16, 32, and 48 weeks), the rats were sacrificed under ketamin anesthesia. They were weighted before sacriﬁcation and several organs such as prostate, pancreas, kidneys, large intestine, small intestine, lung, liver, heart, brain, and stomach were removed and weighed. These tissue samples were used to measure the zinc and β-glucuronidase levels. Zinc levels were measured by Atomic Absorption Spectrophotometry technique. β-Glucuronidase levels were measured by a new and extremely sensitive nuclear measurement technique based on the radioactivity measurement of phenolphthalein radiolabeled with 131I recently developed at our laboratory[1]. In conclusion, no significant correlation between zinc and β-glucuronidase levels was observed in general, and this was attributed to the complexity of metabolic parameters which are very closely related to the aging of animals. However, in pancreas and prostate visible correlations were observed as is seen in Figures 1 and 2.

Figure 1: Relation between Zn and β-glucuronidase levels in the liver tissue of rats.

Figure 2: Relation between Zn and β-glucuronidase levels in the prostate tissue of rats.
SR-90 DETERMINATION IN URINE SAMPLES BY ICP-MS AND RADIOCHEMICAL TECHNIQUES

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$^{90}$Sr is a fission product and because of its long physical (29.12 a) and biological (> 10 a) half-lives it is deemed to be one of the most hazardous radioisotopes and can cause high local radiation damage. $^{90}$Sr and its daughter $^{90}$Y are pure beta emitters. The beta-radiation from $^{90}$Sr is interfered by those from $^{90}$Y and $^{90}$Zr. If the radiochemical techniques (low-level proportional counting or liquid scintillation spectrometry) will be used for $^{90}$Sr determination the different separation procedures would be necessary for isolation of the beta-emitters. If ICP-MS technique will be use for the determination of $^{90}$Sr the presence of $^{90}$Y and $^{90}$Zr in the urine samples and the detection limit would be the limitations.

Many methods have been described for the chemical separation of strontium including, precipitation, liquid-liquid extraction, ion exchange and liquid chromatography [1]. Radiochemical analysis techniques are typically used for the determination of $^{90}$Sr based on isolation of $^{90}$Sr from alkaline-earths and the radioactive isotopes of yttrium, lead, polonium, plutonium, neptunium and potassium. The determination of $^{90}$Sr was performed using low-level anti-coincidence measurements with a proportional counter [2] or LSC [3]. The other way is the separation of $^{90}$Y from $^{90}$Sr and their determination by LSC [2]. The use of sector field ICP-MS or ICP-MS with collision cell eliminates many of the interferences encountered with the radiochemical detection and both have been found to be selective and sensitive means by which to measure various elements. However, difficulties may arise with isotopic interferences of atomic ions or molecular ions that result from the matrix of the sample or the plasma itself. The most critical issue is the appearance of radioactive and stable nuclides at the same mass with a different atomic number. All interferences must be considered and eliminated to obtain accurate and sensitive analysis of radioactive strontium at m/z = 90.

$^{90}$Y is the first decay product of $^{90}$Sr decay. Although yttrium may be removed by the use of strontium-specific resins, once the procedure is completed, $^{90}$Y will be produced by the decay of $^{90}$Sr. This is of concern when using radiochemical detection techniques as they are very sensitive. Therefore, when using thus type of detection, the samples are not analyzed until an equilibrium is reached (2-3 weeks). Alternatively, mathematical correction formulas may be employed. As described later in this paper, detection limits of $^{90}$Sr are quite low. Therefore, because the $^{90}$Y/$^{90}$Sr concentration ratio will be 0.025% in the activity equilibrium, ICP-MS will not be sensitive enough to detect the yttrium in growth that would be expected from typical levels of $^{90}$Sr.
$^{90}$Zr represents a second isobaric interference and its removal may be accomplished by several means. Again, it may be possible for the separation to be specifically conducted prior to analysis. However, the current techniques utilized for strontium isolation prior to measurement, such as precipitation, ion exchange or solvent extraction, are not considered as selective or safe enough and additionally, may require large amounts of resins/ acids and solvents as well as time. A new advance in the isolation of radioactive strontium has been the use of extraction chromatography. Although this preparation technique may serve to eliminate some of the zirconium, others have noted that similar resins may not completely remove all interferences of interest.

Instrumental techniques used for interference elimination may include the utilization of a sector field ICP mass spectrometer at maximum mass resolution (m/Δm) of 12000, the application of a collision cell or a cool plasma in ICP-MS. A sector field ICP-MS may be used to accomplish mass measurements at required mass resolution and subsequently, it may be possible to separate interferences from the isotopes of interest. However, it is generally not possible to separate isobaric singly charged atomic ions, such as $^{90}$Sr$^+$ from $^{90}$Zr$^+$, due to low mass difference (mass of $^{90}$Sr = 89.9077 u and $^{90}$Zr = 89.9047 u) using commercial ICP mass spectrometers, because a mass resolution of approximately 30,000 would be necessary for their separation.

A possible way to solve the interference problem is the application of ICP-MS with collision cell as unwanted ions produced in the plasma can be selectively removed or shifted in m/z ratio prior to mass spectral analysis by the addition of specific reagent gases. In studies of ion/molecule reactions performed by [5], it was shown that Y and Zr react with O$_2$ over two orders of magnitude faster than Sr. Further research showed that Sr$^+$ is not reactive with the choice of O$_2$ as a reaction gas and a stronger oxidant, nitrous oxide, was needed to form strontium oxide with the purpose of separating it from the same mass Rb. Sector field mass spectrometers utilizing an ICP ionization source are used widely in the area of elemental and isotopic analysis, and especially in the determination of long-lived radionuclides, because of two distinct advantages with regard to resolution and sensitivity.

**Polyatomic interferences**

There exists the potential for ion formation of argon-carbon based interferences such as $^{38}$Ar$^{40}$Ar$^{12}$C$^-$. Generally, cool plasma conditions inhibit the formation of argon-based polyatomic ions. In work published by Vanhaucke et al., an r.f. power of 750 W was applied and this was sufficient to reduce the formation of the $^{40}$Ar$^{12}$C$^-$ diatomic ion that interfered with the determination of the major chromium isotope at m/z = 52. The formation of $^{38}$Ar$^{40}$Ar$^{12}$C$^-$ was investigated through the introduction of a solution of 0.01% trichloroacetic acid under the optimized conditions and cool plasma. An increase in background at m/z = 90 was not observed in this experiment.

A second potential contribution to the background at m/z = 90 is the formation of nickel-based interferences, such as $^{58}$Ni$^{18}$O$^-$ or $^{58}$Ni$^{16}$O$^-$, due to the use of nickel extraction cones. With the addition of oxygen, the interferent at m/z = 90 increases by approximately one order of magnitude. Interestingly, there is no change in the abundance of the interferent at m/z = 92 as would be expected due to $^{60}$Ni$^{16}$O$^-$ and this may be due to the elimination of the carbon-based interference under the cooler plasma generated with the addition of oxygen. With the
sector field instrument, a medium resolution setting \((m/\Delta m=4450)\) was adequate to separate these nickel-based polyatomics and therefore eliminate all background at \(m/z = 90\).

A third possible contribution to the background at \(m/z = 90\) is the hydride formation of stable \(^{89}\)Y, although if extraction chromatography is used for sample preparation, yttrium removal is expected. A solution containing only yttrium at a concentration of 200 ppb was prepared and analyzed in conjunction with a nitric acid blank. The background at \(m/z = 90\) was examined for hydride formation and no such phenomena was observed.

In all magnetic sector mass spectrometers, there is a small contribution to peak intensity from adjacent peaks. This abundance sensitivity of sector field instruments is less than that of quadrupole instruments. Average concentration of stable strontium in urine is approximately 50 \(\mu \text{g L}^{-1}\); abundance sensitivity was studied at medium mass resolution \((m/\Delta m=4450)\) using a standard solution with concentration of 1 \(\mu \text{g mL}^{-1}\) of strontium. In order to correct for possible interferences, intensity was measured at the masses \(m \pm 0.5 u\), \(m \pm 1.5 u\), \(m \pm 2.5 u\), etc. Abundance sensitivity was calculated as the intensity at \(m/z = 90\)/intensity at \(m/z = 88\) and in medium mass resolution mode, was found to be \(9 \times 10^{-7} (2 \times 10^{-7})\) in low mass resolution mode. Additionally, peak-tailing can be reduced further by applying a higher mass resolution and abundance sensitivity was measured at \(4 \times 10^{-7}\) at \(m/\Delta m = 12000\), but this was accompanied by a decrease in the intensity of the analyte ions.

In this work, urine samples were prepared as outlined in the Experimental section. As stated previously, the sample preparation procedure represented an effective sample concentration factor of 200. Additionally, as described earlier, natural levels of strontium in urine were in the range of 50 ppb. Taking into account these two facts results in a final extract with a concentration of approximately 10 ppb of natural strontium. Medium mass resolution would therefore not be capable of removing all counts at \(m/z = 90\) due to the peak tail of \(^{86}\)Sr\(^+\) and this was shown experimentally. The background at \(m/z = 90\) was increased by approximately three orders of magnitude. Correction was performed, however, this served to decrease the precision of the measurements and therefore detection limits were increased.

References
DETERMINATION OF URANIUM, THORIUM AND $^{235}$U/$^{238}$U ISOTOPIC RATIO AT TRACE AND ULTRATRACE LEVEL IN URINE BY LA-ICP-MS

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Laser ablation inductively coupled plasma source mass spectrometry (LA-ICP-MS) has become established as a very efficient and sensitive technique for analysis of long-lived radionuclides in solid samples [1,2]. Rapid analysis results are often required for incorporation measurements of long-lived radionuclides in urine [3,4]. Therefore, a new analytical technique for direct determination of uranium and thorium concentration and $^{235}$U/$^{238}$U isotope ratio using LA-ICP-MS was developed.

In sample preparation, possible contaminations represent a problem which can be avoided by a direct analysis (without sample digestion), e.g. by LA-ICP-MS. Synthetic standards (urine matrix) were produced and analysed in order to determine the $^{235}$U/$^{238}$U isotopic ratios and the recovery rate of uranium and thorium determination. The accuracy of the analytical techniques was verified by interlaboratory comparisons.

This contribution discusses the applicability of LA-ICP-MS for routine measurements of uranium and thorium concentration and isotope ratios of uranium in urine. In summary LA-ICP-MS is a powerful analytical method for trace and ultratrace analysis of U and Th and isotope ratio measurements of actinides in urine for a routine control of possible incorporation of exposed persons.

The method allows to minimize sample preparation and contamination danger. For Th lower detection limits are observed in comparison to ICP-MS, because there is no blank problem with nitric acid (see Table 1).

Table 1: Detection limits (3σ-criterion)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>LOD ICP-QMS* µg/L</th>
<th>LOD LA-ICP-MS* µg/L</th>
<th>LOD ICP-SFMS** µg/L</th>
<th>LOD LA-ICP-SFMS** µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{239}$U</td>
<td>4*10^4</td>
<td>6*10^3</td>
<td>1*10^6</td>
<td>5*10^5</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>4*10^4</td>
<td>6*10^3</td>
<td>1*10^6</td>
<td>5*10^5</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>9<em>10^2</em></td>
<td>6*10^3</td>
<td>1*10^4</td>
<td>2*10^4</td>
</tr>
<tr>
<td>$^{238}$Th</td>
<td>4*10^4</td>
<td>6*10^3</td>
<td>6*10^3</td>
<td>2*10^4</td>
</tr>
</tbody>
</table>

* = detection limit Elan 6000; ** = detection limit ELEMENT
Table 2: Results of recovery studies for determination of uranium and thorium (n=10)

<table>
<thead>
<tr>
<th>Concentration of doped Th</th>
<th>LA-ICP-MS value (calculated with Th-230)</th>
<th>Recovery</th>
<th>Concentration of doped U</th>
<th>LA-ICP-MS value (calc. with $^{235}$U/$^{238}$U isotope solution)</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ng/L]</td>
<td>[ng/L]</td>
<td>[%]</td>
<td>[ng/L]</td>
<td>[ng/L]</td>
<td>[%]</td>
</tr>
<tr>
<td>0.5</td>
<td>0.52</td>
<td>104</td>
<td>0.25</td>
<td>0.23</td>
<td>91</td>
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<tr>
<td>1.25</td>
<td>1.25</td>
<td>100</td>
<td>1.25</td>
<td>1.19</td>
<td>95</td>
</tr>
<tr>
<td>2.5</td>
<td>2.49</td>
<td>97</td>
<td>2.5</td>
<td>2.30</td>
<td>92</td>
</tr>
</tbody>
</table>

Figure 1: Investigation of different calibration strategies for determination of uranium and thorium in urine samples (all curves measured with LA-ICP-MS)
References

ION CHROMATOGRAPHIC ANALYSIS OF AQUEOUS IODINE SPECIES BY CONDUCTIVITY AND RADIOACTIVITY MEASUREMENT

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Introduction
Iodine is one of the most essential trace elements in food. The stable isotope $^{127}$I occurs naturally and, together with the long-lived $^{129}$I and the shorter-lived $^{131}$I, is generated as one of the main fission products of uranium and plutonium during nuclear power plants (NPP) operation [1]. Its release into the reactor containment or, especially into the environment as a result of an accident can represent a significant safety issue. One of the problems associated with the iodine is to know its chemical forms and to understand the corresponding reactions in water, in the reactor containment, the environment and during its long-term waste disposal, in order to describe its behaviour. The knowledge of the iodine chemistry and the retention mechanisms of radioactive iodine isotopes is one of the main premises concerning the safety requirements of nuclear reactor containment in the case of a severe accident.

For the high sensitive iodate and iodide analysis, and in particular for post (off-line) test analysis of silver iodide radiolysis reaction products and for specific iodine mitigation experiments, an ion chromatography (IC) method was developed and introduced in the analytical practice. These iodine specification analyses are essential for the investigation of the volatility behaviour and the release minimisation of radioactive iodine isotopes in NPP.

IC is a well-established technique for many applications [2], but iodine was analysed only as the sum by reduction of all species to iodide [3,4]. Only Bichsel et al [5] reported on the determination of iodide and iodate by ion chromatography with postcolumn reaction and UV/visible detection. Iodide/iodate separations are up to now not considered in standard applications of companies like METROHM or WATERS. Additionally, complications arise from the presence of boric acid/borate buffers, which are essential for cooling water of NPP [6]. Thus, a method was developed which allows both the determination of many different anions and of iodine species (iodide, iodate and molecular iodine) simultaneously in one run by measurement of its conductivity and detection of their radioactivity. For cooling water analysis this equipment is required for impurity control.

Equipment
A setup of a system for simultaneous IC analysis of radioactive iodine species and other anions was developed. Isocratic elution was carried out with a METROHM column (Metrosep A-Supp 5) using carbonate-bicarbonate solution as eluent. Conductivity detection (Typ 732 IC detector) was performed with a suppression module (Type 753).

For the radioactivity measurement a new CsI(Tl) scintillation detector (Carroll Ramsey, Berkeley, USA, System Model 105-S-2) was used, which gives an essential improvement of the signal/noise ratio at energies above 300 keV. Thus, solutions with an activity level in the range of kBq can be analysed. Standards were prepared in bi-distilled water and in boric acid/xorate solutions at pH 5-9.
Results
The developed iodine analysis method can be applied to a wide spectrum of sample types. Besides iodide and iodate it is also possible to determine molecular iodine in aqueous solutions. Fig. 1 shows the ion chromatogram of a solution prepared from 6 ppm elemental iodine dissolved in hydrazine containing solution. The detected iodide peak refers to the complete reduction of the iodine to iodide.

Fig. 1: IC analysis of iodine in hydrazine solution (10^{-4} M), 6 ppm iodine at pH 11.0, eluent: 3.2 mM Na_2CO_3/1mM NaHCO_3; flow: 0.7 ml/min, column: A Supp5 from METROHM (Switzerland), conductivity detector with suppression

Figs. 2 and 3 show examples of simultaneous measurement of a boric buffered sample (0.05 M Na_2BO_3/H_3BO_3) spiked with 200 kBq ^{131}I tracer solution and 0.2 ppm iodide/iodate together with other anions.

Fig. 2: IC analysis of a sample solution containing iodine and other anions in 0.05 M boric acid/borate solution, measured with a conductivity detector, eluent: 3.2 mM Na_2CO_3/1mM NaHCO_3, column: A Supp5 (METROHM)

The conductivity measurement allows to determine the general composition of the sample (Fig. 2). The iodide/iodate ratio can be determined with high accuracy by analysing the chromatogram measured with the radioactivity detector (Fig. 3). This device is suitable for the study of carrier free samples. This is of special interest for investigations of cooling water samples from NPP.
**Fig. 2:** IC analysis of an iodine containing sample solution (identical solution as used for Fig. 2), measured with a radioactivity detector, eluent: 3.2 mM Na$_2$CO$_3$/1mM NaHCO$_3$, column: A Supp5 (METROHM)

**Discussion**

An analytical method was developed to provide the previously missing and important information on the iodine behaviour by determining the concentrations of the common species of iodine, i.e. iodide and iodate in the aqueous phase as well as molecular iodine. If the equipment is completed with a previous molecular iodine/organoo-iodine retaining filter [6], then simultaneous determination of molecular iodine, iodide and iodate can be performed from one sample. At first the iodide and iodate species are detected. After that the filter is eluted with hydrazine containing solution, reducing the remaining elemental iodine to iodide, which then can be detected also on the IC column.

For radioactive samples the CsI(Tl) scintillation detector is used. This gives the possibility to identify iodine species on the non-carrier concentration level and in the presence of impurities, interfering in the conductivity measurement. The method can be applied to routine analysis of environmental and technical samples.

To monitor and (specify) contamination in the environment, due to the long-lived iodine fission product $^{129}$I, distribution mass separation (of the iodide and iodate fractions after the IC separation) can be performed. The highest sensitivity is achieved by the use of accelerator mass spectrometry (AMS).

**References**

THE DEVELOPMENT OF A DEPLETED URANIUM SOLID MATRIX REFERENCE MATERIAL

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The National Physical Laboratory (NPL) is the focus for measurement infrastructure in the United Kingdom and maintains appropriate measurement standards for the SI base units and a wide range of derived units, including the Becquerel. Much of NPL's work is concerned with providing absolute, or primary, measurement standards. However, it is not normally practical for the wider measurement community to directly employ such standards, so a significant effort is put into providing secondary standards that are appropriate for the 'routine' user.

Standards of radioactivity are no exception and NPL provides a range of low level radioactivity standards in aqueous and other matrices. This paper describes the development of a reference standard for depleted uranium in a soil/sand matrix.

In response to requests from the user community and growing public concern to the exposure of workers in the non-nuclear workplace (i.e. outside of the nuclear fuel cycle) NPL embarked on a project to generate a solid matrix reference material containing depleted uranium to support measurements of depleted uranium in the environment. A number of candidate materials were considered, including zeolite and kaolin on the grounds that uranium could be chemically incorporated into the matrix. However, this approach was abandoned since both of these materials contain unacceptably high levels of natural uranium and in the environment, recently deposited depleted uranium will not yet be chemically incorporated in the sample matrix and may, indeed, be present as oxide powder of uncertain stochiometry.

Accordingly, the matrix finally chosen was a clean sand with a very low uranium content. The choice of spiking material was to use either very depleted (virtually 100% $^{238}\text{U}$) uranium or 'ordinary' depleted uranium with a $^{235}\text{U}$ content of 0.2-0.3%, the purity being checked by $\alpha$ spectrometry, supported by mass spectrometric and $\gamma$ spectrometric measurements.

In the presentation of this work, we will describe the spiking techniques used and the synthesis and certification of this reference material.

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THE DEVELOPMENT AND APPLICATION OF A
STANDARD FOR ORGANICALLY BOUND
TRITIUM MEASUREMENTS

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United Kingdom

Discharges of tritium to the environment are made either as tritiated water (HTO), or
organically bound tritium (OBT) with some very small discharges of tritiated
hydrogen gas (HT). As with any discharge of a pollutant to the environment, there is
the danger that tritium may enter ecosystems and the food chain.

In this work, we assume that organically bound tritium refers to non-labile tritium that
is bound directly to the carbon skeleton of a molecule (tritium that is bound to other
atoms, such as oxygen or nitrogen can be considered as labile). The radiotoxicity of
tritium is small, due to the low $\beta_{\text{max}}$ (18.6 keV) of tritium decay. For aqueous and
labile tritium, the hazard is further reduced by the short biological half life (~12 days)
 arising from the rapid exchange between hydrated $\text{H}^+$ and $\text{T}^+$ cations in the body. This
is not the case for non-labile organically bound tritium, which may be incorporated
into the fabric of the body, remaining there for considerable periods of time,
depending on the chemical form. In this case, the low $\beta_{\text{max}}$ means that all of the
energy carried by the emitted $\beta$ particles is deposited in a relatively small volume in
the immediate vicinity of the decay site. Thus, there is a requirement to be able to
monitor non-labile OBT.

Radioactivity monitoring laboratories can measure the amount of OBT in a sample by
a number of different techniques, including combustion and freeze drying. However,
these approaches rely on knowing the total efficiency of the analytical technique and
this may not be well known.

This paper describes the generation of a calibrated OBT reference material
characterised for both aqueous and organically bound tritium content and how this
may be employed to support the quality and traceability of OBT measurements.

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STANDARDISATION OF RADIOACTIVITY AT THE NATIONAL PHYSICAL LABORATORY

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The National Physical Laboratory (NPL) is the United Kingdom's national standards laboratory, an internationally respected and independent centre of excellence in research, development and knowledge transfer in measurement and materials science. For more than a century NPL has developed and maintained the nation’s primary measurement standards.

NPL’s new state-of-the-art laboratory is currently being occupied and will eventually provide 36,000 m² of scientific laboratories and other supporting facilities arranged over sixteen interlinking modules. Special attention is being paid to high environmental stability, low vibration and to minimise magnetic and electromagnetic fields. This will allow the most advanced measurement standards to be realised, many exploiting effects at the atomic level. The scientific areas are flexibly designed to meet NPL’s demanding metrology requirements well into the next century. Co-location of all services within one building will increase NPL’s efficiency, enabling us to provide improved services.

The Radioactivity Metrology Group (RMG) has been responsible for radioactivity standards at NPL since 1912, and is funded by the Department of Trade and Industry. Current work in RMG centres on:

- Absolute and primary standardisation
- Secondary standards of radioactivity
- International equivalence
- Environmental radioactivity
- Medical uses of radioactivity
- Radiation protection
- Traceability of measurement of material arising from decommissioning
- Nuclear decay data

This paper will describe the innovative techniques used within RMG to standardise radioactivity, covering nuclides from $^3$H to $^{241}$Am (and beyond) and how these standards are disseminated to the user, providing traceability of measurement to national and international standards of measurement.

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PROMPT GAMMA-RAY ACTIVATION ANALYSIS: MULTIELEMENTAL NON-DESTRUCTIVE ANALYTICAL METHOD FOR GEOCHEMISTRY AND COSMOCHEMISTRY

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Introduction

Prompt Gamma-Ray Activation Analysis (PGAA) is a multi-elemental non-destructive nuclear method used for determination of major and trace elements in a sample. The PGAA method is based on capture of cold neutrons by a nucleus of the target material, the new formed nucleus comes to an excited state and emits characteristic gamma rays, which are detected by a Compton suppressed spectrometer. By identifying the characteristic energies and their intensities, the qualitative and quantitative analysis is performed. An advantage of the PGAA method is that there is no need of any special preparation of the sample. The sample can be solid, liquid or in gaseous form. Solid samples have usually masses in the range of 100 mg up to 10 g. Depending on the amount of the investigated target matrix and the element of interest, the detection limit (DL) for a good quality PGAA installation can reach 10 ppb (e.g for B, Sm, Gd). PGAA is an eligible complementary method to Neutron Activation Analysis (NAA) for detection of H, B, C, N, P, S, Cd, Sm, Gd and Pb. In general, PGAA is an effective technique for the quantitative determination of H, B, Si, S, P, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cd, Sm, Gd, Hg. It is a powerful tool for archeological and geological investigations, helpful in nuclear industry, material science and medicine. Moreover, PGAA is an excellent and sole technique for boron and hydrogen analysis.

At the beginning of the year 2005, a new PGAA installation will be mounted and operated at the new research reactor FRM II in Garching at Munich, Germany. The PGAA facility has been moved from the Paul Scherrer Institute (PSI), Villigen, Switzerland, where it was successfully operated at the end of a curved cold neutron guide of the Swiss spallation source SINQ from October 1997 till January 2002. The neutron flux of the PGAA beam-line at PSI was about $1.4 \times 10^5$ n/cm$^2$s during the last PGAA experiments. According to the latest simulations of the new cold neutron beam guide, the neutron flux at FRM II should reach even $1.5 \times 10^5$ n/cm$^2$s. A thorough description of the PGAA facility at PSI can be found in [1]. Very sensitive measurements of boron concentration in samples were intended already from the very beginning at PSI and the whole PGAA set-up was adapted to it. The detection limits achieved were 0.08 ppm for boron in water solution [2] and 0.0038 ppm for boron in solid geological samples, respectively [1]. A brief overview of detection limits reached for different elements at PSI is presented in Table 1. The expectations are to get more than 3 times better detection limits at FRM II than at PSI.

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Table 1. Brief overview of the detection limit in intervals for selected elements reached with the PGAA facility at PSI.

<table>
<thead>
<tr>
<th>Range in μg/g</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001 - 0.01</td>
<td>B, Sm, Gd</td>
</tr>
<tr>
<td>0.01 - 0.1</td>
<td>Cd</td>
</tr>
<tr>
<td>0.1 - 1</td>
<td>H, Hg</td>
</tr>
<tr>
<td>1 - 10</td>
<td>Na, Cl, K, Ti, Mn, Co, Ni</td>
</tr>
<tr>
<td>10 - 100</td>
<td>Al, Si, S, Ca, Cr, Fe, Cu, Zn</td>
</tr>
<tr>
<td>100 - 1000</td>
<td>C, N, P, Sn, Pb</td>
</tr>
</tbody>
</table>

New applications and outlook
An extensive project of systematic elemental analysis of meteorites in cooperation with the Geochemical Institute of the University of Cologne has started. Although the majority of the meteorites were already submitted to an accurate chemical analysis or NAA, precise analysis of some elements is difficult this way (mainly H, B, C, N, P, S, etc.). PGAA is able to find their amounts in the meteorite sample as well as concentrations of many other important elements for comparison. First test measurements of small amount (hundreds of mg) of meteorites and geological standards were performed at the excellent PGAA facility, operated at the Budapest Neutron Center (BNC), Hungary. The cold neutron flux at BNC was of $5 \times 10^7$ n/cm²·s thermal beam equivalent and the background count rate was as low as 4 cps. Detailed characterization of the Budapest PGAA facility is thoroughly described, e.g. in [3]. In order to improve the detection limits, the measurements lasted for 1100 - 52400 s, depending on the sample size. To demonstrate the reliability of the method, composition of GSP-1 (Granodiorite) international geological standard and meteorite called Orgueil with known composition were determined. Results are compared to nominal values given by [5] and [6] respectively, see Table 2. Homogeneous powders of GSP-1 (335 mg) and of Orgueil (232 mg) were measured for 12500 s and 16500 s, respectively. The spectra were evaluated by the Hypermet-PC program [7], using wide database of kγ-values measured and compiled at BNC, too [8]. Thanks to the significantly higher neutron flux, the time of measurement should be reasonably reduced at the FRM II in Garching, even in case of smaller samples, like 100 – 200 mg.

Conclusions
A new PGAA station will be installed at the FRM II in Garching during the year 2004. The cold neutron flux will be about $1.5 \times 10^7$ n/cm²·s, the beam-size 5.5x5.0 cm². Keeping the background as low as at PSI, then it is realistic to get more than three times better detection limits than at PSI. With a new polycapillary focusing lens, PGAA at FRM II can offer a position sensitive sample analysis with millimeter precision and scanning of heterogeneous samples can be performed. Neutron tomography is also planned to be installed as an exchangeable set-up with the PGAA facility at FRM II. Major- and trace composition of GSP-1 standard and a meteorite sample, determined at the Budapest PGAA facility is presented and compared to nominal values. From these investigations we can draw some useful information about the planned facility in Garching.
Table 2. a) Composition of the Granodiorite standard GSP-1 (4 hours, homogeneous powder of 335 mg) compared to nominal values [5]. b) Composition of Orgueil, meteorite of C1 group (4.5 hours, homogeneous powder of 232 mg) compared to nominal values [6].

<table>
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<tr>
<th>Compound/Element</th>
<th>PGAA, Budapest</th>
<th>US Geological Survey</th>
<th>Nominal [%]</th>
<th>Standard deviation</th>
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<th>Element</th>
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<td>0.88</td>
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<td>10.68</td>
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<td>Cr</td>
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<td>7.94E+03</td>
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<td>Co</td>
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<td>1.13</td>
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</table>

Acknowledgments
This work was supported by the EU5 Framework Project and the University of Cologne.
The authors wish to express their gratitude to Prof. G. L. Molnár of the Department of Nuclear Research, Budapest for his valuable help and to Prof. H. Palme for providing the meteorite samples and standards.

References
DETERMINATION OF ACTINIDES AND $^{90}$Sr IN SPENT ION EXCHANGE RESINS

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According to the IAEA standards all radioactive wastes have to be evaluated, that means determination of physical, chemical and radiological properties. This evaluation assures correct classification, further processing and handling of the wastes. Spent ion exchange resins coming from nuclear power plants are classified as intermediate level waste. They are one of the most problematic nuclear wastes since they are present in large amounts and contain high activities due to activation and fission products. In the present work we focused on determination of some important activation products like $^{238}$Pu, $^{239}$Pu/$^{240}$Pu, $^{241}$Am and $^{237}$Np, and $^{90}$Sr as a fission product. Activation products of interest are alpha emitters, while $^{90}$Sr is beta emitter. Radioactive solutions of $^{243}$Am, $^{242}$Pu, $^{238}$Np, and $^{85}$Sr and pure ion exchange resins were used to prepare artificial samples and trace nuclides during analytical procedure.

Samples were prepared in a suitable form for separation procedure using catalytic wet oxidation, also known as the Fenton reaction. This method was chosen among two other methods, leaching and total destruction. Some problems occurred in leaching and total destruction. Leaching was performed with 8 M HNO$_3$ because it was the most suitable medium for further sample processing. Radionuclides with higher valence states compared to Cs and Sr remained partly bonded to the resin. Leaching was tested also from HCl medium and the results were similar. Losses of radionuclides with higher valence states could not be avoided. The main reason for not using total destruction at 800°C was complete loss of Cs due to volatility. Catalytic wet oxidation gave good results for all selected radionuclides. Optimum pH was determined to be 2-6 and optimum temperature between 50 and 80 degrees.

Determination of selected nuclides requires selective chemical separation prior to alpha spectrometric detection or liquid scintillation counting. The separation was performed by ion exchange chromatography, extraction chromatography and precipitation techniques. We used
the method that was developed by Moreno et al [1]. The method was modified to fit our purpose and available equipment. Some standard solutions and pure ion exchange resins were used for checking the method and five real samples from Institute’s TRIGA MK II reactor were analysed. Radioactive tracers of $^{241}$Am, $^{232}$Pu, $^{239}$Np and strontium carrier were added to each sample. Wet oxidation was performed with Fenton reaction under optimised conditions. Solution was evaporated and the residue was dissolved in 8 M HNO$_3$. Solution was loaded on an anion exchange resin conditioned with 8 M HNO$_3$. Fe, Sr and Am passed through the column. The effluent was used for the analysis of Am and Sr radionuclides. The column was washed with 9 M HCl to elute Th, if present. Pu was stripped with NH$_4$I/9MHC1, while Np with 4M HCl. Both load solutions were evaporated to dryness. Evaporating with 1-2 mL of concentrated nitric acid destroyed ammonium iodide. Thin sources for alpha spectrometry measurement were prepared by co-precipitation on NdF$_3$. Am/Sr effluents from the ion exchange column were evaporated to dryness and diluted with deionized water. Up to 5g of Ca$^{2+}$ and 10g of oxalic acid were added to the solution. pH was adjusted to 5.5-6 with ammonia solution so that both Am and Sr were co-precipitated. Iron forms complexes with oxalic acid and remains in solution. After centrifugation, washing with deionised water oxalate precipitate was destroyed by evaporation with concentrated nitric acid. The residue was dissolved in 2 M HNO$_3$ and loaded on a TRU Resin from ElChrom. The column did not retain Sr. Am was stripped with 4M HCl. Am load solution was evaporated, co-precipitated on NdF$_3$ and measured on an alpha spectrometer. Sr fraction was cleaned on a Sr column and recovery was determined gravimetrically by weighing the strontium oxalate precipitate. Precipitate was dissolved in 1M nitric acid, mixed with scintillation cocktail and analysed by liquid scintillation counting. Table 1 shows yields for various radionuclides after separation according to described procedure.

Table 1: Yield intervals for various radionuclides after separation of artificially made samples.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$^{241}$Am</th>
<th>$^{90}$Sr</th>
<th>$^{239}$Np</th>
<th>$^{232}$Pu</th>
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</thead>
<tbody>
<tr>
<td>Yield interval (%)</td>
<td>54-72</td>
<td>77-85</td>
<td>56-94</td>
<td>83-88</td>
</tr>
</tbody>
</table>

Table 2 shows specific activities of selected activation products in five real samples of spent ion exchange resins from Institute’s TRIGA MK II reactor. Selected activation products were low in all samples. Sample 1 has high activity of $^{90}$Sr. This sample was also analysed by
gamma spectrometry and results showed high activities of Cs-137 and Co-60 in the sample. Eu-152 and Eu-154 were also detected.

Table 2: Specific activities of $^{90}$Sr, $^{241}$Am, $^{239/240}$Pu, $^{238}$Pu and $^{237}$Np in spent ion exchange resins from Institute's TRIGA MK II reactor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr-90 (Bq/kg)</th>
<th>Am-241 (Bq/kg)</th>
<th>Pu-239/240 (Bq/kg)</th>
<th>Pu-238 (Bq/kg)</th>
<th>Np-237 (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.5 \times 10^2 \pm 1 \times 10^3$</td>
<td>0.60 ± 0.06</td>
<td>7.2 ± 0.6</td>
<td>0.66 ± 0.06</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>2</td>
<td>88 ± 4</td>
<td>0.07 ± 0.02</td>
<td>0.18 ± 0.05</td>
<td>0.05 ± 0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>3</td>
<td>144 ± 3</td>
<td>0.04 ± 0.01</td>
<td>0.67 ± 0.06</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>4</td>
<td>129 ± 3</td>
<td>0.06 ± 0.02</td>
<td>0.65 ± 0.06</td>
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<tr>
<td>5</td>
<td>108 ± 2</td>
<td>0.09 ± 0.03</td>
<td>0.23 ± 0.05</td>
<td>0.02 ± 0.01</td>
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</table>

Reference

A TRLFS STUDY OF AQUEOUS CARBONATE COMPLEXES: COMPARISON OF Eu(III) AND Cm(III) AT 25°C, AND TEMPERATURE INFLUENCE ON CmCO$_3$$^+$ STABILITY

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INTRODUCTION

Actinide chemistry in natural environments is of great interest to predict radionuclide migration from possible radioactive waste repositories. In particular Am(III) aqueous speciation in groundwaters can be dominated by carbonate complexes [1]. The solubility of Am(III) solid compounds, and the stoichiometries and thermodynamic stabilities of its aqueous complexes have been critically reviewed by the NEA-TDB (Thermodynamic Data Base project of the OECD) [2]. The NEA-TDB have pointed out (i) that the species AmCO$_3$$^+$, Am(CO$_3$)$_2$$^-$ and Am(CO$_3$)$_3$$^-$ have been well established, but other carbonate complexes may be stable under environmental conditions, particularly hydroxo-carbonate mixed complexes; (ii) a lack of available data at temperatures above 25°C; (iii) discrepancies in the literature, so that it has not been possible to determine the ion interaction coefficients, e, for ionic strength connections with the specific ion interaction theory: the NEA-TDB has reported values among which many estimated coefficients.

Lundqvist et al. determined lg $\beta_1 = 5.81 \pm 0.04$ and $5.91 \pm 0.05$, and lg $\beta_2 = 9.72 \pm 0.10$ and $10.72 \pm 0.08$ for Am(III) and Eu(III) respectively for in 1M NaClO$_4$ [3]; Kim et al. have proposed lg $\beta_1$ of $6.65 \pm 0.07$ and $6.57 \pm 0.08$ for Cm(III) and Eu(III) respectively in 0.1M NaClO$_4$ [4]. The comparison of lg $\beta$ values for Am, Cm, and Eu measured by the same author suggests that they are good chemical analogues. Thus we have chosen to study Eu(III) and Cm(III) by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Thanks to its high sensitivity [5], TRLFS enables the detection of metal ion species below solubility limits, so that there is no ambiguous interpretations due to the nature of the solid phases [6]. This technique has already been used to determine stabilities of Cm(CO$_3$)$_3$$^{2-}$ (i = 1-4) and CmHCO$_3$$^-$ in NaCl media [7]; the bicarbonate complex has also been proposed at higher CO$_2$(g) pressure [8]. However the analogous AmHCO$_3$$^-$ has not been observed even under up to 1-atm CO$_2$(g) pressure [1]. Moreover both M(CO$_3$)$_3$$^{2-}$ [1,4,9] and M(CO$_3$)$_3$$^-$ [7,10] have been proposed for the stoichiometries of lanthanides and actinides limiting carbonate complexes, which also affects the determination of other complexation constants in data treatments.

We will present our experimental data on Eu(III) and Cm(III) using TRLFS. Our experimental conditions have been chosen on the basis of Am(III) data. Quantitative results on Eu(III) carbonate complexation are obtained and speciation models considering Eu(CO$_3$)$_3$$^{2-}$ or Eu(CO$_3$)$_3$$^-$ as the limiting complex are tested. This study has been extended to Cm(III) at temperatures from 10 to 50°C.

SENSITIVITY ANALYSES

A sensitivity analysis of Am(III) complexes in hydroxo-carbonate solutions has first been conducted using data from [1,4,9]. We use in particular solubility experiments with correct measurements of [H$^+$] at high ionic strength, taking into account the junction potential of the
electrode and the activity coefficient of $\text{H}^+$ by a calibration method with adequate buffer solutions [1,9]. Figure 1 shows the speciation of Am(III). Only validated complexes [2] are represented on this diagram and dotted lines are drawn when other possible stoichiometries could be considered. The chemical conditions of interest for our studies have been extracted from such calculated speciation diagrams.

![Figure 1: Speciation of Am(III) as a function of $-\log [\text{H}^+]$ and $\log [\text{CO}_3^{2-}]$ calculated with [Am(III)] = $10^{-5}$M and [Na$^+$] = 0.1M according to validated stoichiometries of soluble complexes and solid compounds and using stability constants from [1] and [2]. The dots represent our conditions for the experimental study of Eu(III).](image)

**CARBONATE COMPLEXES OF Eu(III)**

Each Eu(III) species is characterised by specific fluorescence lifetime and spectrum (Figure 2). Our sensitivity analysis suggests the presence of at least the species $\text{EuCO}_3^{2+}$, $\text{Eu(CO}_3)_2^{3-}$ and $\text{Eu(CO}_3)_3^{4-}$. Only mixtures of these can be obtained by varying the chemical conditions in the solutions, except the limiting carbonate complex that could be isolated at high ionic strength taking advantage of its elevated charge. Thermodynamic constants are determined by curve fitting based on fluorescence intensity ratios as shown on Figure 3. No bicarbonate or hydroxo-carbonate mixed complex seems to be significant under our experimental conditions.

![Figure 2: Variation of fluorescence spectra with $\log [\text{CO}_3^{2-}]$, measured in Eu(III) solutions with [Na$^+$] = 0.1M under 100% CO$_2$ atmosphere; formation of $\text{EuCO}_3^{2+}$.](image)
Indications on stoichiometries result from the fluorescence spectra and lifetimes measured at various [CO$_3^{2-}$]. Two interpretations are tested depending on the nature of the limiting complex Eu(3CO$_3$)$_2$ or Eu(3CO$_3$)$_3$. but no definitive conclusion is obtained (Figure 3). To conclude this point, solubility measurements of NaEu(3CO$_3$)$_2$ in concentrated carbonate solutions at high ionic strength are currently carried out.

**TEMPERATURE DEPENDENCE OF Cm(III) FLUORESCENCE SPECTRA**

At constant [CO$_3^{2-}$], the spectra of thermostatically-controlled Cm(III) solutions between 10 and 50°C show differences in their shapes and intensities from that at 25°C: in addition to the effect of temperature on spectroscopy, values of the stability constants should change with temperature since complexion reactions are not athermous. TRLFS is then used for a determination of enthalpy variations corresponding to the formation of Cm(3CO$_3$)$_2$.

![Figure 3: Measured fluorescence intensity ratios plotted against lg [CO$_3^{2-}$]. Comparison of fitted curves depending on the limiting complex Eu(3CO$_3$)$_2$ or Eu(3CO$_3$)$_3$.](image)

**ACKNOWLEDGMENTS**

The authors are grateful to ANDRA for financial support for this work and PhD grant.

**REFERENCES**

ELECTROCHEMICAL BEHAVIOUR OF U (IV) AND U (VI) IN PHOSPHORIC ACID

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‡ Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc
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For both technical and historical reasons, most light water moderated nuclear reactors use uranium dioxide as fuel. Alternate chemical forms (e.g., uranium metal, uranium carbide, uranium nitride, uranium phosphide and uranium sulphide) were also considered but were never used on a large industrial scale. Indeed, uranium dioxide presents attractive advantages such as a high melting point (3113 K), good dimensional stability under radiation, and good chemical compatibility with structural reactor materials. It has also some drawbacks like a rather low thermal conductivity (< 10 W m⁻¹ K⁻¹) which leads to large temperature gradients inside the fuel pins. Beside several factors influencing the thermal conductivity (e.g., the porosity, the burn-up, the temperature), the stoichiometry of UO₂ plays an essential role. Indeed, solid uranium dioxide reacts easily with oxygen, leading to a hyper-stoichiometric state (UO₁⁺₇), the oxygen to uranium ratio becoming slightly greater than 2. Oxygen occupies interstitial locations into the crystal lattice. Deviations from stoichiometry have significant effects on fuel performance [1] and lead to a decrease of the fuel thermal conductivity, which results in even higher fuel temperatures. This affects the rate at which fission-product gases are released from the fuel, thereby exerting pressure on the fuel clad. In extreme conditions, the thermal expansion of hyper-stoichiometric fuel may become large enough to cause further increase of mechanical pressure exerted by the fuel on the clad when a zero-gap situation is achieved. These factors may, in turn, affect the integrity of the fuel pin and determine the useful life of a fuel element.

Therefore, the measurement of the stoichiometry of UO₂ is essential for predicting the remaining lifetime of fuel elements. Among several methods to achieve such measurements, differential pulse polarography or alternate electroanalytical methods have been widely used under various conditions [1-4]. Besides the analytical determination, the electrochemical behaviour of the couple U (VI)/U (IV) in various conditions has also been widely studied [5-8]. However, the reported results do not allow to consistently conclude on the exact mechanism of the reduction of U (VI) to U (IV) under highly concentrated phosphoric acid. For instance, El Kacem et al. [7] found that the reduction is quasi-reversible, while it would involve the exchange of one electron. Since they found also that the global number of electrons (as determined by coulometry) is 2, they conclude that the reduction proceeds in two steps: the reduction of U (VI) to U (V), followed by the dismutation of U (V) to U (IV) and U (VI). But Plazanet et al. [5] found that the reduction is irreversible and involves two electrons.

In order to elucidate the mechanism governing the electro-reduction of U (VI) on a mercury electrode in relatively high concentrations of phosphoric acid (5 M), we carried out cyclic voltammetry experiments. As is shown in Fig. 1, using a solution containing 6.10⁻⁶ M of U
(IV) and 2.10^{-4} \text{ M of U (VI)} and cycling from +200 \text{ mV to } -600 \text{ mV}, then back to +200 \text{ mV vs. Ag/AgCl (KCl sat.), does not show any oxidation peak during the scan. Based on a further analysis of the displacement of the reduction wave with respect to the scan rate, we concluded that the reduction is electrochemically irreversible. The product of the transfer coefficient ($\alpha n$) by the number of electron exchanged by the rate determining step (n) was found to be 0.97. Assuming that the electrochemical activation barrier is symmetrical (i.e. $\alpha = 0.5$), we conclude that the number of exchanged electrons is 2.

Figure 1: Cyclic voltammetry of a solution containing 6.10^{-4} \text{ M U (IV)} and 2.10^{-4} \text{ M U (VI)} in H_3PO_4 5 \text{ M at 298 K. All potentials measured w.r.t. Ag/AgCl (KCl sat.) reference electrode.}

Further, we used the theoretical models published by Nicholson and Shain [9] to fit our results. We found that the theoretical predictions for an irreversible process were much better adapted to our measurements than the model corresponding to a reversible process. This approach delivered a second estimation of $\alpha n = 1.06$, which confirms the conclusions derived from the displacement of the linear sweep voltammetric wave with the scan rate. Further calculations will allow us to estimate both the diffusion coefficient of the U (VI) species and the kinetic constant associated to the reduction.

Finally, we standardised a differential pulse polarographic method to quantify U (VI) in UO_2 samples, thereby allowing characterising the degree of hyper-stoichiometry. As expected, the differential pulse method allowed us to carry out the quantification using much less material than along the standard polarographic method. We found a detection limit equal to 10^{-5} \text{ M in U (VI), while the calibration curve remains linear for U (VI) concentrations ranging from 10^{-4} to 2.10^{-3} \text{ M. The relative precision of the method is better than 3 \% when at least five measurements are averaged.
References


SEPARATION OF THORIUM (IV) FROM CERIUM (IV) AND LANTHANUM (III) IN AQUEOUS SOLUTIONS BY EXTRACTION CHROMATOGRAPHY TECHNIQUE

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Extraction chromatography is a type of liquid-liquid chromatography in which the stationary phase is either an extractant or a solution of an extractant in an appropriate solvent supported on an inert substrate. This technique thus combines the selectivity of solvent extraction with the multistage character of a chromatographic process and the ease of handling associated with an ion-exchange resin [1]. Extraction chromatographic columns are prepared by simply coating or impregnating a solid support (e.g., kieselguhr, silica or various polymers) with the extractant. The extraction chromatography technique has been utilized for the separation and recovery of actinides and lanthanides [2-4].

The common minerals containing rare earth elements are monazite, a phosphate mineral, and bastnaesite, a carbonate mineral [4]. It was found that the ore contained rare earths (REEs) in bastnaesite mineral were present in mid-west of Turkey. These deposits, Eskişehir-Beylikahır ore deposits, have approximately 3.8x10⁵ tons of ThO₂ and 4.5x10⁶ tons of REE ores [5]. Several studies have been reported to recovery of thorium and REE in these deposits [6-9].

In this study, the separation of thorium (IV) from aqueous solutions containing lanthanum (III) was investigated by extraction chromatography technique. Acidic extractants have been used for separation and recovery of actinides and lanthanides [10]. Solvation in these extractants occurs by means of their P—O groups. Di(2-ethyl/hexyl)orthophosphoric acid (DEHPA), which is one of the acidic organophosphorous compounds, was selected as the extractant. Silica gel was chosen as the inert support. Glass columns of 0.8 mm internal diameter were packed with 0.5 g of the silica gel coated with DEHPA. Experiments were
carried out by using synthetic Th and La solutions. Extraction of these elements on DEHPA/silica gel column was tested in hydrochloric and sulphuric media. Fig. 1 shows the yield of extraction (E %) as a function of HCl concentration. Extraction yields for La and Th are quite low. The extraction yield of thorium increases with increasing sulphuric acid concentration (Fig 2). The parameters affecting the efficiency of extraction such as extractant concentration, flow rate, solutions and different diluents were studied. Optimum conditions were determined. In addition, the influence of several ions (cations and anions) on the extraction performance was also investigated. Various elution solutions were tested for the elution experiments. Elution curves were made to separate Th(IV) in binary mixture. The process obtained in this work can be applied especially for separation and recovery of thorium from Bastnasite or Monazite minerals.

Fig. 1. Effect of HCl concentration on extraction of Th(IV) and La(III) on 0.5 g DEHPA/Silica gel column. Thorium (IV): 50 μg mL⁻¹, 25 mL; Lanthanum (III): 50 μg mL⁻¹, 25 mL. Flow-rate of aqueous phase: 0.7 mL min⁻¹.
Fig. 2. Effect of $\text{H}_2\text{SO}_4$ concentration on extraction of Th (IV) on 0.5 g DEHPA/Silica gel column. Thorium (IV): 50 $\mu$g mL$^{-1}$, 25 mL. Flow-rate of aqueous phase: 0.7 mL min$^{-1}$.

References


239Np AS A TRACER OF 237Np IN EFFlUENT SAMPLES AND LOW LEVEL NUCLEAR WASTE

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In this paper a technique to separate and measure 239Np using 229Np as a tracer, is presented. For the case of the most known actinides such as Pu, Am, Th, U and Cm, it is possible to quantify the chemical recovery in a separative process through the corresponding tracers 240Pu, 241Am, 232U and 230Th (the Cm is determined along with the Am). However, there is no alpha tracer that could be added to the sample and measured together with 239Np. In addition to the time required for the chemical separation, which implies the use of two stages of a chromatographic system (either for anionic exchange or partition chromatography), it is important to take into account the time required for the conditioning of the medium and electrodeposition of the column eluent, with the resulting risk of a decrease in the chemical recovery due to loss of material.

Taking into account the above mentioned drawbacks, an interesting alternative is the combined measurement of liquid scintillation with shape pulse discrimination and gamma spectrometry, which permits a measurement right after separation adding only a predetermined amount of L.S. cocktail.

The determination of 239Np is accomplished within a scheme of radiochemical separation that implies the use of three EICHROM chromatographic columns, in tandem (in which U, Pu, Am, Cm are also separated), as shown in the figure 1.

![Diagram](image)

Figure 1
After the radiochemical separation, a liquid scintillation measurement with pulse decay discrimination and a gamma measurement on the same vial is performed. The method also allows to perform an electrodeposition and an ulterior alpha and gamma measurement.

The conditions to set the best discrimination of beta/gamma emitters (\(^{60}\)Co and \(^{137}\)Cs included) are described in comparison to different scintillation cocktails and % spillover vs. t-SIE correction curves.

Details of a simple radiochemical procedure based on separations of Np nuclides on a TEVA column are also given.

The separative technique was applied to a liquid sample of an evaporator tank at Atucha I Nuclear Power Plant (CNA1).

The \(^{237}\)Np spectrum obtained by liquid scintillation shows a less pronounced peak of the spectrum, when compared with that obtained from the pure standard in the same region, allowing to verify the presence of \(^{60}\)Co by gamma spectrometry.

The absence of other actinides was assessed by alpha spectrometry on an aliquot of the sample electrodeposited.

![Figure 2: Linear LSC spectrum of \(^{237}\)Np standard. Efficiency of alpha measurement (optimized region 116-294): 93.7%](image)

![Figure 3: Linear LSC spectrum of \(^{237}\)Np (TR 71 CNA1)](image)
In this case, the chemical recovery obtained by spectrometry is 85.2%. The MDA obtained by alpha spectrometry is 0.08 Bq/l and, by LSC, 0.22 Bq/l; being the measurement efficiency 93.7% and the chemical recovery 98.0%.

REFERENCES


SETTING UP LASER ABLATION – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (LA-ICP-MS) IN A HOT-CELL ENVIRONMENT FOR THE ANALYSIS OF IRRADIATED NUCLEAR MATERIALS

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The characterisation of irradiated material is very demanding as the UO\textsubscript{2} ceramic considerably changes during the irradiation process. Due to significant temperature gradients (±500K over ~5mm) the fission products show a concentration profile along the fuel pellet radius. Furthermore neutron capture reactions at the pellet periphery and fuel cladding interactions enhance the inhomogeneous distribution of fission products and transuranium elements. The techniques mainly used today to characterise these materials are Electron Probe Micro Analysis (EPMA), Secondary Electron Microscopy (SEM) and X-ray fluorescence. These techniques have deficits especially regarding the fission gas analysis and the sensitivity. Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) offers the potential to considerably improve the analyses of irradiated nuclear fuel. The possibilities of accessing almost 80% of the elements in the Periodic Table with sufficient sensitivity for trace determinations, having both in situ local and bulk analysis capabilities, and performing quantitative analysis using non-matrix-matched calibration standards are major advantages of this technique [1].

\textbf{Fig 1} : Schematic configuration of LA-ICP-MS in a hot-cell environment
Setting up LA-ICP-MS in a hot-cell environment requires an original design, with the main (technical) objective to install only the minimum amount of equipment into the hot-cell. This limitation comes from practical considerations that all handling (also repairs) inside the hot-cell is only possible with master-slave manipulators, that sensible electronics should be kept out of the heavy radiation environment of a hot-cell and that all equipment inside the hot-cell in the end becomes expensive radioactive waste.

The principle of the LA set-up adapted for a hot-cell environment is illustrated schematically in Fig. 1. The laser is installed in front of the hot-cell and the laser beam is guided to the sample through a periscope. A ‘visual channel’ is also provided in the periscope so that the sample can be clearly observed from outside the hot-cell. A housing around the periscope shields it from the hot-cell atmosphere. From the ablation cell, the ablated material is transported through a long carrier gas line to the ‘nuclearised’ ICP-MS (with a sample introduction system in a glove-box) behind the hot-cell. Distances from laser to ablation cell and from ablation cell to ICP-MS torch are each time around 6m long. The detailed technical characteristics and first results with this set-up as tested in a ‘cold lab’ will be shown.

Once operative, the LA-ICP-MS technique will be able to provide detailed (down to ppb level), spatially bound (crater diameter ≥ 20µm), isotopic data of highly radioactive samples, e.g. the distribution of fission and activation products (including fission gas) across an irradiated fuel pellet.

Reference
NAA OF LONG-TIME IRRADIATED HAFNIUM FOR AN IMPROVED HALF-LIFE VALUE OF \(^{182}\text{Hf}\)

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Long-time irradiated hafnium samples were investigated in the framework of a new half-life determination of \(^{182}\text{Hf}\). The now extinct \(^{183}\text{Hf}\) was present in the early solar system, and thus it is used for dating the earliest history of the Earth and the Moon on the basis of hafnium-tungsten separation during core formation [1-3]. The \(\beta\)-decay of \(^{183}\text{Hf}\) with a half-life of about 9 million years produces stable \(^{182}\text{W}\) via \(^{182}\text{Ta}\) (half-life 114 days) and leads to tungsten isotopic anomalies in early fractionated materials. The only half-life measurements from 40 years ago were performed directly in connection with the discovery of \(^{183}\text{Hf}\), yielding a value of \(\pm 2\) million years [4]. The large uncertainty of \(\pm 22\%\) is not satisfactory for the application mentioned above.

Neutron activation was used to quantify hafnium in a material produced by Helmer and Reich more than 30 years ago, initially for the study of the high-spin isomer of \(^{178m}\text{Hf}\). They irradiated hafnium for up to 2 years with \(>4 \times 10^{14}\) neutrons cm\(^{-2}\)s\(^{-1}\) in the Materials Testing Reactor and the Engineering Test Reactor at Idaho Falls, USA [5,6]. The half-life can be calculated according to the basic decay law, when both the number of \(^{182}\text{Hf}\) atoms and their activity are measured in the sample material. The isotopic ratio of \(^{182}\text{Hf}\) to \(^{180}\text{Hf}\) can be precisely determined by mass spectrometry. NAA contributes the quantity of \(^{180}\text{Hf}\) in the same sample and gamma-spectrometry adds the activity of \(^{182}\text{Hf}\). The material of Helmer and Reich was deposited originally on a white fibrous filter, covered with adhesive tape on both sides and mounted on cardboard. After removing the tape and the cardboard the actual hafnium material was detached from the filter by using an ultrasonic bath with HNO\(_3\) and H\(_2\)O tridest. After drying at 50\(^\circ\)C a quantity of 97.7 mg of white powder remained for the investigations, which was split into five samples for NAA and activity measurements.

First measurements by ICP-MS indicated a certain amount of boron in the sample. This contamination was probably due to glass filter fibres, which had not been removed quantitatively in order to minimize hafnium losses. As a boron contamination impairs NAA by neutron absorption, for one sample an additional chemical purification step was performed by dissolution in HF suprapure and calcination at 1500\(^\circ\)C. Volatile boron compounds and other fluorides were evaporated and stable H\(_2\)O \(_2\) was produced. By comparing the hafnium determination before and after the purification, a boron content of 1.28±0.03\% was found, which was included in the corrections for neutron shielding.

The irradiation for NAA was performed at the TRIGA Mark-II reactor of the Atom Institute of the Austrian Universities. To produce similar count rates for \(^{183}\text{Hf}\) and the activation product \(^{185}\text{Hf}\) (half-life 42.39 days) in the sample, an irradiation at a moderate flux of \(10^8\) neutrons cm\(^{-2}\)s\(^{-1}\) (reactor operation at 25W) was chosen. High purity H\(_2\)O \(_2\) was used as hafnium
standard. Several hafnium standard samples were irradiated together with the $^{182}$Hf containing samples, and the rotation (2 turns s$^{-1}$) of the capsule containing the samples guaranteed a homogeneous activation. Altogether four irradiation runs were performed, one test irradiation, two irradiations of $^{182}$Hf containing samples and one irradiation of the purified $^{182}$Hf sample with high neutron flux.

Activities were measured by gamma-spectrometry in several independent measurement series. These measurements were carried out using a HPGe-detector with 50% relative photo-peak efficiency connected to a Canberra DSP amplifier and a loss-free counting system. One measurement series was performed with an HPGe detector with 30% relative photo-peak efficiency. Corrections for self-attenuation of gamma rays were taken into account.

The measurements lead to a value of 9.034±0.251 million years (My) for the half-life of $^{182}$Hf. Parallel investigations with another material from Helmer and Reich using isotope dilution for the determination of the amount of $^{182}$Hf atoms gave 8.896±0.089 My [7]. For the activity of $^{182}$Hf, in both cases the 270 keV decay line was used with a branching ratio of 0.79±0.006 [8]. The results are in satisfactory agreement and a weighted mean (considering correlated uncertainties) of 8.904±0.088 My will be proposed.

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References

APPLICATION OF X-RAY FLUORESCENCE METHODS FOR ANALYTICAL CONTROL OF PYROCHEMICAL REPROCESSING OF NUCLEAR FUEL

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At present the procedures applied to on-line control of granulated uranium and mixed uranium-plutonium fuel production, when scientific studies and experimental pyrochemical reprocessing irradiated fuel, include spectrophotometric and radiometric (in some cases emission-spectral) methods of analysis. However these methods do not quite meet current requirements, especially in respect of accuracy and rapidity. Thus X-ray fluorescence analysis [1] that allows simultaneous multi-elemental analysis and does not require any complex and long sample preparation was selected as an advanced method for the process on-line control.

X-ray fluorescence analyzer SKS 07P-RT (developed by “Green Star”, Russia) used for the analysis consists of the following principle of units:
- measuring module containing an excitation source, a detecting unit and a measuring cell;
- power supply source for the excitation source;
- excitation source control plate;
- pulse signal processor plate SBS-59;
- personal computer.

The spectrometer measuring unit may be placed in shielded equipment that allows measurement of samples containing Pu and Am with the total activity up to $10^7$ Bq. The close accommodation geometry of the excitation source and the detector provides the high sensitivity and possibility to determine elements at units of μm level. Design of the measuring module allows decontamination of its surfaces in case of radioactive contamination.

In order to improve the analysis sensitivity and to reduce the activity of the samples being measured, an effort was made to study the effect of sample preparation method on the measurement of the target elements. An aliquot of the measured solution is applied on the polyethylene film (less than 0.1mm thick) of the substrate that is used as a sample for taking spectrum. The analysis of a sample as an aqueous solution droplet as compared with the sample obtained after the solution evaporation shows that a significant contribution into the background signal level is made by the radiation scattered in water (Fig.1). This is most evident in the energy range of 15 to 22 keV and the effect is more significant for small concentrations of elements being measured. Thus the samples evaporated to dry residue are more preferable for quantitative determination of elements using SKS-07P-RT spectrometer.
The boundary conditions for determination of uranium, plutonium, neodymium, cerium, samarium, europium, copper and barium as well as the cross effect of these elements during their qualitative and quantitative determination in the same sample were studied.

To shorten the quantitative analysis procedure the internal standard method with copper as a standard element was selected. The quantity of copper required for the quantitative determination of the target elements in different concentration range was determined. Fig. 2 shows the typical spectrum of real process sample.

The measurement errors were determined for the elements subjected to the quantitative analysis. According to the preliminary investigation the quantitative analysis error for primary elements (uranium, plutonium, lanthanides) ranges 10 to 15%. Owing to calibration of the spectrometer by references and application of the regression analysis by the references, the analysis error was reduced to less than 10% [2].

The studies suggest that the fluorescence analysis allows determination of the target elements (uranium, plutonium) and the main fission products in the same sample with rather high accuracy. The time taken to prepare a sample and obtain the analysis results by this method is less than applying the traditional methods. Thus the fluorescence analysis may be used to control the pyrochemical reprocessing of irradiated fuel.
Fig. 2. Spectrum of real process sample

References


ULTRATRACE ANALYSIS OF $^{129}\text{I}$ IN SEDIMENTS BY ICP-MS WITH COLLISION CELL

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Determination of the long-lived radioactive nuclide $^{129}\text{I}$ is of interest in monitoring radioactive emissions from nuclear facilities as well as in studying geological and cosmic processes. $^{129}\text{I}$ is released continuously into the environment by nuclear fuel reprocessing plants. Today its fallout is even larger than the fallout from nuclear weapon tests in the 1960s. The Chernobyl accident in April 1986 resulted in widespread contamination of the environment with radioactive materials, including $^{129}\text{I}$. All this makes it the research target of a growing scientific community. However, detection of $^{129}\text{I}$ in environment samples by radiometric methods is very difficult because of its long half-life. Radiochemical neutron activation analysis (RNAA) and accelerator mass spectrometry (AMS) allow low detection limits to be achieved, but these methods are very expensive and time-consuming [1,2].

The problems in $^{129}\text{I}$ determination by ICP-MS are the high background caused by $^{129}\text{Xe}$ impurities in argon plasma gas and in the insufficient abundance ratio sensitivity of $^{129}\text{I}/^{127}\text{I}$. Application of ICP-MS with collision cell is advantageous for reducing disturbing background intensity of $^{129}\text{Xe}^+$. The aim of the work was the development of a rapid and high-sensitive analytical method using ICP-MS with hexapole collision cell (ICP-CC-MS) for the determination of low $^{129}\text{I}/^{127}\text{I}$ isotope ratios in synthetic lab standards and environmental samples. A special direct sample introduction device for iodine extraction via the gas phase from solid environmental material coupled on-line to ICP-CC-QMS was developed. The detection limit for $^{129}\text{I}^+$ determination in aqueous solution and soil samples via gas-phase extraction was determined to be of 0.8 pg/g and 30 pg/g, respectively.

The measurement of the isotope ratio of $^{129}\text{I}/^{127}\text{I}$ in contaminated soil samples using ICP-CC-QMS down to $10^{-6}$ yielded good accuracy and precision. The sample introduction system by application of a cooling finger (between oven and ICP) in order to enrich the analyte and to improve the detection limit of 0.4 pg/g for $^{129}\text{I}$ determination was achieved.

ON THE USE OF CE-ICP-MS (CAPILLARY ELECTROPHORESIS - INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY) TO DETERMINE THERMODYNAMIC CONSTANT. APPLICATION TO THE UO_2^{2+}/H_2SO_4 SYSTEM


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During the last years speciation studies have gained more and more popularity since their knowledge is necessary to understand the transfer mechanisms observed for various elements. Among them, radionuclides or chemical pollutants become a subject of interest, especially to predict their behaviour in the biosphere and their potential impact on health and population. Indeed, migration in the environment and toxicity depend on the chemical species with respect to the thermodynamic conditions encountered in nature such as pH, pE, ionic strength and temperature. Furthermore, the very low concentration of these radionuclides and their repartitions in several chemical species necessitate on the one hand the use of a sensitive detector and, on the other, their separations necessitate efficient chromatographic techniques with high separation factors. That is why, we have combined capillary electrophoresis and ICP-MS. Indeed, the univocal attribution of a peak to an element is then only possible if the reproducibility in terms of migration time is high enough to attribute any peak without ambiguity to a unique species. In addition, the detector may exhibit very low detection limits for actinides and a resolution high enough to discriminate between neighbouring masses.

Therefore, studies were carried out in order to check the capacity of the CE / ICP-MS coupling as a speciation instrument for actinides at trace level and to define the associated analytical procedures[1]. Focusing on actinides speciation, several axes were identified and investigated. The coupling turned out to be a suited instrument for the determination of absolute electrophoretic mobilities at infinite dilution[2] (physico-chemical property which allows to predict the migration time of an ion under an electrical field), the separation of different actinide oxidation states in solution and the determination of thermodynamic constants. Among those, the knowledge of thermodynamic constants is essential to predict species distribution. Therefore, the potentialities of the coupling were checked on well characterized equilibria[3] [T = 298 K et I = 0]:

\[
\begin{align*}
\text{UO}_2^{2+} + \text{SO}_4^{2-} & \leftrightarrow \text{UO}_2\text{SO}_4, & \log \beta_1^{\text{u}} &= 3.15 \pm 0.02 \\
\text{UO}_2^{2+} + 2\text{SO}_4^{2-} & \leftrightarrow \text{UO}_4^{2+} (\text{SO}_4)^2, & \log \beta_2^{\text{u}} &= 4.14 \pm 0.07
\end{align*}
\]

Moreover, the complexation of the uranyl ion by the sulphate is characterised by a fast kinetic. Therefore, the system is always in equilibrium and a single peak of uranium appears on the electropherogram. The observed mobility will then depend on the mobility and molar fraction of the various chemical forms:

\[
\mu = \sum [f_i \mu_i]
\]

by taking into account the various uranium species: UO_2^{2+}, UO_2SO_4, UO_4^{2+}(SO_4)^2.
\[ \mu_i^t = \phi_{10j} \mu_{10j}^{i+} + \phi_{10s0} \mu_{10s0}^i + \phi_{10s0j} \mu_{10s0j}^i \cdot \]

Focusing on the first complexation in a first stage and using the mobility of the uranyl ion \((\mu_{10j}^{i+} = 5.29 \times 10^{-4}\text{ cm}^2\text{V}^{-1}\text{s}^{-1})\) as reference this average mobility was determined experimentally using the following equation.

\[
\Delta \mu_{op}^t = \frac{L^2}{V} \left( \frac{1}{t_{10j}^+} - \frac{1}{t_v} \right)
\]

\(V\) voltage (V)
\(L\) capillary length (m)
\(t_{10j}^+\) and \(t_v\) migration time

The following experimental conditions were used: uranium concentration of 1 mg L\(^{-1}\) (4.2 \times 10^{-6} \text{ M}), overall sulphate concentration ranging from 10^{-6} to 10^{-2} \text{ M}, pH equal to 3.55 and ionic strength of 0.11M. The experimental and calculated values of uranium complexation versus sulphate concentration (Fig. 1) are in very close agreement, indicating thus the interest of the coupling for such studies. From those experimental data, the log \(\beta_1^{0,11}\) was determined: log \(\beta_1^{0,11} = 2.31 \pm 0.07\) using the following equation.

\[
C_{so} = \left( \frac{\phi_{10j}^{i+}}{1 - \phi_{10j}^{i+}} \right)^i \left( \frac{1}{\beta_1} + \frac{C_u}{2} \right)
\]

\(V\) voltage (V)
\(\phi_{10j}\) uranyl ion molar fraction
\(C_u\) overall uranium concentration (M)

Then, the value was extrapolated to zero ionic strength using the Davis equation[4].

\[
\log \beta_1^t = 3.19 \pm 0.09
\]

This first result demonstrates the interest of the coupling EC/ICP-MS for the determination of thermodynamic constants.

However, to implement the knowledge of uranium complexation in the sulphate system the determination of the second constant \(\beta_2^t\) is a challenging task. Indeed, to ensure the reproducibility of the data further work are in progress to develop a double detection system taking benefit of the UV detector to determine the electroosmotic flow and using the caesium reference with the ICP-MS. Important results might be obtained validating the use of the Cs reference at higher sulphate concentration despite its small ability to be complexed (log \(K^t = 0.87\)[5]). It will lead to the validation of the analytical procedure developed for thermodynamic constant determination and the calculation of the \(\beta_2^t\) value. Moreover, a first
approach of the mobility of the anionic complex will also be attempted and an estimated value of $\mu_{\text{ion}(\text{SO}_4)}^0$ will be given.

![Graph](image)

**Figure 1**: Comparison of theoretical and experimental complexation data

Electrolyte: $I = 0.11$ mol L$^{-1}$, pH = 3.55 par HClO$_4$, β-alanine buffer

Conditions: $L = 68.3$ cm, $V = 10$ kV, $T = 298$ K

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THE USE OF MOSS AS BIOMONITORS OF ATMOSPHERICAL DEPOSITION IN ROMANIA: AN EXAMPLE FROM THE EASTERN CARPATHIAN MOUNTAINS

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Introduction

In the last thirty years, the use of naturally growing mosses as biomonitors in the study of atmospheric deposition of the heavy metals became a common method for monitoring air pollution. Naturally growing mosses have a primitive structure with no specialization of cells within the tissue. Mosses are able to concentrate and to solubilize some chemical species of environmental pollutants. Because the contact between the moss and the soil (or rock) is very weak, it is possible that the moss can not absorb notable quantities of metal ions from the soil.

The principal sources of pollution are dry and wet atmospheric deposition. The naturally growing mosses like Hylocomium splendens, Hypnum cupressiforme, and Pleurozium schreberi were employed for the first time by Ruhling and Tyler in Scandinavia [1]. One of the first applications in Norway was carried out in 1976 by Steinnes [2]. In Romania this method was recently used in monitoring an industrial and mining area from the Northern and Eastern Carpathian mountains [3], in a close co-operation Trondheim University from Norway [4].

The purpose of the present study was to use thermal neutron activation analysis to determine the element concentrations in the moss samples of Hylocomium splendens and Hypnum cupressiforme types. The samples were harvested in 1995. The elements: Al, As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, K, La, Mn, Na, Rb, Sc, Sm, Th, U, V and Zn have been determined thirty-six sampling sites selected from a total of one hundred and twenty sampling sites in an industrial area in the Bacau district in the Eastern zone of Romania.

Another object of this study was to test the feasibility of a particular analytical scheme, based on instrumental thermal neutron activation analysis for the survey of environmental pollution in Romania.

Experimental

The method regarding for the preparation of the moss samples for the analysis has been described in other works [3]. The irradiations were performed at the VVR-S reactor at NIPNE-HH Bucharest in a thermal neutron flux of \(1.1 \times 10^{10} \text{ n cm}^{-2}\text{s}^{-1}\) to determine the elements. For the determination of Al, Mn and V content, the irradiations were done in a horizontal channel of the VVR-S reactor in a thermal neutron flux of \(2.3 \times 10^{12} \text{ n cm}^{-2}\text{s}^{-1}\) using a pneumatic rabbit with an inner diameter of 14 mm and a polyethylene ampoule 2 cm³ volume.

The moss DK-1 [5] was used for calibration of along with IAEA-356, P-alfalfa lucerne and geochemical material G-2. The gamma ray measurements of irradiated moss and reference materials were run on a 4096 channel analyser connected with a Ge (Li) detector of 7% efficiency and a FWHM = 1.9 keV for the \(^{60}\text{Co}\). The counting statistics errors between 5% and 10%.

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Results
The results of the analysis of Hylocomium splendens and Hypnum cupressiforme moss types from thirty-six sampling sites are given. The analysed samples from the two naturally growing mosses have permitted a better characterization of eight elements namely Al, Cr, Fe, K, Mn, Na, Th, and Zn. We have also determined the concentrations of Ce, Eu, La, and Sm. These elements are of crustal origin and they are found also as elemental composition of the solid phase of rainwater (Fe, K, Mn, Na, Zn, La, and Sm).
Significant sources of the atmospheric contamination are the combustion products of fossil fuels and wastes. These products are mainly contained in a finely dispersed very leachable and/or mobile form[3].

Discussion
In the same sampling site point, for aluminium there are high and uniform concentrations, but there are high deviations between the sampling points and between the studied mosses type. The highest concentration is situated in S19, T30, T21 and T22 sampling sites.
Chromium is better represented in the Hylocomium splendens moss samples with the highest concentrations in the Q25, R31, S18, S20, S22 and S24 sampling points.
The high iron concentrations are especially in the Hylocomium splendens moss. The highest levels of iron were found in the S23-S24 and T22-T23 sampling sites.
Manganese is in varying concentration present from one sampling site to other. It has a higher content in the Hylocomium splendens moss samples. Most probably, the source of Mn in moss is the leaching from living and dead materials. Its highest concentration was found in the R18 and R20 sampling sites.
Zinc was present in all the sample sites investigated and this content varies between 350 ppm to 550 ppm. It is better represented in Hylocomium splendens samples with the highest value in the S22 and R24 sites.
The four lanthanides: lanthanum, cerium, europium and samarium may originate from coal and ash deposits, being transported through the air and falling out on the moss where absorption occurs. In Table 2 we can have a representative view about the environmental pollution in the mining and industrial sites. In these investigated sites there are gas and oil drilling and refining as well as thermal power stations.

Conclusions
The obtained results by the method of thermal neutron activation analysis prove that the NAA can successfully be applied for the identification of many elements in environmental samples like mosses.
Our study has demonstrated that Hylocomium splendens moss type samples can be successfully utilized. This moss was present at all sampling points.
Furthermore, it is easy to distinguish the Hylocomium splendens from other mosses and its annual growing yield can be readily defined.

References
<table>
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<th>Element</th>
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<th>R-20</th>
<th>R-23</th>
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Nd=not determined
PHOSPHORIC ACID PURIFICATION: REMOVAL OF THORIUM AND OTHER CHEMICAL SPECIES

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The largest uranium reserve known in Brazil is the Itataia deposit, located in the Ceará state. The ore consists of uraniferous, apatite-ferruginous geological characteristics of phosphorus and uranium association. Total estimated reserves are 13.8 million tons P2O5 and 142.5 thousand tons U3O8 [1].

When fully operational for the simultaneous recuperation of phosphorus and uranium, the Itataia phosphate rock milling will make use of the wet-process phosphoric acid production by dihydrate method. The uranium contained in the phosphoric acid will be recovered by solvent extraction using DEHPA and TOPO extractant mixture. After separation from the phosphoric acid, the uranium will be precipitated as ammonium diuranate.

The distribution of long half-life radionuclides of the 238U and 232Th decay series in the products and wastes generated during phosphate rock milling was evaluated showing that 226Th, 230Th and 232Th remained in the phosphoric acid after uranium extraction [2]. Thorium concentration in the Itataia phosphoric acid after uranium removal is about 50 times higher than other phosphoric acids available in the Brazilian market.

Separation techniques like solvent extraction, ion exchange resin retention, precipitation and inorganic adsorption showed very low efficiency in removing thorium from the phosphoric acid. Then the process was directed to the extraction of phosphoric acid with tri-n-butyl phosphate (TBP) for its purification [3] which consequently removed the thorium isotopes. This phosphoric acid purification was established to use the mixer-settler cells in countercurrent system. The operational conditions were defined first in discontinuous tests at the laboratory scale and thereafter consolidated in a continuous unit.

Experimental

Discontinuous tests

Free-uranium phosphoric acid was produced using phosphate rock leaching (sulfuric acid and dihydrate route) and further uranium solvent extraction (DEHPA/TOPO). Based on a solvent extraction method with TBP to extract the phosphoric acid, the process conditions for thorium and other chemical species removal were obtained at the laboratory scale. McCabe-Thiele methods [4] were employed to determine the operational conditions of the continuous processes, which have established three units, i.e. the phosphoric acid extraction, the scrubbing of the load organic phase and the purified phosphoric acid stripping.
**Continuous pilot plant**

The phosphoric acid purification unit using mixer-settler cells in countercurrent system encompassed three steps:

- **Phosphoric acid extraction**: free-uranium phosphoric acid was fed in countercurrent flow with pure TBP (Daichi, Japan). At the ends of the extraction unit there were obtained the loaded organic solvent and the raffinate phosphoric acid.
- **Scrubbing**: the loaded organic solvent was contacted with deionized water to remove entrained raffinate phosphoric acid that contains impurities.
- **Stripping**: the scrubbed loaded organic solvent was contacted with deionized water to strip the extracted phosphoric acid. The purified phosphoric acid (aqueous phase from stripping) and the stripped solvent were obtained in this unit.

The equipment employed in the purification unit consisted of mixer-settler cells, fabricated with stainless steel 316 L. Volumetric capacities of the mixer and settler were 1700 mL and 1400 mL, respectively. The operational conditions established for the continuous pilot plant are presented in Table 1.

<table>
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<th>Reextraction</th>
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</table>

**Results**

Table 2 depicts the results of chemical and radiochemical analyses of the aqueous solutions obtained in the process, i.e. feed phosphoric acid, raffinate phosphoric acid, scrubbing aqueous solution and purified phosphoric acid. The existing impurities in the feed phosphoric acid were concentrated in the barren phosphoric acid.

The P_{2}O_{5} initially present in the phosphoric acid, which fed the extraction continuous unit, was distributed among raffinate phosphoric acid (40 %), scrubbing aqueous solution (10 %) and purified phosphoric acid (50 %).

**Conclusions**

Results obtained for the continuous unit of phosphoric acid extraction with TBP, using the established operational conditions, demonstrated that the process of extraction removed the thorium and other impurities contained in the phosphoric acid. The promoted purification can convert the phosphoric acid to a technical grade, aggregating commercial values. The operational conditions defined in discontinuous tests were consolidated successfully in continuous unit.
Complementary tests like previous treatment of feed phosphoric acid with phosphate rock and sand to decrease the sulfate and fluorine concentrations are underway.

Table 2. Concentration (mg L\(^{-1}\)) and activity (Bq L\(^{-1}\)) of chemical and radiochemical species in the aqueous solutions of the process

<table>
<thead>
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References

DIGITAL SIGNAL PROCESSING GAMMA-RAY SPECTROMETERS IN HIGH COUNT RATE APPLICATIONS

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D-52425 Forschungszentrum Jülich, Jülich, Germany

Introduction
In gamma-ray spectrometry the digital signal processing devices conquer the market of digital electronics. Most digital devices have some advantages, especially concerning their capability of full software control via standard connections. In our laboratories we operate DSP based systems for some years. From this experience some further main advantages were observed as stability of the energy calibration and linearity of the energy calibration over a large range of energies.

The suppliers often argue that DSP based systems also have advantages concerning higher throughputs and are therefore useful especially in high count rate applications. To examine this, the performance of a digital signal processing gamma-ray spectrometry system was compared with a high end analogues device in a field of high count rate applications. Both systems were exposed to high gamma-ray fluxes. The performance was evaluated by means of dead time, dead time correction, energy resolution, energy stability and throughput. The description of the measurements and the results are presented in the following.

Experimental Set-Up
The following table shows a compilation of the equipment used to examine the differences in performance of DSP based and analogues electronics.

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<th>DSP based system</th>
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<td>Ortec 921 Multi Channel Buffer</td>
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<tr>
<td></td>
<td>Detector</td>
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<td>Canberra HPGe-detector, n-type</td>
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<td></td>
<td>DSP electronics</td>
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<td>Ortec DSpec Plus</td>
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</table>

The analogous electronics were operated at 1 µs shaping time and with 8 k resolution. For the DSP based system the DSpec Plus of Ortec was used. The DSpec Plus was operated in ZDT (zero dead time) mode as well as in conventional LT (life time) mode. In the ZDT mode the LT representation and the ZDT representation of the spectral data were used for the analysis. Both systems were optimised for high throughput. Therefore, deterioration in energy resolution has to be accepted. In addition to the equipment mentioned above a pulse generator at 50 Hz was used to investigate dead time effects.
To establish varying count rate situations with stable analysis conditions, two radioactive sources were used in the measurement. A $^{60}$Co source was placed close to the detector front. For the performance comparison the $^{60}$Co line at 1333 keV was analysed. A strong $^{137}$Cs was placed at different distances in front of the detector resulting in dead times up to 98%.

To investigate the performance of the systems the dead time versus input rate and the net area, the net count rate, the energy centroid and the width at half maximum of the 1333 keV $^{60}$Co line were determined and compared. The input rate was determined from the sum of all events in the spectrum. As the result of the investigation of the performance of the dead time correction led to a positive result, this was thought to be the best way to estimate the input rate. Although, this procedure leads to an underestimation of the true input rate as the pile-up events are only counted once, these effects were shown to be below 11%.

Results
Comparing the dead times no significant difference could be observed for analogous and digital electronics (Fig. 2). Both types tend to slightly overestimate the dead time at input rates higher than 100 kHz. For the ZDT mode the dead time is zero by definition.

Fig. 2: Dead time versus input rate.

The net area of analogous and digital electronics behave similarly. In ZDT mode some fluctuations were observed (Fig. 3). But this occurs far beyond 100 kHz or 60% dead time. Ortec guarantees the dead time correction to work properly within 3% up to this value of 60%.

Figure 4 shows the net count rate normalised to the value of lowest input rate as a function of input rate. Within the region up to 100 kHz there is no difference in the behaviour of digital and analogous electronics. The net count rates are correct within 2% which is lower than the value guaranteed by the supplier.
Fig. 3: Net area of the 1333 keV line of $^{60}$Co versus input rate.

Fig. 4: Relative net count rate versus input rate.

Looking at the energy shift at trend to lower energies was observed (Fig. 5) for the digital electronics for very high input rates beyond 100 kHz. In this region the analoguous electronics show fluctuations. For input rates below 100 kHz the shift and fluctuation are within 0.1 keV which is acceptable for most high count rate applications.

Fig. 5: Shift of peak centroid versus input rate.  Fig. 6: FWHM versus input rate.

Obviously the digital electronics performs better concerning the energy resolution. According to Fig. 6 for the analoguous electronics a resolution of about 3.75 keV was obtained while the value for the digital electronics is about 2.5 keV depending on the mode. However, if one accepts only slightly higher dead times for constant input rate the energy resolution for the analoguous electronics could be improved significantly.

Conclusions
For the digital and analoguous systems under consideration no significant advantage could be observed for one or the other system. In very high count rate situations the digital system seems to perform better concerning the energy resolution. However, this happens at such high input rates and dead times that the supplier does not guarantee a proper dead time correction. For that, operating either system in beyond this boundary is not recommended at all. Therefore, from the pure scientific point of view there seems to be no advantage to use digital electronics but there might be some from the economic and handling aspects.
APPLICATION OF k-f-BASED NEUTRON ACTIVATION ANALYSIS FOR STUDIES ON SERPENTINES, DOLERITE AND DOLOMITES

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Serpentines are a class of secondary minerals derived by alterations in magnesium rich silicate minerals. They are two layered hydrous phyllosilicates and have formula of \([\text{Mg}_8\text{Si}_2\text{O}_{5}(\text{OH})_4]_2\) with varying concentrations of other elements [1]. Serpentine and asbestos formation in Vempalle, Cuddapah basin of Andhra Pradesh, India has been discussed by several workers. Serpentine and associated asbestos are formed due to hydrothermal solutions accompanying the dolerite intrusive. It was also reported that hydrothermal solutions accompanying the igneous sills have rendered serpentinisation in the magnesium rich limestone by supplying silica, magnesium and water [2]. Many are of the opinion that magnesia and a major part of silica and hydroxyl molecules are introduced from the emanations derived from the intrusive [3]. Two varieties of serpentines viz. serpentine black and serpentine yellow along with the altered and unaltered dolomites and intrusive dolerite were systematically collected in the asbestos mines of Brahmanapalle in Cuddapah basin. The altered dolomite is a combination of dolomite and serpentine yellow and is collected near the contact of yellow serpentine whereas the unaltered dolomite is collected around 2-3 m away from the contact region. In the present study only black and yellow serpentines are investigated as there are no noticeable differences between black and green serpentines. Investigations on the composition of the altered and unaltered dolomites, serpentines and dolerite from the same location are expected to provide clues to understand the process of serpentinisation.

In the present studies, two types of serpentines, two types of dolomites (unaltered and altered dolomites) and one intrusive rock dolerite obtained from the asbestos mines of Cuddapah basin, were analyzed for major, minor and trace elements by 4 NAA method [4-6]. As many as 21 elements having significance on geological formations were measured. The elemental concentrations were used for distinguishing and characterizing these minerals. The accuracy of the method was evaluated by analyzing two certified reference materials (CRM's) namely USGS W-1 and IAEA Soil-7.

Accurately weighed samples of mass in the range of 50-100 mg and gold (5 μg), packed in polypropylene tube and doubly sealed in polyethylene, were irradiated in E8 position of APSARA reactor, BARC, Mumbai. The duration of irradiation was varied from 5 minutes to 7 hours depending on the half life of the nuclide of interest. The neutron flux at E8 position of APSARA reactor is \(\sim 10^{12} \text{ cm}^{-2} \cdot \text{s}^{-1}\). The sub-cadmium to epi-thermal neutron flux ratio (f) and epithermal neutron flux shape factor (a) at E8 position of APSARA reactor are 52.2±2.7 and \(\sim 0.016±0.004\) respectively [4]. Samples were assayed for gamma activity using an efficiency calibrated HPGe detector coupled to a PC based 4K channel analyzer. The detector system had a resolution of 2.0

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ceV at 1332 keV. Relevant nuclear data were taken from the compilations of De Corte et al [6]. Details of the calculations and input parameters like f and α are given in references [4,5].

The measured elemental concentrations in CRMs were within ±10%. The elemental concentrations given in Table 1 are the average values from quadruplicate measurements. The %RSD on the measured values are within ±10 %. The major constituents that are present in these five varieties are Mg, Ca, Fe and Al (Ca is absent in black serpentine). From the results, it is clear that the Mg content in black and yellow serpentines are more than that in dolerite and altered dolomites. The concentration of calcium is higher in host rocks, dolerite and unaltered dolomite. The absence of Ca in black serpentine might be attributed to its replacement by Mg during serpentinisation. Yellow serpentine which is in contact with dolomite is having small amount of Ca (0.55 %). These elements might have migrated during the process of metamorphism. It is observed that altered dolomite is having lesser amount of Na than that of unaltered dolomite and dolerite is also having very high amount of Na. Barium is not detected in dolerite and black serpentine and it increases in the following order: unaltered dolomite → altered dolomite → serpentine yellow. The Ba content, which is concentrated in yellow serpentine, might be due to its migration from the host rock dolomite, which is several times larger than the values in yellow serpentine. This conjecture is supported by the absence of Ba in dolerite and black serpentine. Thus it could be understood that Mg is the main element that replaces Ca, Ba and Na from dolomite resulting in serpentinisation.

The amounts of three diagnostic elements, Sc, Cr and Co of serpentines are in good agreement with the results of Faust et al [7]. The concentrations of Sc and Co are higher in black serpentine than in yellow serpentine and Cr is present in dolerite and black serpentine (Table 1). These three elements could be used to distinguish the black and yellow serpentines. Cobalt, Cr, Ti and V are contributed by dolerite during mineralisation process. Rare earth elements (REE) like La, Ce, Sm, Eu, Dy, Yb and Lu are present in dolerite, black serpentine and yellow serpentine. A few REEs are also present in dolomite. The REEs in these samples decrease in the following order: dolerite → black serpentine → yellow serpentine → dolomite. Chlorine is absent in dolerite. Black serpentine is having high amount of Cl than in yellow serpentine. Both Al and Fe (except in dolomites) are present as major constituents. Both of these elements might have been contributed by the dolerite to the serpentines.

In conclusion, the random distribution of elements among the host rock (dolomite), serpentines and intrusive rock (dolerite) could be the result of chemistry of serpentinisation at a higher temperature brought in by dolerite. The current understanding is that dolerite supplies silica, water vapour and thermal gradient in serpentine formation. It is clear from the present studies that Mg is supplied both by dolerite and dolomite and Ca is depleted from the serpentine in the form of calcite vein. Our studies suggest that dolerite also contributes many elements during serpentinisation. The elements like Sc, Cr and Co can be used to classify the serpentines.
References
Murthy, P. B., Econ. Geol., 45, 681 (1950).

Table 1. Elemental Concentrations of Dolerite, Serpentines and Dolomites
(in mg kg⁻¹ unless % or ng g⁻¹ is indicated).

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Element</th>
<th>Dolerite</th>
<th>Black Serpentine</th>
<th>Yellow Serpentine</th>
<th>Altered Dolomite</th>
<th>Unaltered Dolomite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>1325.47±79.51</td>
<td>162.37±7.46</td>
<td>93.28±5.02</td>
<td>86.90±5.87</td>
<td>654.67±18.15</td>
</tr>
<tr>
<td>2</td>
<td>Mg%</td>
<td>9.22±1.1</td>
<td>22.72±1.86</td>
<td>18.11±0.58</td>
<td>8.28±0.18</td>
<td>12.91±1.4</td>
</tr>
<tr>
<td>3</td>
<td>Al%</td>
<td>1.89±0.11</td>
<td>4.00±0.17</td>
<td>0.11±0.005</td>
<td>0.11±0.005</td>
<td>0.17±0.001</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>N.D.</td>
<td>400.10±11.20</td>
<td>255.23±2.92</td>
<td>288.67±9.12</td>
<td>133.23±5.21</td>
</tr>
<tr>
<td>5</td>
<td>Ca%</td>
<td>8.75±1.15</td>
<td>N.D.</td>
<td>0.55±0.02</td>
<td>18.10±1.32</td>
<td>25.46±1.76</td>
</tr>
<tr>
<td>6</td>
<td>Sc</td>
<td>27.13±1.12</td>
<td>25.29±1.07</td>
<td>0.16±0.01</td>
<td>0.50±0.02</td>
<td>0.22±0.01</td>
</tr>
<tr>
<td>7</td>
<td>Ti%</td>
<td>0.48±0.03</td>
<td>0.70±0.04</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>8</td>
<td>V</td>
<td>209.50±14.12</td>
<td>172.42±8.53</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>9</td>
<td>Cr</td>
<td>70.1±4.12</td>
<td>53.66±3.23</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>10</td>
<td>Mn</td>
<td>292.1±160</td>
<td>2722±54</td>
<td>28.69±0.09</td>
<td>144.02±9.45</td>
<td>145.31±3.59</td>
</tr>
<tr>
<td>11</td>
<td>Fe%</td>
<td>7.94±0.20</td>
<td>5.00±0.38</td>
<td>0.22±0.01</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>12</td>
<td>Co</td>
<td>30.51±1.85</td>
<td>37.31±2.33</td>
<td>4.26±0.23</td>
<td>5.63±0.31</td>
<td>4.73±0.26</td>
</tr>
<tr>
<td>13</td>
<td>As</td>
<td>4.99±0.18</td>
<td>13.41±1.16</td>
<td>6.21±0.11</td>
<td>0.76±0.05</td>
<td>0.76±0.05</td>
</tr>
<tr>
<td>14</td>
<td>Ba</td>
<td>N.D.</td>
<td>545.00±53</td>
<td>222.02±17.06</td>
<td>158.58±9.23</td>
<td>0.75±0.05</td>
</tr>
<tr>
<td>15</td>
<td>La</td>
<td>13.72±1.05</td>
<td>10.94±0.68</td>
<td>1.82±0.04</td>
<td>3.07±0.06</td>
<td>1.28±0.08</td>
</tr>
<tr>
<td>16</td>
<td>Ce</td>
<td>41.32±2.16</td>
<td>24.25±1.51</td>
<td>N.D.</td>
<td>N.D.</td>
<td>8.32±0.67</td>
</tr>
<tr>
<td>17</td>
<td>Sm</td>
<td>2.97±0.15</td>
<td>1.77±0.08</td>
<td>0.48±0.03</td>
<td>0.23±0.01</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td>18</td>
<td>Eu¹</td>
<td>990.05±60.10</td>
<td>350.23±20.11</td>
<td>100.16±5.10</td>
<td>50.28±2.12</td>
<td>20.06±1.13</td>
</tr>
<tr>
<td>19</td>
<td>Dy</td>
<td>N.D.</td>
<td>9.19±0.57</td>
<td>0.27±0.01</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>20</td>
<td>Yb</td>
<td>2.99±0.13</td>
<td>2.22±0.10</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>21</td>
<td>Au²</td>
<td>N.D.</td>
<td>13.20±1.01</td>
<td>N.D.</td>
<td>20.25±1.52</td>
<td>10.12±0.85</td>
</tr>
</tbody>
</table>

N. D. - not detected, "" - ng g⁻¹
DEVELOPMENT OF A SOFTWARE PACKAGE FOR IMPROVING ACCURACY AND PRECISION IN NON-DESTRUCTIVE DECLARATION OF RADIOACTIVE WASTE

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Introduction
Huge amounts of different waste streams arise during the decommissioning of nuclear installations. The characterization of these waste streams is frequently supported by non-destructive assay techniques. Depending on the objective, different techniques are applied like integral gamma-counting for free-release measurements or gamma-scanning for activity determination.

In practice, all techniques have in common that the measurement result strongly depends on the activity and matrix distribution throughout the measuring object which are only specified/known in rare cases and are approximated by rather simple models. A statement concerning accuracy and corresponding uncertainties is therefore usually based only on counting statistics. In some applications the uncertainties are „corrected” by empirical factors which should take into account the lack-of-knowledge on the real matrix and/or activity distribution.

To overcome this unsatisfactory situation, a software package was developed for the determination of activities and their uncertainties on a more reliable basis using all available information and considering different density and activity distributions being consistent with the measured data. Figure 1 shows the schematic representation of the main part of the software package as a flowchart. Additionally, the software package is applicable for reducing the efforts for calibration, evaluation and QA/QC for both declaration and free-release measurements.

The Software Package
Information on an object to be characterized non-destructively may be available from different sources. While conventionally measuring data for the individual techniques are evaluated independently, the software package aims to relate this information, i.e. it considers all available information to set the data evaluation and analysis of an object on a more reliable basis. Since this information is manifold and diverse, a special module for data acquisition is the first step of data processing using the software package. Based on this data, an iterative evaluation and analysis routine is applied, resulting in the most probable nuclide specific activities, their uncertainty ranges and the corresponding matrix compositions. The software package is set up by individual modules, thus enabling easy adaptation of future extensions, e.g. when considering additional data or new consistency checks.
Figure 1: Schematic representation of the main part of the software package.

Figure 2: Import of measurement data: Measurement results of digital radiography, tomography and segmented gamma-scanning to be used for activity determination by the software package.
Types of information
Three different types of information are considered by the software package:
- measuring data
- a-priori information
- databases
Measurement data that actually can be processed result from simple weighing, integral gamma-counting, segmented gamma-scanning, digital radiography and tomography. A-priori information is information on the container (dimension, mass, material etc.), type of conditioning, limiting the possible density range of the matrix, nuclide inventory etc. Finally, databases offer nuclide and matrix specific information like transmission probabilities, mass attenuation coefficients etc.

Example
A simple example using only little information should illustrate the principle operation of the software package. A small aluminum container, partly filled by a sand matrix containing a homogeneous activity distribution ($^{241}$Am: 4.9E+7 Bq, $^{152}$Eu: 1.9E+6 Bq) was characterized. Using a-priori data on the container and measurement data from simple weighing, segmented gamma scanning and digital radiography, two independent evaluation runs were performed. For the first run no information from digital radiography was considered, i.e. the matrix distribution and composition is not known. This results in quite large uncertainties:

$^{241}$Am: $A = \left( \frac{6.9 + 78.0}{-6.9} \right) E + 09$ Bq; $^{152}$Eu: $A = \left( \frac{2.1 + 2.5}{0.7} \right) E + 06$ Bq

The second run took into account the filling height and the density of the matrix, drastically decreasing the uncertainty ranges, specially at low gamma energies.

$^{241}$Am: $A = \left( \frac{2.4 + 2.5}{-1.9} \right) E + 07$ Bq; $^{152}$Eu: $A = \left( \frac{1.2 + 0.7}{0.5} \right) E + 06$ Bq

As can be seen by the comparison of the results of the two runs, the uncertainty range could be drastically reduced when considering additional information.

Conclusion
The software-package in its actual status is already applicable to consider a certain number of different information for data evaluation, but there is still a large potential for further improvement, many of them will be considered in the ongoing development.

Acknowledgment
The authors are very much indebted to BMBF (Bundesministerium für Bildung und Forschung) for the financial support of this work (Förderkennzeichen: 02 S 8081) and the Ingenieurbüro Marschelke, Reichenau, Germany, for the professional realisation of the software package.
5. Nuclear Technology
Determination of Nuclear Constants of Reactions Induced on Zinc by Short Irradiations with the Epithermal and Fast Components of a Reactor Neutron Spectrum


The knowledge of the constants associated to the generation of nuclear reactions with epithermal or fast reactor neutrons, i.e. resonance integrals and fission averaged cross-sections, is an important tool to improve or validate the already existing methods of parametric activation analysis, currently based on thermal neutron capture reactions, and also to provide alternative analytical methods. In addition, a set of simultaneously produced threshold reactions on a single element can be used for characterisation of the fast component of the reactor spectrum.

Several works have been carried out by the authors, in connection with the importance of the reactions other than those induced by thermal neutrons, the determination of nuclear constants for these reactions, and the development of methods for measurements of the reactor spectrum components [1-10]. The present work deals with the determination of fission averaged cross-sections, and the measurement of working values of the resonance integrals, for some reactions induced on zinc by the epิดmium spectrum (epithermal and fast neutrons) of a reactor. The reactions studied were: $^{64}\text{Zn}(n,p)^{64}\text{Cu}$; $^{64}\text{Zn}(n,2n)^{63}\text{Zn}$; $^{66}\text{Zn}(n,p)^{66}\text{Cu}$; $^{68}\text{Zn}(n,p)^{68}\text{Ni}$; $^{68}\text{Zn}(n,\alpha)^{71}\text{Zn}$; and $^{70}\text{Zn}(n,\gamma)^{70}\text{Zn}$. Zinc foils with masses of about 70 mg and aluminium standards were irradiated for times between 3 and 20 min, under cadmium cover, using the pneumatic facility of the RA-6 reactor of Centro Atómico Bariloche. The fast component of the neutron flux at the irradiation position follows a distribution similar to that of an undisturbed $^{235}\text{U}$ fission spectrum [4, 5]. The epithermal flux in this position has not been fully characterised, with respect to the departures of the ideal behaviour, although low values of the $\alpha$ parameter were found in some primary measurements [3] and other recent experiments [11]. The mean values of the fast flux and the epithermal flux per unit of $E$, as measured from the standard reaction: $^{27}\text{Al}(n,p)^{28}\text{Mg}$ and the $^{68}\text{Zn}(n,\gamma)^{69}\text{Zn}$ reaction, which was used as internal standard, were respectively $1.7 \times 10^{12} \text{n.cm}^{-2}.\text{s}^{-1}$ and $8.4 \times 10^{10}$. The relevant data for the first reaction can be found in ref. [8]; the resonance integral of the $^{68}\text{Zn}(n,\gamma)^{69}\text{Zn}$ reaction was extracted from the compilation of Gyntakis et al. [12].

Initial sets of measurements by high resolution gamma spectrometry of about 5 min duration were performed, with 1 – 15 min decay; then, after decay times of between 1 to 2 h, the samples were measured for 1 – 3 h.

The nuclear constants related with the studied reactions are shown in Table 1. The
methodology followed for the activity measurements, as well as the calculation of the averaged cross-section values and the assessment of uncertainties, have been described elsewhere [4,5]. Since the reactions: $^{64}$Zn(n,p)$^{64}$Cu; $^{65}$Zn(n,p)$^{65}$Cu; and $^{68}$Zn(n,α)$^{65}$Ni could be interfered by the capture reactions: $^{64}$Cu(n,γ)$^{64}$Cu; $^{65}$Cu(n,γ)$^{65}$Cu; and $^{64}$Ni(n,γ)$^{64}$Ni, the possible presence of copper and nickel in the samples was specifically investigated. Copper was determined by inductively coupled plasma emission spectrometry, finding a concentration of 29 μg·g$^{-1}$; a 25 μg·g$^{-1}$ upper limit was estimated for nickel in the spectrum generated by long duration measurements of the irradiated samples, through the search of $^{55}$Co, eventually produced by the (n,p) reaction on $^{59}$Ni. The calculations demonstrated that the contribution of both elements to the activities of the nuclides of interest was negligible.

Table 1. Parameters for the Studied Reactions.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Nuclear reaction</th>
<th>Product</th>
<th>Half life (13)</th>
<th>Gamma-ray energy, keV (14)</th>
<th>Emission probability, % (14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative atomic mass (13)</td>
<td>Isotopic abundance, % (13)</td>
<td>$^{64}$Zn(n,p)$^{64}$Cu</td>
<td>(12.700 ± 0.002) h</td>
<td>1345.77</td>
<td>0.473 ± 0.010</td>
</tr>
<tr>
<td>65.39 ± 0.02</td>
<td>48.63 ± 0.60</td>
<td>$^{65}$Zn(n,2n)$^{64}$Zn</td>
<td>(38.47 ± 0.05) min</td>
<td>669.62</td>
<td>8.2 ± 0.3</td>
</tr>
<tr>
<td>27.90 ± 0.27</td>
<td>$^{65}$Zn(n,p)$^{65}$Cu</td>
<td>(5.120 ± 0.014) min</td>
<td>1039.2</td>
<td>9.23 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>18.75 ± 0.51</td>
<td>$^{65}$Zn(n,α)$^{65}$Ni</td>
<td>(3.75 ± 0.05) min</td>
<td>525.9</td>
<td>73.3 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>0.62 ± 0.03</td>
<td>$^{70}$Zn(n,γ)$^{71}$Zn</td>
<td>(2.45 ± 0.10) min</td>
<td>121.52</td>
<td>2.98 ± 0.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>390.0</td>
<td>3.84 ± 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>910.3</td>
<td>7.84 ± 0.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{70}$Zn(n,γ)$^{71}$Zn</td>
<td>(3.96 ± 0.05) h</td>
<td>121.48</td>
<td>2.88 ± 0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>389.87</td>
<td>2.60 ± 0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>910.1</td>
<td>0.307 ± 0.030</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In connection with the determination of the resonance integral of the reactions: $^{70}$Zn(n,γ)$^{71}$Zn and $^{70}$Zn(n,γ)$^{71m}$Zn, no pure peaks could be used for the discriminated measurements of the products. Two methods were used for decomposition of the counting relative contributions of the complex peaks, both based on the generation of two equation systems with two unknowns: a) evaluation of two peaks in a single measurement from the different emission probabilities; b) evaluation of a single peak in two measurements performed with different decay times, taking advantage of the dissimilarity of half-lives. Both methods showed a reasonable agreement. From these data, a satisfactory value was obtained for the resonance integral of the $^{70}$Zn(n,γ)$^{71}$Zn reaction. On the other hand, the contribution of $^{71m}$Zn to the total activity was found with a very high uncertainty, thus affecting the uncertainty of the resonance integral value. This value was verified through a measurement of one of the samples, after a decay long enough to assure a negligible influence of $^{71}$Zn.

The results for the cross-sections measurements are summarised in Table 2. As far as the authors know, these are the first values for the cross-sections of the $^{64}$Zn(n,2n)$^{64}$Zn and $^{68}$Zn(n,p)$^{68m}$Cu reactions. Some discrepancies exist for the other reactions, in comparison with the published data. Most of them are old determinations, included in the Calamand’s compilation [15]. It is worth mentioning that the present values are the result of measurements carried out with modern technology and calculations based on new data, particularly relevant in the case of isotopic abundances and emission probabilities. They allowed, for example, the
direct measurement of the 1345.77 keV peak from $^{64}\text{Cu}$, while the previous cross-section values were based, primarily, on the measurement of the annihilation radiation.

Table 2. Results of the Fission-Averaged Cross-Sections of the Threshold Reactions

<table>
<thead>
<tr>
<th>Nuclear Reaction</th>
<th>Averaged Cross-Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{64}\text{Zn}(\alpha,p)^{67}\text{Cu}$</td>
<td>$(37.4 \pm 1.4)$ mb</td>
</tr>
<tr>
<td>$^{64}\text{Zn}(n,2n)^{67}\text{Zn}$</td>
<td>$(23.4 \pm 2.0)$ μb</td>
</tr>
<tr>
<td>$^{64}\text{Zn}(\alpha,p)^{67}\text{Cu}$</td>
<td>$(0.775 \pm 0.079)$ mb</td>
</tr>
<tr>
<td>$^{64}\text{Zn}(n,p)^{69}\text{Cu}$</td>
<td>$(5.32 \pm 0.65)$ μb</td>
</tr>
<tr>
<td>$^{64}\text{Zn}(n,\alpha)^{60}\text{Ni}$</td>
<td>$(52.1 \pm 2.3)$ μb</td>
</tr>
</tbody>
</table>

No previous data were found on the discriminated resonance integrals for the capture reactions on $^{70}\text{Zn}$. The present results are $(0.1350 \pm 0.0093)$ b, for the $^{60}\text{Zn}(\alpha,p)^{67}\text{Zn}$ reaction (average of four measurements) and $(0.157 \pm 0.029)$ b, which corresponds to a single measurement of the resonance integral for the $^{70}\text{Zn}(\alpha,p)^{77}\text{Zn}$ reaction. As it was mentioned, no corrections of the departures from the ideal behaviour of the epithermal flux were performed, and literature data on the mean effective resonance energy are lacking for these reactions. Therefore, these results should be considered as informative or working values.

References
FISSION SPECTRUM AVERAGED CROSS SECTION MEASUREMENTS OF SOME NEUTRON THRESHOLD REACTIONS OF RELEVANCE TO MEDICAL RADIONUCLIDE PRODUCTION

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A programme of work on nuclear reaction cross section measurements relevant to the production of some biologically important radionuclides has been underway for quite some time at PINSTECH. Initial studies were carried out in collaboration with the Institut für Nuklcarchemie, Forschungszentrum Jülich, Germany [cf. 1-3], but in recent years systematic studies have been performed independently. The basic aims are:

(i) To study the formation of a few radionuclides in a nuclear reactor which are normally produced at a cyclotron.

(ii) To investigate neutron threshold reactions which could lead to a higher specific activity of some (n,γ) produced radionuclides.

We describe here some recent measurements in detail. In each case extensive radiochemical work was involved.

In many chemical and biological tracer studies, such as the investigation of physicochemical bond characteristics of technetium complexes, radioisotopes with suitable half-lives are required. For these purposes, the half-life of $^{99m}\text{Tc}$ is too short. whereas that of $^{99}\text{Tc}$ is too long ($T_{1/2} = 2.14 \times 10^5 \text{ y}$). Consequently, $^{96}\text{Tc}$ ($T_{1/2} = 4.28 \text{ d}$) is recommended as a more suitable radioisotope for such studies. Fission neutron spectrum averaged cross sections were measured by the activation technique in combination with radiochemical separations and high-resolution γ-ray spectroscopy for several (n,2n), (n,p) and (n,α) reactions on isotopes of ruthenium. Of special interest was the investigation of the $^{98}\text{Ru}(n,p)^{96}\text{Tc}$ reaction for the production of $^{96}\text{Tc}$ in a nuclear reactor[4].

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$^{45}$Ti is generally produced in a cyclotron, either by proton or deuteron irradiation of scandium via the $^{45}$Sc(p,n)$^{45}$Ti or $^{45}$Sc(d,2n)$^{45}$Ti reaction [5-7], or with α-particle irradiation of calcium by the $^{42}$Ca(α,n)$^{45}$Ti reaction [8]. There is an inherent disadvantage in the production of $^{45}$Ti via these channels since the long-lived $^{44}$Ti ($T_{1/2} = 47.3$ y) may also be produced simultaneously as an impurity via $^{45}$Sc(p,2n)$^{44}$Ti, $^{45}$Sc(d,3n)$^{44}$Ti and $^{42}$Ca(α,2n)$^{44}$Ti reactions, respectively. Its production in a nuclear reactor has been reported for the first time by us. Such a study involved the investigation of the reaction cross section of the nuclear process $^{46}$Ti(n,2n)$^{45}$Ti. Therefore, integral cross-sections for several threshold reactions on natural titanium were measured and a small-scale production method has been described [9].

Production of $^{153}$Sm ($T_{1/2} = 1.9$ d) is generally carried out via the $^{152}$Sm(n,γ)$^{153}$Sm reaction, but the specific activity is low [10]. Production of no-carrier-added $^{153}$Sm by fast neutrons involved an investigation of the $^{153}$Eu(n,p)$^{153}$Sm for the nuclear process. A small scale production method of no-carrier-added $^{153}$Sm has been described for the first time [11]. Similarly the production of no-carrier-added $^{153}$Gd was investigated via the $^{159}$Dy(n,α)$^{153}$Gd process [12]. A summary of the most relevant measured data is given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Cross sections of some nuclear reactions induced by fission neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear reaction</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>$^{90}$Ru(n,p)$^{90}$Tc$^1$</td>
</tr>
<tr>
<td>$^{90}$Ti(n,2n)$^{89}$Ti</td>
</tr>
<tr>
<td>$^{153}$Eu(n,p)$^{153}$Sm</td>
</tr>
<tr>
<td>$^{159}$Dy(n,α)$^{153}$Gd</td>
</tr>
</tbody>
</table>

$^1$ Cross-section value for this reaction is the sum of $\sigma_{\alpha}$ and $\sigma_{\gamma}$; independent values could not be measured.

$^*$ Cross-section value expressed in $\mu$b.
References


[5] Mitchell M. W., Anderson M. R., Kennett S. R., Sargood D.G.: Cross sections and thermonuclear reaction rates for $^{42}$Ca(p,$\gamma$)$^{43}$Sc, $^{46}$Ca(p,$\gamma$)$^{47}$Sc, $^{44}$Ca(p,n)$^{44}$Sc and $^{46}$Sc(p,n)$^{48}$Ti, Nuclear Physics A380, 318 (1982).


[8] Cheng C. W., King J. D.: Cross sections for the $^{42}$Ca(p,$\gamma$)$^{43}$Sc, $^{42}$Ca($\alpha$,n)$^{45}$Ti and $^{44}$Ca(p,n)$^{44}$Sc reactions, J. Phys. G: Nucl. Phys. 5, 1261 (1979).


NEW CROSS SECTION DATA FOR PRODUCTION OF THE THERAPEUTIC RADIONUCLIDES $^{64}$Cu, $^{67}$Cu, $^{140}$Nd and $^{192}$Ir

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The use of radionuclides in internal radiotherapy is gaining significance. In this regard, radionuclides emitting $\alpha$-particles, low-energy $\beta$-radiation, or conversion and Auger electrons are needed for different applications. We investigated the formation of $^{64}$Cu, $^{67}$Cu, $^{140}$Nd and $^{192}$Ir via novel routes. The radionuclide $^{64}$Cu ($T_{1/2} = 12.7$ h, $E_{\beta^-} = 0.6$ MeV, $E_{\gamma} = 0.7$ MeV) is interesting because of its suitable half-life and low energy $\beta$-radiation. It has the extra advantage of $\alpha$-vivo detection possibility via Positron Emission Tomography (PET). $^{67}$Cu ($T_{1/2} = 61.9$ h, $E_{\beta^-} = 0.6$ MeV) is also a nuclide of interest for therapy because of its suitable radiation and half-life. The radionuclide $^{140}$Nd ($T_{1/2} = 3.37$ d, 100% EC, no $\gamma$-radiation) is almost a pure Auger-electron emitter. The available database for its production is rather weak. The radionuclide $^{192}$Ir ($T_{1/2} = 78.83$ d, $E_{\beta^-} = 0.7$ MeV) is well established in therapy. However, since it is commonly produced in a reactor, it is obtained with low specific activity.

Copper-64 and Copper-67

The $^{nat}$Zn(d,x)$^{64}$Cu and $^{66}$Zn(d,$\alpha$)$^{64}$Cu reactions were investigated from 5 to 14 MeV. The $^{68}$Zn(p,ux)$^{64}$Cu process was studied from threshold up to 35 MeV and the $^{64}$Ni(p,$\alpha$)$^{65}$Cu reaction from 5 to 27 MeV. In each case the stacked-foil technique was used. The thin target samples were prepared via electrolytic deposition. Measurements on the first three reactions involved extensive radiochemical work. The radioactivity of $^{67}$Cu was measured via HPGe detector $\gamma$-ray spectrometry and that of $^{64}$Cu via a careful decay curve analysis of the annihilation peak. Some yield and cross section information on these reactions were available in the literature. However, for all the four reactions our data constitute the first systematic cross section measurements.

A comparison of the various production routes of $^{64}$Cu [1-7] is given in Table 1. The reactions $^{64}$Ni(p,$\alpha$)$^{61}$Cu and $^{64}$Ni(d,2n)$^{64}$Cu appear to be most promising. At a small-sized cyclotron, however, the best route is the $^{64}$Ni(p,$\alpha$)-reaction [4]. It has been technically developed [8] to deliver large batch yields. The $^{68}$Zn(p,ux)$^{64}$Cu reaction is of interest to obtain $^{64}$Cu as a byproduct in the production of $^{67}$Ga. The reaction $^{nat}$Zn(d,x)$^{64}$Cu could be interesting if deuteron energy of about 25 MeV would be available. For production of $^{67}$Cu, several reactions like $^{68}$Zn(p,2p)$^{67}$Cu, $^{60}$Zn(p,$\alpha$)$^{67}$Cu and As,Ge(p,spall)$^{67}$Cu are used. The database of the presently investigated route, namely the $^{64}$Ni(p,$\alpha$)$^{64}$Cu reaction, is now established, but the integral yield is rather low.

A new approach to the production of $^{64}$Cu and $^{67}$Cu involves the use of a 14 MeV d(Be) neutron field. The broad neutron spectrum has a mean neutron energy of 4.95 MeV. Cross sections for the $^{64}$Zn(n,p)$^{64}$Cu and $^{67}$Zn(n,p)$^{67}$Cu reactions were measured radiochemically and found to be about four to five times higher than with fission neutrons. Those data show that the two therapeutic radionuclides can be advantageously produced at a fast neutron spectral source, e. g. a spallation source.

*Guest scientist from KIPT, Kharkov, Ukraine.
Table 1 Comparison of $^{64}$Cu-producing reactions

<table>
<thead>
<tr>
<th>Production route</th>
<th>$E_{\text{max}}$ [MeV]</th>
<th>$\sigma_{\text{max}}$ [mb]</th>
<th>Suitable energy range [MeV]</th>
<th>Integral yield [MBq/μA·h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{64}$Zn(n,p)$^{64}$Cu [1]</td>
<td>FS</td>
<td>48.3$^1$</td>
<td>whole spectrum</td>
<td>14.5$^2$</td>
</tr>
<tr>
<td>$^{65}$Zn(n,p)$^{65}$Cu [2]</td>
<td>14 MeV d(Be)</td>
<td>$132 \pm 25^3$</td>
<td>whole spectrum</td>
<td>0.65$^4$</td>
</tr>
<tr>
<td>$^{64}$Ni(d,2n)$^{64}$Cu [3]</td>
<td>16</td>
<td>-</td>
<td>$19 \rightarrow 15$</td>
<td>389</td>
</tr>
<tr>
<td>$^{64}$Ni(p,n)$^{64}$Cu [4]</td>
<td>11</td>
<td>$738 \pm 94$</td>
<td>$12 \rightarrow 9$</td>
<td>241</td>
</tr>
<tr>
<td>$^{94}$Zn(d,x)$^{64}$Cu [5-7]</td>
<td>$&gt; 25$</td>
<td>~ 40</td>
<td>$25 \rightarrow 10$</td>
<td>50</td>
</tr>
<tr>
<td>$^{65}$Zn(d,α)$^{64}$Cu [5]</td>
<td>$11.7 \pm 0.3$</td>
<td>$22 \pm 4$</td>
<td>$13 \rightarrow 7$</td>
<td>6.6</td>
</tr>
<tr>
<td>$^{64}$Zn(p,αn)$^{64}$Cu [5]</td>
<td>$28.8 \pm 0.7$</td>
<td>$23 \pm 4$</td>
<td>$35 \rightarrow 20$</td>
<td>65</td>
</tr>
</tbody>
</table>

$^1$ Average cross section for fission neutron spectrum.
$^2$ MBq/mg Zn at a fast flux of $8.7 \cdot 10^{17}$ n·cm$^{-2}$·s$^{-1}$ for 150 h.
$^3$ Average cross section for break-up neutron spectrum.
$^4$ MBq/g Zn at a flux of $10^{19}$ n·cm$^{-2}$·s$^{-1}$ for 1 h.

Neodymium-140

Cross sections were measured for the reactions $^{94}$Ce$(^3$He,xn)$^{140}$Nd and $^{141}$Pr(p,2n)$^{140}$Nd, again using the stacked-foil technique. The samples were, however, prepared via the sedimentation technique. The $^{94}$Ce$(^3$He,xn)$^{140}$Nd reaction was studied from 15 to 36 MeV for the first time. Previously only some yield data had been reported [9]. The side reactions $^{94}$Ce$(^3$He,xn)$^{139}$Nd were also investigated. The results of the $^{94}$Ce$(^3$He,xn)$^{140}$Nd reaction are shown in Fig. 1. A maximum cross section of about 800 mb was obtained for this reaction at 27 MeV. The results deduced via direct X-ray counting and measurement of the annihilation radiation of the daughter nuclide $^{140}$Pr were compared and found to be consistent. In Fig. 1 no recommended energy range for the production of $^{140}$Nd is given, because all the side reactions lead to shorter-lived isotopes of neodymium. The theoretical calculated yield over the $^3$He-particle energy range of $35 \rightarrow 20$ MeV amounts to 22 MBq/μA·h.

Measurements on the $^{141}$Pr(p,xn)$^{140,141}$Nd reactions were done from 10 to 45 MeV. The $^{141}$Pr(p,2n)$^{140}$Nd reaction shows a maximum cross section of about 850 mb at about 18 MeV. This reaction had been studied earlier [10] and our results are in agreement. A comparison of the two production routes of $^{140}$Nd, viz. $^{94}$Ce$(^3$He,xn)$^{140}$Nd and $^{141}$Pr(p,2n)$^{140}$Nd reactions, was done. The latter reaction gives a higher yield but needs a higher energy cyclotron.
Fig. 1 Excitation function of the $^{nat}$Ce($^{2}$He,xn)$^{141}$Nd reaction

**Iridium-192**

A study of the $^{192}$Os(p,n)$^{192}$Ir reaction has been recently recommended by the IAEA [11]. Measurements on this reaction are underway in our laboratory using natural and isotopically enriched osmium targets over the proton energy range of 5 to 20 MeV. The shape of the excitation function appears to be similar to that of other (p,n) reactions in this mass region.

The suitability of the reactions investigated in this work will be discussed with regard to the production of the respective therapeutic radionuclide in high yield and high radionuclidic purity.

**References**


NEW DATA OF INTERMEDIATE ENERGY NUCLEAR REACTIONS
FOR THEORY AND MEDICAL APPLICATIONS

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Yu. Shubin\textsuperscript{1}, S. Spellerberg\textsuperscript{1}, N. van der Walt\textsuperscript{2}, S. M. Qaim\textsuperscript{1}, H. H. Coenen\textsuperscript{1}

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Data of nuclear reactions in the intermediate energy range are of considerable importance in testing nuclear models as well as for practical applications, e.g. in medicine. We studied several reactions induced by intermediate energy protons using the stacked-foil technique. The radioactive reaction products were identified via high resolution gamma ray spectrometry. The present investigations were oriented in two directions.

Proton induced positron emitters formation

The formation of short-lived positron emitters in the interactions of protons with biological elements, e.g. carbon, nitrogen and oxygen, is of considerable interest. The reactions studied included \(^{14}\text{C}\text{(p,x)}^{11}\text{C}\), \(^{14}\text{N}\text{(p,x)}^{11}\text{C}\), \(^{16}\text{O}\text{(p,x)}^{13}\text{C}\), \(^{15}\text{N}\text{(p,x)}^{13}\text{N}\) and \(^{16}\text{O}\text{(p,x)}^{13}\text{N}\). The energy range covered extended up to 200 MeV. For most of those reactions extensive data existed till about 20 MeV \cite{1} but only scanty information was available in the higher energy range. The experimental results obtained in this work fill some gaps in the existing database and were compared with calculations performed using the modified hybrid nuclear model code ALICE-IPPE \cite{2}.

![Graph](image)

Fig. 1: Excitation function of the \(^{15}\text{N}\text{(p,x)}^{13}\text{C}\) process. Experimental data are shown by symbols and theoretical data by the solid line. The dashed line is the recommended curve published by the IAEA \cite{1}.

* Guest scientist from IPPE, Obninsk, Russia
An accurate theoretical description was difficult because of the non-statistical properties of light nuclei. Using individual input-parameters, however, it was possible to obtain fairly good agreement between the experiment and theory. The results for, e.g. the $^{14}$N(p,x)$^{13}$C reaction are shown in Fig.1.

The major contributing process are at energies up to about 30 MeV is the $^{14}$N(p,α)$^{11}$C process; at higher energies, however, this reaction as well as the $^{14}$N(p,2p2n)$^{12}$C reaction should be important. The theory appears to reproduce the experimental trend fairly well. The cross section data developed in this work could be used for estimating the total activity formed in tissue during proton therapy. Similar nuclear reaction data were obtained for the other processes mentioned and compared to ALICE-IPPE modell calculations.

**Production of $^{124}$I**

The $^{126}$Te(p,3n)$^{124}$I reaction is a potentially interesting alternative route for the production of the important positron emitting radionuclide $^{124}$I ($T_{1/2} = 4.18$ d). Excitation functions of all the (p,xn) reactions on 99.8 % enriched $^{126}$Te were measured up to 70 MeV and the experimental data were compared with the results of ALICE-IPPE [2] calculations performed using standard parameters. The agreement was found to be generally good. For practical applications, the theoretical yields of the various iodine isotopes were calculated from the measured excitation functions. The energy range $E_p = 38 \rightarrow 28$ MeV was found to be very suitable for the production of $^{124}$I via the (p,3n) reaction. A comparison of the various production routes of $^{124}$I is given in Table 1. The yields and impurities were calculated from our recent cross section measurements [cf. 3-5].

<table>
<thead>
<tr>
<th>Energy range [MeV]</th>
<th>Nuclear reaction</th>
<th>Thick target yield of $^{124}$I [MBq/µA-h]</th>
<th>Impurity [%]</th>
<th>$^{123}$I</th>
<th>$^{125}$I</th>
<th>$^{126}$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 $\rightarrow$ 8</td>
<td>$^{124}$Te(p,n)</td>
<td>16</td>
<td>1.0</td>
<td>$&lt;0.1$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>14 $\rightarrow$ 10</td>
<td>$^{124}$Te(d,2n)</td>
<td>17.5</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>21 $\rightarrow$ 15</td>
<td>$^{125}$Te(p,2n)</td>
<td>81</td>
<td>7.4</td>
<td>0.9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>38 $\rightarrow$ 28</td>
<td>$^{126}$Te(p,3n)</td>
<td>148</td>
<td>84</td>
<td>1.5</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

The results show that the two intermediate energy reactions, viz. $^{125}$Te(p,2n)$^{124}$I and $^{126}$Te(p,3n)$^{124}$I, are high yield reactions. However, the levels of the $^{125}$I and $^{126}$I impurities need to be critically considered.
References


PRODUCTION AND SEPARATION OF PROTON RICH RADIONUCLIDES BY HEAVY ION ACTIVATION

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Introduction
Over the last few years, our laboratory has been engaged in heavy ion assisted production and separation of no-carrier-added (n.c.a) radionuclides. The programme started with the aim to produce and separate no-carrier-added rare earth radionuclides. The separation of n.c.a rare earth radionuclide from the adjacent bulk rare earth matrix is a difficult task due to the pronounced chemical similarity of the adjacent rare earth elements. If the rare earth targets are irradiated with heavy ions like \(^{7}\)Li, \(^{11}\)B, \(^{12}\)C, \(^{16}\)O, etc., there will be a large atomic number difference between the product and target radionuclides, which would result in better separation of n.c.a rare earth radionuclides. Using heavy ion projectiles, some lighter rare earth radionuclides can even be produced from non-rare earth targets and the separation would be easier. Moreover, the heavy ion induced radionuclides are proton rich and short-lived compared to light charged particle induced radionuclides. Thus we have not only studied the production and separation of n.c.a rare earth radionuclides by heavy ion activation but also extended our studies to other region of the Periodic Table. Radioanalytical methodologies were developed to separate the product radionuclides from the bulk target matrix mainly by liquid-liquid extraction using different liquid ion exchangers.

Production and Separation of No-Carrier-Added Rare Earth Radionuclides
In order to produce n. c. a radionanthenes, \(^{139}\)La, \(^{140}\)CeO\(_{2}\), \(^{147}\)Nd\(_{2}\)O\(_{3}\), \(^{153}\)Gd and \(^{169}\)Tb were irradiated with 6–7 MeV/A heavy ion projectiles like \(^{7}\)Li, \(^{11}\)B, \(^{12}\)C, \(^{16}\)O, etc., with a beam current in the range of 50-150 nA at BARC-TIFR Pelletron, India. Different radionuclides were produced through the following reactions when \(^{12}\)C was used as projectile [1-5]:

\[
\begin{align*}
\text{\(^{165,167}\)Eu} & \quad (n = 4,5), \\
\text{\(^{147}\)Ce} & \quad (n = 5), \\
\text{\(^{153}\)Nd} & \quad (n = 4,5), \\
\text{\(^{159-153}\)Dy} & \quad \rightarrow \quad 150-153\text{ Tb} \\
\text{\(^{157,167}\)Gd} & \quad \rightarrow \quad 155-157\text{ Tm} \\
\text{\(^{159}\)Tb} & \quad \rightarrow \quad 165-167\text{ Lu} & \quad (n = 4,5,6)
\end{align*}
\]

The irradiated oxide targets were dissolved in appropriate acids and finally brought into HCl solutions of desired concentrations. Appropriate trace of the target element was spiked to the stock solution to monitor the fate of the bulk target radiometrically during the separation process. The liquid cation exchanger, di-(2-ethylhexyl)phosphoric acid (HDEHP) diluted in cyclohexane or HCl was used as organic or aqueous phase, respectively. \(^{165}\)Eu radionuclides were separated from the bulk lanthanum oxide target using 10\(^{-3}\)M HCl and 1% HDEHP with a separation factor ~1000. \(^{147,153}\)Gd radionuclides were separated from a cerium oxide target with a separation factor >3000. Similarly, highly pure terbium and thulium radionuclides were also separated from their corresponding parent, dysprosium and ytterbium as well as their respective targets \(\text{Nd}_2\)O\(_{3}\) and Gd. Terbium foil when irradiated with \(^{12}\)C beam results in the formation of n. c. a \(^{165-167}\)Lu and their corresponding decay products, \(^{165-167}\)Yb.
and $^{165-167}$Tm in the matrix. Methodologies were developed for separation of n. c. a. lutetium and ytterbium isotopes from the terbium bulk target matrix using HDEHP.

A few lanthanide as well as non-lanthanide targets such as $^{112}$Sb$_2$O$_5$, $^{112}$CsNO$_3$, $^{112}$La$_2$O$_3$, $^{112}$Ce$_2$O$_3$, and $^{112}$Eu$_2$O$_3$, were also irradiated by ~80 MeV $^{16}$O projectile with an average beam current 50-200 nA, in order to produce $^{133,135}$Ce, $^{145,146}$Eu, $^{151,153}$Tb, $^{153,155}$Dy and $^{161,162}$Tm radionuclides respectively [6-10]. Methods were developed for isolation of these radionuclides. For example, no-carrier-added $^{133}$Ce radionuclide was produced by irradiating CsNO$_3$ target with $^1$Li beam of energy 44 MeV. A complete separation of $^{133}$Ce (separation factor >80,000) from the bulk cesium was achieved when extracted with HDEHP in the HCl medium. $^{11}$B projectile was also used in order to produce no-carrier-added $^{147,149}$Gd, $^{145}$Eu, $^{157-159}$Ho and $^{157-159}$Dy radionuclides from metallic $^{149}$Pr and $^{149}$Eu$_2$O$_3$ targets [11,12].

Production and Separation of No-Carrier-Added Radionuclides of Transition Series

No-carrier-added radionuclides, like $^{192,193}$Hg and $^{192,193}$Au, $^{170,171}$Hf and $^{170,171}$Lu, $^{176,177}$W and $^{176,177}$Ta, $^{181}$Ir were produced by medium energy $^{16}$O irradiation of tantalum, terbium, holmium and thulium targets respectively [13-16]. Separation of $^{192,193}$Hg and $^{192,193}$Au from the target tantalum was achieved by extracting with the mixture of trioctylamine (TOA) and tributyl phosphate (TBP), using HNO$_3$ as an aqueous phase. Tm$_2$O$_3$ irradiated with 90 MeV $^{16}$O results in the formation of carrier free short-lived $^{181}$Ir and $^{181}$Os, which ultimately decay out to $^{181}$Re in the matrix. Rhenium was separated from the bulk thulium in HDEHP-HCl system, when thulium got extracted into the organic phase in lower acidity due to the formation of [Tm(4H$_2$O)$_3$]$^{2+}$, leaving rhenium in aqueous phase. $^{188,189}$Pt and $^{188,189}$Ir radionuclides were produced from their precursor short-lived $^{188,189}$Au, in $^{12}$C irradiated tantalum matrix. Again $^{187,189}$Pt and $^{187,189}$Ir were produced in tantalum by activation with 57 MeV $^{11}$B beam [17]. Separation of platinum and iridium from the bulk tantalum was performed in TOA and HCl system while the separation between n.c.a platinum and iridium was possible with Aliquat-336 and HNO$_3$. Production and separation of n.c.a radionuclides of first transition series elements like $^{45}$V and $^{45,47}$Cr in $^1$Li irradiated Sc$_2$O$_3$ target was also carried out [18].

Production and Separation of No-Carrier-Added Radionuclides of S and p-Block

We have proposed alternative production route of gallium radionuclides by heavy ion activation of naturally occurring mononuclidic cobalt target. Thick cobalt foil was irradiated with either 52 MeV $^{11}$B or 73 MeV $^{12}$C$^{6+}$ resulting in the formation of carrier free short-lived $^{66,67}$Ga and $^{66,68}$As radionuclides respectively in the matrix with their corresponding decay products, $^{66,67}$Ga. The carrier free gallium radionuclides were separated from the bulk target matrix with a separation factor of more than 10$^6$ [19]. Alternative production and separation route of clinically important $^{115}$In by $^1$Li activation of silver target has been developed [20]. We have also reported the alternative production and separation procedure of $^{199}$Tl by $^1$Li activation of gold. $^{199}$Tl has comparable property with $^{201}$Tl for clinical application, with a shorter half-life [21]. Apart from this, carrier free arsenic and selenium radionuclides were produced and separated from $^{16}$O irradiated cobalt target using HDEHP-NH$_4$OH and TOA-HCl system [22]. Metallic silver target was irradiated with 60 MeV $^{11}$B in order to produce $^{145,146}$Tc, and $^{145,147,143,141}$Tc radionuclides which were separated using Aliquat 336 from HNO$_3$ medium [23]. Amongst the s-block elements, no-carrier-added $^{24}$Na and $^{24}$Mg were produced and separated from $^1$Li-irradiated aluminium target matrix [24].
Conclusion
The radioanalytical procedures developed for production of carrier free radionuclides by heavy ions and effective separation from their bulk target matrix are rapid and simple. High radiochemical purity was achieved but high radioisotopical purity was not achieved in all the cases due to the use of natural targets. The use of enriched isotope will lead to the production of radionuclides of high radiochemical and high radionuclidic purity. The thick target yields of the radionuclides in most of the cases are between 0.5–10 MBq/μAh, which is obviously much lower than neutron or light charged particle induced activation yield, but on the contrary, the separation factors are much higher in case of heavy ion activation.

References
BULK PROCESSING OF RADIONUCLIDE GENERATOR PARENTS AT THE LOS ALAMOS HOT CELL FACILITY


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Bulk radionuclide processing at Los Alamos includes isotopes ("generator parents") with short-lived radioactive daughter nuclides for medical applications: Germanium-68, 88Sr, 185Zr and 105Cd are regularly prepared at the Los Alamos Hot Cell Facility. Nuclear chemical aspects related to the production and processing of these generator parents are briefly outlined below.

Radionuclide production and processing

Germanium-68 (T1/2 = 270.8 d) solely decays via electron capture (EC) to 68Ga, a positron emitter (T1/2 = 67.6 min, β+ 88%), which finds use in Positron Emission Tomography [cf. 1]. Germanium-68 can be obtained at relatively low proton energies via 87Ga(p,xn) reactions using 36 MeV protons and gallium metal targets, which is the production route currently pursued within the U.S. DoE Medical Radioisotope Distribution Program. Irradiated Ga targets are mechanically removed from Nb capsules, and dissolved in aqua regia. The 68Ge activity is first extracted from the aqueous phase using tetrachloromethane, and then re-extracted into aqueous HCl. The overall processing yield is typically > 92 %, with respect to the theoretical thick target yield of (1586 ± 30) MBq / μAh of the radionuclide.

Strontium-82 (T1/2 = 25.5 d, EC=100%) is primarily used to generate the PET diagnostic radioisotope 82Rb (T1/2 = 1.3 min), which has been utilized in myocardial perfusion studies [cf. 2]. At Los Alamos, 88Sr is produced via the process 89Rb(p,xn)88Sr using Rb metal or RbCl targets. In the case of Rb metal targets, the alkaline metal is dissolved in propan-2-ol, and the resulting rubidium propylate, in turn, is decomposed with aqueous HCl. The separation of n.c.a Sr from the RbCl matrix is achieved by the use of a chelating resin. 88Sr2+ is retained while Rb+ elutes. Subsequently, 88Sr2+ is desorbed from the column with HCl (6 mol/L), and evaporated to dryness. The final product species is 88SrCl2 (1-14 GBq per batch, 90-98% of the theoretical yield).

Cadmium-119 (T1/2 = 462.6 d, EC=100%) has been suggested as a generator parent nuclide for 119Ag. 119Ag (T1/2 = 39.6 s) possesses properties of a Single Photon Emission Tomography (SPECT) imaging radionuclide, especially for use with first pass radionuclide angiography [cf. 3]. One possible 109Cd/119Ag generator principle is based on Cd/Ag separation via sorption on a column of particulate tin phosphate as an ion exchanger [cf. 4].

105Cd processed at Los Alamos is predominantly obtained from targets containing pure indium metal of natural isotopic composition, irradiated with proton beams of 65 MeV incident energy. Experimental 105In(p,x)105Cd cross section values [cf. 5] were compared to ALICE-IPPE modeling results. It was found that the model is in good agreement for the low energy part of the

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excitation function, while values differ strongly for energies > 50 MeV. The thick target yield
curve calculated from experimental data is shown in Figure 1.

![](image)

**Fig. 1.** Thick target yield function for the process \(^{116}\text{In}(p,xn)^{109}\text{Cd}\) calculated from the smoothed excitation function given in Ref [5].

Indium targets are dissolved in HCl, and contacted with an anion exchanger, where Cd is re-
tained. The exchanger is washed with HCl, Cd is subsequently eluted with HNO\(_3\) and the
solution is evaporated to dryness. The dry residue is again taken up in a small volume of HCl, and
loaded onto a second anion exchange column, which is then treated with HCl of increasing con-
centration (gradient elution), whereby isotopes of In, Rh and Ag are removed. Cd is then eluted
with concentrated HCl, while Sn isotopes remain on the solid phase. Cadmium-109 is assayed indi-
directly by detection of \(\gamma\)-rays of the daughter \(^{109}\text{Rh}\)Ag after decay in-growth. \(\gamma\)-ray counting
results are compared against a liquid \(^{109}\text{Cd}/^{108}\text{Ag}\) standard source. Decontamination factors for
In, Rh, Sn and non-\(^{109}\text{Rh}\)Ag silver isotopes are >500. Typically, 80 % of the theoretical \(^{109}\text{Cd}\) ac-
tivity can be recovered experimentally.

Zirconium-88 (83.4 d, EC=100%) is the parent nuclide of \(^{88}\text{Y}\) (106.7 d, EC+\(\beta^+\)), which has been
considered a useful label surrogate for \(^{88}\text{Y}\) in cancer radioimmunotherapy [cf. 6]. Although
the half-life of the daughter is longer than the parent’s, the system \(^{88}\text{Zr}/^{88}\text{Y}\) appears suitable as a nu-
clide generator. Within the distribution program at Los Alamos, \(^{88}\text{Zr}\) is recovered from Nb cap-
sules and beam windows irradiated with protons of 65 MeV incidental energy. To the best of our
knowledge, experimental reaction cross section for the process \(^{71}\text{Nb}(p,\alpha n+2p4n)^{88}\text{Zr}\) have not
been published as yet. Figure 2 shows the theoretical excitation function as predicted by ALICE-IPPE.

Niobium targets are carefully dissolved in HNO\(_3\)/HF. In order to remove any traces of Y carrier,
the solution is then contacted with a cation exchanger resin. The eluting Y mass depleted \(^{88}\text{Zr}\)
containing solution constitutes a liquid “reverse phase” radionuclide generator, and it is kept in
stock. After \(^{88}\text{Y}\) activity in-growth, the isotope is separated by passing through a cation ex-
changer, where \(^{88}\text{Y}\) is retained on the solid phase. The column is washed, and \(^{88}\text{Y}\) with a very
high specific activity is subsequently eluted with HNO\(_3\). Yttrium-88 separation batches typically
yield to 6 – 300 mCi of \(^{88}\text{Y}\), and overall experimental \(^{88}\text{Zr}\) product yields amount to ~89 % of
the theoretical thick target value [514.3 MBq(13.9 mCi)/μAh] calculated from ALICE-IPPE modeled cross section data.

![Graph showing cross section vs. proton energy](image)

**Fig. 4.** ALICE-IPPE model calculation results for the process $^{94}$Nb(p,α2n+2p4n)$^{90}$Zr: accumulative reaction cross sections

**Conclusion**

The Los Alamos Hot Cell Facility regularly prepares bulk amounts of radionuclide generator parents for medical applications. Targets irradiated at different sites are shipped to Los Alamos for chemical processing 1-6 times yearly with batch nuclide activities ranging from 40 MBq to 75 GBq. Radiochemical separation methods based on liquid-liquid extraction and ion exchange were specifically developed or modified to suit remote control operations in a hot cell. Overall experimental yields generally correspond to more than 90% of the theoretical thick target yields calculated on the basis of reaction cross section data.

Comparison of experimental reaction cross sections with ALICE-IPPE model calculation results reveals that the model describes nuclear processes on medium-mass target nuclei in a satisfactory manner, while giving poor results for heavier target elements.

**References**

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STUDY ON RECLAMATION OF LOW RADIOACTIVE WASTE BY CHEMICAL PROCESSES

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After the accident at Chernobyl, it was necessary to conduct radioactive decontamination in areas heavily polluted by fallout. As a result of efforts to decontaminate various industrial and municipal commodities, significant volumes of radioactive decontamination solutions (containing predominantly $^{137}$Cs and $^{90}$Sr) were generated. These solutions included surface active substances, complexing agents and ions of salts. Recovery and disposal of these solutions was a major effort in this project. The goal is to create a system for recovering solutions contaminated by radioactive materials and thereby to reduce the quantity of radioactive waste in need of disposal by burial.

At present, radioactive pollutants are defined basically by the radioisotopes $^{137}$Cs, $^{90}$Sr, $^{239}$Pu and $^{240}$Pu. The area of the territory, where density of pollution by $^{137}$Cs exceeds 37 kBq/m$^2$, totals 46,450 km$^2$. Millions of persons currently live and work in areas contaminated by this fallout. Because of secondary soiling, the atmospheric air in spring-summer season is in constant need of decontamination.

It is necessary to first conduct deactivation of roofs and sewer of buildings by using ventilation equipment. Undertaking decontamination of the industrial equipment brings about formation of more than 20 tons of liquid radioactive waste. This waste requires special conversion, and following this, hard setting remediation in the repositories. After processing, solutions derived from decontamination have a radioactivity of $^{137}$Cs and $^{90}$Sr lower than $1 \times 10^{-5}$ Ci/l. These decontamination solutions are considered as low-active, fluid, radioactive wastes. With regard to surface-active substances, the solutions contain complexing agents, as well as salts of heavy metals.

To date, remediation of radioactive solutions derived from decontamination was conducted by hardening through cementing. Cement blocks were buried in repositories. However after only 19 months of aging, the leaching of sour soils is about 1% of the $^{90}$Sr and more than 3% of $^{137}$Cs. Since water constitutes about 80% of these solutions it is more expedient to clear the water from the surface-active substances, complexing agents and radionuclides and thus allowing the water to be recovered for re-use. Greater volumes generally are typical for the low-level radioactive wastes. The present researches will make it possible to reduce the volume of liquid radioactive wastes by 80%. Not more than 15-20% of their original amount of decontamination waste solutions is suitable for direct burial in the repositories.

The study of remediation of radioactive solutions derived from decontamination, which contain surface-active substances, complexing agents, heavy metals salts, have shown that, firstly, it is necessary to clear these solutions from surface-active substances. In this case, therefore, traditional thermal methods of remediation sharply reduce the cleaning degree;
however during the process of evaporation strong foam is formed from decontamination solutions.

For remediation by sulphonates of radioactive solutions derived from decontamination, studies were conducted on methods for precipitating hydroxides of aluminium, iron (III), and reagent N1 and N2. To date, remediation of radioactive solutions derived from decontamination was conducted by hardening through cementing. Cement blocks were buried. Remediation by direct burial will apply to not more than 15 % of the whole amount of radioactive solutions resulting from decontamination.

For remediation by sulphonates of radioactive solutions derived from decontamination, studies were conducted on methods for precipitating calcium salts from solutions, since alkylarilsulphonates of calcium are not very soluble substances.

The results on surface-active substances precipitation by varying the pH of the solution have shown that the change in precipitation in acid medium was small when the pH was varied from 2 to 4: 92.9 % precipitated under pH = 2 and 92.0 % precipitated under pH = 4. With increasing pH with neutral and alkaline media, the precipitation of surface-active substances decreased down to 85-78 %.

The study on the process of precipitating surface-active substances by the reagent N1, containing hydroxide calcium and nitrate calcium in the correlation $8 \times 10^{-5}$ mol :1 g-eq., have shown that the precipitate mass formed rises to 9-13 % of the solutions. The maximum percentage of precipitated formed was 84.4 %.

Table 1 shows the results of clearing of radioactive solutions derived from decontamination from surface-active substances as a function of reagent N1 and remediation solution positive-displacement correlation.

<table>
<thead>
<tr>
<th>Reagent N1 and remediation solution positive-displacement correlation</th>
<th>Surface-active substances precipitation %</th>
<th>Surface-active substances precipitation $10^{-5}$ mol</th>
<th>Precipitation and remediation solution ratio %</th>
<th>Process - Temperature °C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.0</td>
<td>64.0</td>
<td>0.21</td>
<td>10.2</td>
<td>20</td>
<td>12.6</td>
</tr>
<tr>
<td>1:1.5</td>
<td>69.0</td>
<td>0.23</td>
<td>10.7</td>
<td>25</td>
<td>12.1</td>
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<tr>
<td>1:2.0</td>
<td>53.0</td>
<td>0.20</td>
<td>9.5</td>
<td>35</td>
<td>13.8</td>
</tr>
<tr>
<td>1:2.5</td>
<td>65.3</td>
<td>0.22</td>
<td>10.5</td>
<td>40</td>
<td>12.0</td>
</tr>
<tr>
<td>1:3.0</td>
<td>84.4</td>
<td>0.28</td>
<td>13.4</td>
<td>50</td>
<td>10.5</td>
</tr>
<tr>
<td>1:4.0</td>
<td>80.3</td>
<td>0.26</td>
<td>11.8</td>
<td>40</td>
<td>10.0</td>
</tr>
<tr>
<td>1:5.0</td>
<td>72.0</td>
<td>0.24</td>
<td>11.0</td>
<td>30</td>
<td>9.8</td>
</tr>
<tr>
<td>1:6.0</td>
<td>77.2</td>
<td>0.25</td>
<td>11.2</td>
<td>25</td>
<td>10.0</td>
</tr>
</tbody>
</table>

The studies on the process of precipitation of surface-active substances by the reagent N1 have shown a decrease in the $\alpha$- and $\beta$-activities of the decontamination solutions.
RADIOACTIVE TARGETS FOR NEUTRON-INDUCED CROSS SECTION MEASUREMENTS

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Measurements using radioactive targets are important for the determination of key reaction paths associated with the synthesis of the elements in nuclear astrophysics (s-process), advanced fuel cycle initiatives (transmutation of radioactive waste), and stockpile stewardship. High precision capture cross-section measurements are needed to interpret observations, predict elemental or isotopical ratios, and unobserved abundances.

There are two new detector systems that are presently being commissioned at Los Alamos National Laboratory for very precise measurements of (n,γ) and (n,f) cross-sections using small quantities of radioactive samples. DANCE (Detector for Advanced Neutron-Capture Experiments) a 4π gamma array made up of 160 BaF$_2$ detectors, is designed to measure neutron capture cross-sections of unstable nuclei in the low-energy range (thermal to ~500 keV) [1]. The high granularity and high detection efficiency of DANCE, combined with the high TOF-neutron flux available at the Lujan Center provides a versatile tool for measuring many important cross section data using radioactive and isotopically enriched targets of about 1 milligram. Another powerful instrument is the Lead-slowing down spectrometer (LSDS), which will enable the measurement of neutron-induced fission cross-section of U-235m and other short-lived actinides in an energy range from 1 to 200 keV with sample sizes down to 10 nanograms [2]. Due to the short half-life of the U-235m isomer (T$_{1/2}$=26 minutes), the samples must be rapidly and repeatedly extracted from its 239Pu parent. Since 239Pu is itself highly fissile, the separation must not only be rapid, but must also be of very high purity (the Pu must be removed from the U with a decontamination factor $>10^{15}$). Once extracted and purified, the 239Pu isomer would be electrodedeposited on solar cells as a fission detector and placed within the LSDS for direct (n,f) cross section measurements.

The production of radioactive targets of a few milligrams will be described as well as the containment for safe handling of these targets at the Lujan Center at LANSCE. To avoid any contamination, the targets are electrochemically fixed onto thin Ti foils and two foils are placed back to back to contain the radioactive material within. This target sandwich is placed in a cylinder made of aluminum with thin translucent windows made of Kapton. Actinide targets, such as 234,235,236,238U, 237Np, and 239Pu are prepared by electrodeposition or molecular plating techniques. Target thicknesses of 1-2 mg/cm$^2$ with sizes of 1 cm$^2$ or more have been made. Other
targets will be fabricated from separation of irradiated isotopically enriched targets, such as $^{155}$Eu from $^{154}$Sm, $^{151}$Tm from $^{150}$Er, and $^{147}$Pm from $^{146}$Nd, which have been irradiated in the high flux reactor at ILL, Grenoble. A radioactive sample isotope separator (RSIS) is in the process of being commissioned for the preparation of other radioactive targets. A brief summary of these experiments and the radioactive target preparation technique will be given.

INVESTIGATIONS ON ADSORPTION AND TRANSPORT 
BEHAVIOUR OF CARRIER-FREE SILVER, GOLD, PLATINUM, 
TECHNETIUM AND RHENIUM IN QUARTZ COLUMNS AT LOW PRESSURE

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Introduction
The absence of a carrier gas enables a fast separation, which is necessary for nuclear spectroscopy of species having short half-lives. Another advantage of vacuum-chromatography is the direct use of the separated species to feed an ion source for radioactive ion beams (RIB), which is normally operated under vacuum conditions [1,2]. The use of nuclides of non-volatile refractory elements (e.g. Tc, Re, Os) as RIBs requires the separation of volatile compounds of these elements formed at low pressures.

Experimental
Carrier-free amounts of different silver, gold and platinum nuclides were produced by irradiation of Pb/Hg, Cd/Hg or pure Hg targets with neutrons at the spallation neutron source SINQ at PSI. The activity was separated from the target via dry distillation. For the production of Re activity a target of tungsten was irradiated with 72 MeV protons at the injector 2 at PSI. Re activity was separated from the target material via dry distillation in an Ar/O₂-flow (59 ml/min). ⁹⁹ᵐTc was taken from a ⁹⁹Mo/⁹⁹ᵐTc-generator.

We used quartz columns with one closed end, 1 m length and 3 mm inner diameter for our thermochromatographic experiments with Ag, Au, and Pt activity. After small pieces of quartz fleece containing the activity were positioned at the closed end, the column was evacuated to a final pressure of 10⁻⁵·5·10⁻⁸ mbar and placed inside an oven with a negative temperature gradient between 18-22 K/cm. After 1 or 2 hours of exposure time the distribution of activity inside the column was determined using standard γ-ray spectroscopy with a lead collimator in front of an HPGe detector. A typical vacuum thermochromatogram of gold on quartz is shown in Fig. 1.

The rhenium and technetium compounds were reduced in H₂-atmosphere at 1100°C for one hour in order to start the experiments from the elemental state. After this step the activity was placed at the end of quartz columns with one closed end, 3 mm inner diameter and a length of 0.5 or 1.0 m. Because Re and Tc are not volatile in the elemental state, it was necessary to add small amounts of O₂ to the experimental setup to form the volatile compounds ReO₂ and TeO₂. For the controlled transport of O₂ into our setup we used an electro chemical approach. A ZrO₂/Y₂O₃ ceramic tube with one closed end was connected with our setup. Depending on
the voltage and the temperature of the tube it was possible to control the O₂ flow inside. For our release experiments the quartz columns were evacuated to 10⁻³ mbar and then heated up to 1100°C. After the temperature was reached a constant O₂ flow was adjusted to enable a constant pressure of 10⁻³ – 10⁻¹ mbar in our setup.

![Graph of yield vs. distance with temperature gradient](image)

**Fig. 1** Vacuum thermochromatogram of gold on quartz. The result of the Monte Carlo simulation is shown as solid line, the temperature gradient as dotted line.

**Results**

From the thermochromatograms of Ag and Au on quartz the adsorption enthalpies were calculated by using Monte Carlo simulations [3] or a thermodynamic approach [4]. The average adsorption enthalpies for Ag and Au are in good agreement with literature values. A transport of Pt could not be observed. Hence, only an upper limit of the adsorption enthalpy was determined. Our results together with literature values [5] are summarized in table 1.

**Table 1** Adsorption enthalpies of Ag, Au and Pt on quartz

<table>
<thead>
<tr>
<th>Element</th>
<th>ΔHₐdh, MCS (kJ/mol)</th>
<th>ΔHₐdh, TD (kJ/mol)</th>
<th>ΔHₐdh, Lit (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>-267</td>
<td>-232</td>
<td>-223</td>
</tr>
<tr>
<td>Au</td>
<td>-306</td>
<td>-279</td>
<td>-283</td>
</tr>
<tr>
<td>Pt</td>
<td>-80</td>
<td>&lt;40</td>
<td></td>
</tr>
</tbody>
</table>
Additional MCS have been performed for isothermal experiments (shown in Fig.2). To simulate a continuous regime the experimental time was set as 100 hours. It is straightforward that higher temperatures of the column increase the yield of short-lived isotopes.

![Graph showing temperature vs. percentage of a substance over time]

Fig. 2 Results of Monte Carlo Simulations of an isothermal chromatography: The amounts of atoms, leaving a quartz column with an inner diameter of 3 mm and a length of 1 m within a time period of 100 h as a function of temperature for different half-lives.

In the case of Re and Tc only preliminary release experiments have been done. A release of activity could be observed with pressures higher than $5.5 \times 10^{-3}$ mbar. The amount of released Tc-activity strongly depends on the concentration of O$_2$. Release rates between 5% and 85% for $^{99m}$Tc within 1 hour could be reached. Re shows a similar behaviour.

Acknowledgement
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References
OSCILLATORY EXTRACTION OF LANTHANIDES AND URANIUM

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The discovery of a new type of reaction, the oscillatory Belousov-Zhabotinsky reaction (BZ reaction) [1, 2], made possible the implementation of an extraction reaction under non-equilibrium nonstationary conditions. During an oscillating chemical reaction the concentrations of intermediates or catalyst species oscillate while the conversion of reactants to products approaches towards equilibrium. Oscillations in the concentrations of intermediates and catalyst species are driven by a monotonic decrease in free energy as the overall reaction occurs [3]. One of the key components of the BZ reaction is cerium, which is present in both the +3 and +4 oxidation states. This rare-earth metal ion plays the role of a catalyst in the process of oxidation of an organic acid by potassium bromate. In the reaction the [Ce(IV)]/[Ce(III)] ratio changes periodically not allowing the system to reach equilibrium for a time varying from several seconds to several hours.

Oscillatory extraction is a process in which the BZ reaction is used in the aqueous phase to drive the extraction of components into an organic phase [4, 5]. In a heterogeneous solvent extraction system, the periodic transition of one form into another influences the partition of Ce and another metal ion present between the organic and the aqueous phase since the various species have different distribution coefficients.

The chemical separation of isotopes and similar chemical elements such as lanthanides has been recently investigated rather extensively. The latest developments of chemical uranium and rare earths isotope separation have demonstrated new ways to separate heavy and medium isotopes [6, 7]. It was shown that the non-steady-state separation could be effectively used for the enrichment of isotopes [6]. The use of reduction/oxidation reactions coupled with liquid-liquid extraction gives high enrichment factors in the case of the isotope exchange reaction U(III)/U(IV) in the extraction system [7]. Isotope fractionation is typically large during microbial processes such as denitrification [8], sulfate reduction [9], and methanogenesis [10], with preferential microbial metabolism of isotopic light compounds. The phenomenon of Pu isotope fractionation by bacteria during the Pu reduction [11] and isotope fractionation phenomenon by bacteria for selenium [12] were observed. The chemical red/ox fractionation of iron isotopes reported in [13] could be expected during microbial reduction / oxidation of iron and plutonium [11].

The study of dynamic non-linear processes linked to unsteady-state (oscillatory) or chaotic behavior leads to new, optimum processes and operating techniques. As a result, improvements might be found with cyclic or transitory operation [14]. Liquid-liquid extraction driven by oscillatory oxidation-reduction reaction in aqueous phase gives the opportunity to separate similar elements and isotopes using repetition of extraction/stripping in two extractors coupled by liquid membrane as analogue of in vivo isotope separation processes performed by bacteria. Use of bulk liquid membranes in oscillatory extraction systems gives the technical possibility to multiply the separation of elements/isotopes using synchronization of time-dependent separation coefficient profiles in extractors. This operation mode should improve the separation by magnifying the small kinetic differences between similar metal ions or isotopes.

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The kinetics of U, Ce, Eu, Pr and Nd extraction by tri-n-butyl-phosphate (TBP) and the red/ox potential behavior in the aqueous phase have been investigated in oscillatory extraction systems. The extraction has been followed continuously by UV-visible spectroscopy, potentiometry, and radioactive counting methods. Data collected showed the oscillatory changes of Ce(IV), Eu(III), Pr(III) and UO₂(²⁺) concentrations in organic and aqueous phases with time. Uranium, praseodymium and europium actively responded to the red/ox potential fluctuations. The uranium, europium and praseodymium distribution coefficient changed repeatedly and was out-of-phase with Ce(IV) fluctuations. The experimental setup is described elsewhere [4, 5, 15, 16]. It is found that cerium, being the catalyst of the BZ reaction, which takes place in the aqueous phase, also participates in the solvent extraction process. Obviously, cerium alternately extracts and back extracts due to the BZ reaction. The time dependence of the optical density of the organic phase at a cerium(IV) specific wavelength (400 nm) is very close to periodic.

The effect of U, Pr, Nd and Ce concentration on the parameters of an oscillatory BZ reaction is investigated. It is shown that the two metals, under conditions of non-equilibrium extraction, mutually influence their distribution. Periodic oscillations of a platinum electrode potential \( E(t) \) are observed when both Ce and U or REE are present in the extraction system with a BZ reaction. Oscillations of cerium distribution coefficient \( D_{Ce} \) are synchronous with \( E(t) \). Oscillations of uranium and praseodymium are observed which are both in-phase and out-of-phase with oscillations of \( E(t) \). The concentration dependences of the parameters of the oscillatory reaction and the distribution coefficients of the elements are obtained.

The change of the parameters of the oscillatory reaction with increasing U, Ce or other REE concentration and its termination at some defined metal concentration (at fixed concentrations of Ce and other components of the oscillatory reaction) is the indirect proof of metal ions participation in the redox process, i.e., affecting the BZ reaction. The existence of mutual effect of the oscillatory BZ reaction and the extraction of uranium or REE in the presence of cerium under non-equilibrium conditions is established. The principle possibility of controlling the parameters of REE extraction, and also of U extraction in the presence of cerium by means of BZ reaction was found.

The new separation extraction system was created based on the oscillatory extraction/stripping process in two extractors coupled by bulk liquid membrane. To induce the extraction/stripping process the BZ reaction was used [5]. Two extractors were connected by loop of bulk liquid membrane (0.5 M TBP in tetradecane). In aqueous phases in both extractors the solutions of equimolar Nd(NO₃)₃ and Pr(NO₃)₃ in 6 M NaNO₃ in presence of potassium bromate and malonic acid were used. Continuous flow stirred tank reactor (CSTR) mode of operation was investigated. In this mode the reagents were continuously fed to the aqueous phase of extractors and the aqueous phases were continuously pumped from the extractors with appropriate flow rate. The composition of cerium isotopes was measured using MI-1201 apparatus by thermo ionizing mass-spectrometry method (TIMS). The concentrations of HNO₃ in the extractors were different, so as to maintain different frequencies of oscillatory reactions in the extractors. Some samples of aqueous phases were prepared for TIMS analysis of cerium and neodymium isotopes. The separation of Ce¹⁴⁰ and Ce¹⁴² isotopes between the aqueous phases of extractors with magnitude about 3.5% was observed.

Applying the electrochemical reduction-oxidation of cerium gives the opportunity to reduce of amount chemicals needed to disturb chemical equilibrium in extraction system. It was proposed that the electrochemical method of initiating oscillation allows to reach high
separation coefficients of elements in organic phase. To induce the cyclic extraction/stripping process electrochemical oxidation/reduction of cerium ion were used. Two extractors were coupled by bulk liquid membrane stream (0.5 M tri-butyl-phosphate (TBP) in alkanes or in kerosene). Concentration ratio of Pr with respect to Nd in organic phase during the experiment was reached 5. Usage of this method for separation of elements requires further research.

It is experimentally established, that the extraction system is induced by chemical or by electrochemical technique in which the non-stationary, non-equilibrium extraction process takes place, the separation factor of the pair Pr/Nd increases in comparison with separation of these metals using equilibrium membrane extraction.

The alternating current influence to oscillatory extraction system also was investigated. It was found that alternating current with special “resonant” frequency allows relatively easy to control the transfer rate of metals between the phases in extraction system due to controllable changing of phase boundary area.

The mathematical model of the oscillatory extraction system with U, Ce and REE extraction by TBP and the red/ox potential behavior in the aqueous phase have been created and tested. The algorithm of the solution of a reverse kinetic problem is designed. The program calculating of the reaction rate constants of an extraction system is built. In this program the Gear method was used [17] to calculate the solution of ordinary differential equations system using Fletcher and Powell method of optimization [18] to calculate the reaction rate constants of chemical reactions. The reaction rate constants of extraction and stripping of Ce\(^{3+}\), Ce\(^{4+}\), Pr, Nd and U are computed, which adequately describes the behavior of extraction systems in the studied conditions. The perspectives of nonstationary oscillatory extraction to separate similar elements and isotopes of medium and heavy weight are discussed.

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References
PRODUCTION POSSIBILITY OF COPPER RADIOISOTOPES FROM COBALT TARGET FOR PET STUDIES

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Introduction

The increasing number of clinical PET equipment strongly stimulates the quick evolution of new practical production ways of ‘metallic’ PET radioisotopes, especially in the case of copper. Recently four radioisotopes of copper ($^{60,61,62,64}$Cu) have been widely used for PET studies. Their routine production is based on Ni+p and Ni+d reactions [1-3]. Unfortunately, the ‘nickel’ way requires highly enriched (expensive) target materials. The necessity of the recovery of the targets after production and the material losses during irradiation, separation and recovery steps are major disadvantages of these production methods. To avoid the above problems comprehensive investigations have been started recently in several laboratories to find other reactions which also form these copper radioisotopes with efficient yields, but employing natural targets or cheaper enriched materials. Possible candidates are the Zn+p, Zn+d [4-7], Co+α and Co+3He reactions. Here we report on our new results on the practical production of $^{60,61,62}$Cu radioisotopes via $^{59}$Co+3He and $^{59}$Co+α reactions.

Experimental

To evaluate the optimum production circumstances of $^{60,61,62}$Cu radioisotopes via Co+3He,α reactions, excitation functions of the $^{59}$Co(3He,n)$^{60}$Cu, $^{59}$Co(3He,2n)$^{61}$Cu, $^{59}$Co(α,3n)$^{60}$Cu, $^{59}$Co(α,2n)$^{61}$Cu and $^{59}$Co(α,n)$^{62}$Cu nuclear reactions were measured up to 60 MeV using the activation technique. Details of the experimental circumstances were already discussed elsewhere [8,9]. Alpha (44.5 and 60 MeV) and 3He (70 and 42.5 MeV) beams of the AVF-930 cyclotron of NIRS, Chiba were used for irradiations. Thin metallic Co foils (10-15 μm) were activated in the form of stacks together with different monitor (Ti, Cu), catcher and degrader foils. The measurement of foil activities was performed with HPGe-detectors coupled to MCA’s operating on PCs. The cross-sections were calculated by using the well-known activation formula. The total error in each cross-section value was obtained by summing all the individual errors in quadrature. The combined uncertainty on the cross-sections varied between 10-15%.

Results

The excitation functions of the above reactions obtained by us are shown up to 60 MeV in Fig.1. Using these curves one can calculate the thick target yields of the required radioisotope
as well as the yields of the contaminants. Based on these calculations we elaborated the ‘practical’ production circumstances for each copper radioisotope. These results are collected in Table 1.

![Graph showing cross-section vs. bombarding particle energy](image)

**Fig.1.** Measured excitation functions of $^{59}\text{Co}(a,2n)^{61}\text{Cu}$, $^{59}\text{Co}(a,3n)^{60}\text{Cu}$, $^{59}\text{Co}(a,n)^{62}\text{Cu}$, $^{59}\text{Co}(^{3}\text{He},2n)^{60}\text{Cu}$ and $^{59}\text{Co}(a,n)^{62}\text{Cu}$ nuclear reactions.

**Table 1.** Practical production circumstances of $^{60,61,62}\text{Cu}$ PET radioisotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Reaction</th>
<th>Energy (MeV)</th>
<th>Irradiation time (min)</th>
<th>Cooling time (min)</th>
<th>Available EOC/EOB** yields (MBq/μA)</th>
<th>Contamination at EOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}\text{Cu}$ (23.2)</td>
<td>$^{59}\text{Co}(^{3}\text{He},2n)$</td>
<td>26 → 10</td>
<td>23</td>
<td>23</td>
<td>59.2/114.7</td>
<td>$^{60}\text{Cu}(2.5%)$</td>
</tr>
<tr>
<td>$^{61}\text{Cu}$ (205)</td>
<td>$^{59}\text{Co}(a,2n)$</td>
<td>39 → 18</td>
<td>205</td>
<td>60</td>
<td>636/777</td>
<td>$^{61}\text{Cu}(1.2%),$ $^{62}\text{Cu}(1.2%)$</td>
</tr>
<tr>
<td>$^{62}\text{Cu}$ (9.74)</td>
<td>$^{59}\text{Co}(\text{LD})$</td>
<td>18.5 → 46</td>
<td>29</td>
<td>30</td>
<td>70.3/599.4</td>
<td>$^{62}\text{Cu}(1%)$</td>
</tr>
</tbody>
</table>

EOC*: End of Cooling; EOB**: End of Bombardment.

Since the Co/Cu separation methods reported in the literature are rather slow especially in the case of $^{60}\text{Cu}$ production, we developed a new quicker and simple ‘one column method’ using chelating resin. We have already tested it in the case of $^{61}\text{Cu}$-ATSM production via $^{59}\text{Co}+\alpha$ reaction [10]. The target was quickly dissolved in c-HNO$_3$ (3mL) and was adjusted to pH 3-5 using 32 mL of 2M AcONa. This solution was passed through a Chelex 100 column (4 mm I.D., × 80 mm, 1.0 mL, 0.4 meq) with a peristaltic pump. The resin was preconditioned with acetate buffer (20 mL, 0.1 mol/L, pH = 4.4) before use. The cobalt ($^{59}\text{Co}^+$ ions) adsorbed on the chelating resin was eluted with 50 mM phosphate buffer (pH = 2) at a flow rate of 1.0 mL/min. Finally, the $^{61}\text{Cu}^{2+}$ was eluted from the resin with 1N HCl (5 mL). The separation yield was higher than 95%. On the bases of the preliminary results, the use of a considerably
shorter column may be possible, which enables the elution of Cu$^{2+}$ ions with smaller amount of the eluent in a much shorter time (~20 min). It gives the possibility to employ this method (after automation) also for $^{60}$Cu and $^{62}$Cu production. For the synthesis of $^{61}$Cu-ATSM, the $^{61}$Cu$^{2+}$ solution was evaporated to dryness under reduced pressure. The residue was dissolved in 0.1 M acetate buffer (pH = 5.6, 1 mL). To this solution 200 μL. of H$_2$ATSM in DMSO solution (1 mg/mL) was added. The obtained $^{61}$Cu-ATSM was purified on a reversed phase HPLC column with mobile phase of CH$_3$CN/H$_2$O (40/60) at flow rate of 1.5 mL/min. After removal of the HPLC solvent under reduced pressure, the $^{61}$Cu-ATSM was dissolved in saline (5 mL) and passed through a sterile 0.22 μm Milipore filter to be collected in a sterile vial. The determination of the radiochemical purity was performed with radio-HPLC. The labelling yield exceeded more than 90% and the total processing time was around 60 min.

Conclusion

The Co-$^3$He,$\alpha$ routes seem to produce enough activity of $^{60,61,62}$Cu (with low contamination level) to be selected for practical purposes. It not only employs very cheap target material but the separation method of Cu/Co is also simple and quick.

Acknowledgement

We thank the operators of the cyclotron of NIRS, Chiba, for performing the irradiations. This work was supported by the Hungarian Research Found (OTKA: T037219), the Japanese Society for Promotion of Sciences (Tokyo) and the Hungarian Academy of Sciences (Budapest).

References

HIGHLY-PURE RADIOISOTOPES FOR LIFE SCIENCE RESEARCHES PRODUCED AT THE FLNR JINR ACCELERATORS

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A short review of latest data concerning development of production methods of some radioisotopes at FLNR JINR is presented [1-3]. Among these isotopes there are: $^{149}$Tb, $^{211}$At and generator-pairs $^{99m}$Mo/$^{99m}$Tc, $^{225}$Ac/$^{225}$Bi (for nuclear medicine); $^{26}$Al, $^{237}$Pu (for metabolism studies); $^{97}$Tc, $^{235}$Np, $^{236}$Np, $^{238}$Pu (as tracers for radioecological studies). Nuclear reactions, targets, yields, radiochemical separation procedures for production of highly-pure radionuclides are given (Tables 1 and 2).

**TABLE 1. Production methods**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$T_{1/2}$</th>
<th>Reaction</th>
<th>$E_{\text{MeV}}$</th>
<th>Thick target yield, Bq/μAh</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{149}$Tb</td>
<td>4.1 h</td>
<td>$^{142-144}$Nd($^{12}$C,xn)</td>
<td>108→90</td>
<td>$4 \times 10^6$</td>
</tr>
<tr>
<td>$^{211}$At</td>
<td>7.2 h</td>
<td>$^{209}$Bi($^4$He,2n)</td>
<td>30→10</td>
<td>$2.8 \times 10^7$</td>
</tr>
<tr>
<td>$^{99m}$Tc</td>
<td>66 h</td>
<td>$^{100}$Mo(γ,n)</td>
<td>25</td>
<td>$2 \times 10^3$ / mg $^{99}$Mo</td>
</tr>
<tr>
<td>$^{225}$Ac</td>
<td>10 d</td>
<td>$^{228}$Ra(γ,n)</td>
<td>25</td>
<td>$5 \times 10^7$ / mg $^{226}$Ra</td>
</tr>
<tr>
<td>$^{223}$Bi</td>
<td>45.6 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{26}$Al</td>
<td>$7.2 \times 10^7$ y</td>
<td>Mg($^4$He,xn)</td>
<td>35→15</td>
<td>0.4</td>
</tr>
<tr>
<td>$^{237}$Pu</td>
<td>45.6 d</td>
<td>$^{235}$U($^4$He,2n)</td>
<td>27→24</td>
<td>$3.12 \times 10^3$</td>
</tr>
<tr>
<td>$^{97}$Tc</td>
<td>$4 \times 10^6$ y</td>
<td>$^{99}$Mo($^4$He,2n)</td>
<td>36→104</td>
<td>0.06</td>
</tr>
<tr>
<td>$^{230}$Pu</td>
<td>2.86 y</td>
<td>$^{235}$U(d,n)</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{235}$U($^4$He,3n)</td>
<td>36→30</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{235}$Np(γ,n)</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>$^{233}$Np</td>
<td>291.1 d</td>
<td>$^{235}$U(d,2n)</td>
<td>18</td>
<td>330</td>
</tr>
<tr>
<td>$^{236}$Np</td>
<td>1.54 y</td>
<td>$^{237}$Np(γ,n)</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 2 Radiochemical methods

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Target</th>
<th>Chemical procedure (main operations)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{99m}$Mo($^{99m}$Tc) $^{149}$Tb $^{211}$At $^{225}$Ac</td>
<td>Mo$_{met}$ Nd$_2$O$<em>3$ Bi$</em>{met}$ Ra(NO$_3$)$_2$</td>
<td>Ion-exchange chromatography Cation exchange chromatography Gas-thermochromatography Cation exchange chromatography</td>
</tr>
<tr>
<td>$^{26}$Al $^{233}$Pu</td>
<td>Mg$_{met}$ U$_3$O$_8$</td>
<td>Cation exchange chromatography Co-precipitation with LaF$_3$, anion exchange chromatography, electromagnetic mass separation</td>
</tr>
<tr>
<td>$^{97}$Tc $^{235}$Np $^{236}$Np $^{236}$Pu</td>
<td>Mo$_{met}$ U$_3$O$_8$ U$_3$O$_8$ U$_3$O$_8$ NpO$_2$</td>
<td>Distillation Co-precipitation with LaF$_3$, anion exchange chromatography Anion exchange chromatography Co-precipitation with LaF$_3$, anion exchange chromatography, electromagnetic mass separation Anion exchange chromatography</td>
</tr>
</tbody>
</table>

The choice of methods is determined by the physical and chemical properties of the target material and the generated radioactive elements in it, on the one hand, and by the requirements for quality of the preparation (high degree of purity, carrier-free, high specific activity), on the other. The time factor plays an important role for separation of short-lived isotopes. Different processes for preparation of highly-pure carrier-free isotopes were developed at FLNR, including targets, radiochemical methods, electromagnetic separation.

**References**
CYCLOTRON PRODUCTION OF RADIONUCLIDES IN AQUEOUS TARGET MATRICES AS ALTERNATIVE TO SOLID STATE TARGETRY: PRODUCTION OF Y-86 AS EXAMPLE


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Commonly used “organic” positron emitting radionuclides $^{18}$F, $^{11}$C, $^{13}$N, and $^{15}$O are simply obtained from gaseous or aqueous targets, which enable an automated handling of target, i.e. both, filling and radionuclide delivery to a hot cell containing a chemistry processing and/or labelling module. In the recent years other – mostly metallic – radionuclides for PET gained more and more interest, since they can be used as surrogates for therapeutic nuclides attached to biomolecules like peptides or antibodies. The implication for surrogate nuclides results from the circumstance that an optimum dosimetric regime in endo radiotherapy relies on quantitative pharmacokinetic data obtained only by non invasive in vivo PET scans [1]. However, for production of these alternative positron emitters the vast majority of them affords solid targets in form of metal foils, oxide or salt pellets [2, 3] which can not be operated by an automated processing. Those solid target systems have to be mounted and dismounted after irradiation by man, leading to two major disadvantages. First, manual cyclotron intervention is practically unsuited for daily routine radionuclide production and second the operating staff receives high radiation doses from the activated target. An alternative could be the irradiation of aqueous salts of target isotopes, allowing automated target operation. The major requirements are firstly a thermal stability of the dissolved compound, secondly the avoidance of counter ions containing nuclides which produce long-lived radionuclides under irradiation and thirdly a high solubility of the salt in the aqueous matrix. Here we report the proof of principle of the new radionuclide production concept by irradiation of strontium nitrate dissolved in water in order to produce $^{86}$Y (cf. [4, 5]).

Methods

A “Nitrogen-13 target” liquid target (cf. Figure 1) was filled with a Sr(NO$_3$)$_2$ solution (natural isotopic composition, 81 % of maximum solubility: 6.0 g Sr(NO$_3$)$_2$ [MERCK, Germany] were dissolved in 11.2 mL pure water (FLUKA, Switzerland)) and irradiated with 16 MeV protons for 60 minutes at 6 µA. After end of bombardment (EOB) the target content was delivered to a 25 mL glass vial containing phosphate buffer pH 7. Then, the target was flushed 5 times by a 25 mM HNO$_3$ solution and these fractions were collected in the same vial resulting in a total final volume of about 16 mL. Two aliquots of 10 and 100 µL were transferred to an Eppendorf cap respectively, containing already 100 µL of the phosphate buffer. Exact aliquot fraction was determined by measuring totally collected activity and the aliquot activities immediately afterwards using a “dose calibrator”. Both aliquots were measured several times applying gamma spectrometry (HPGe detector). The smaller aliquot was measured immediately after sample preparation to observe nuclides with short half-lives and the other one was measured over a period of 4 weeks starting with the following day. Nuclear decay and emission data were taken from Ref. [6].
Results

The activities of the yttrium radionuclides produced by this experiment are listed in Table 1 together with the derived and extrapolated activities for higher beam currents, irradiation times and $^{86}$Sr enrichment.

Table 1: Produced and extrapolated activities of yttrium radioisotopes generated by irradiation of aqueous solutions of $\text{Sr(NO}_3)_2$. 1) target nuclide and nuclear reaction with the most contribution to the respective radionuclide, 2) isotopic composition of enriched $^{86}$Sr taken from Ref. [4], 3) EOB activities effectively produced in this experiment, 4) derived activities for maximum possible beam current [under these conditions target material corrosion by hydrolysis might occur], 5) further extrapolated activities for longer irradiation time, 6) further processed data for the case of enriched $^{86}$Sr, 7) finally calculated activities after 3 hours cooling time (while *Y may be separated from the product matrix).

<table>
<thead>
<tr>
<th>Nuclide:</th>
<th>$^{88}$Y</th>
<th>$^{87}$Y</th>
<th>$^{87m}$Y</th>
<th>$^{86}$Y</th>
<th>$^{86m}$Y</th>
<th>$^{85}$Y</th>
<th>$^{85m}$Y</th>
<th>$^{84m}$Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Half-life:</td>
<td>106.65 d</td>
<td>80.3 h</td>
<td>13 h</td>
<td>14.74 h</td>
<td>48 min</td>
<td>2.68 h</td>
<td>4.86 h</td>
<td>39.5 min</td>
</tr>
<tr>
<td>Nuclear reaction$^1$</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td>(p,n)</td>
<td></td>
</tr>
<tr>
<td>Target nuclide$^2$</td>
<td>$^{88}$Sr</td>
<td>$^{87}$Sr</td>
<td>$^{87m}$Sr</td>
<td>$^{86}$Sr</td>
<td>$^{86m}$Sr</td>
<td>$^{85}$Sr</td>
<td>$^{85m}$Sr</td>
<td>$^{84m}$Sr</td>
</tr>
<tr>
<td>Natural Sr composition [%]</td>
<td>82.58</td>
<td>7.00</td>
<td>7.00</td>
<td>9.86</td>
<td>9.86</td>
<td>9.86</td>
<td>9.86</td>
<td>0.56</td>
</tr>
<tr>
<td>Composition of enriched $^{86}$Sr [%]$^3$</td>
<td>2.68</td>
<td>1.02</td>
<td>1.02</td>
<td>96.30</td>
<td>96.30</td>
<td>96.30</td>
<td>96.30</td>
<td>0.002</td>
</tr>
<tr>
<td>Produced EOB activities $A_{\text{EOB}}$ [MBq]$^4$:</td>
<td>1.2</td>
<td>4.5</td>
<td>16.8</td>
<td>21.6</td>
<td>46.7</td>
<td>$\leq 3.2$</td>
<td>not detectable</td>
<td>$\leq 7.8$</td>
</tr>
<tr>
<td>$A_{\text{EOB}}(6 \rightarrow 30\mu\text{A})$ [MBq]$^4$:</td>
<td>5.9</td>
<td>22.6</td>
<td>83.8</td>
<td>108.1</td>
<td>233.4</td>
<td>$\leq 16.0$</td>
<td>$\leq 39.2$</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{EOB}}(1\ h \rightarrow 5\ h)$ [MBq]$^4$:</td>
<td>29.6</td>
<td>110.8</td>
<td>377.9</td>
<td>493.1</td>
<td>397.4</td>
<td>$\leq 50.6$</td>
<td>$\leq 59.9$</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{EOB}}(\rightarrow ^{86}\text{Sr})$ [MBq]$^4$:</td>
<td>1.0</td>
<td>16.1</td>
<td>55.1</td>
<td>4815.6</td>
<td>3881.6</td>
<td>$\leq 494.1$</td>
<td>$\leq 0.2$</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{EOB}}(\rightarrow ^{86}\text{Sr})$ [MBq]$^4$:</td>
<td>1.0</td>
<td>15.7</td>
<td>46.9</td>
<td>4182.0</td>
<td>288.5</td>
<td>$\leq 227.4$</td>
<td>$\leq 0.01$</td>
<td></td>
</tr>
<tr>
<td>$\pm$ Error [%]</td>
<td>5.6</td>
<td>13.2</td>
<td>16.4</td>
<td>6.6</td>
<td>16.4</td>
<td>25.6</td>
<td>25.6</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion

In case the beam upsampling for the described target system works without physico-chemical complications, PET nuclide $^{88}$Y would be produced in activities of more than 4 GBq by proton irradiation of aqueous dissolved $^{86}$Sr(NO$_3$)$_2$ with the parameters: 96.3 % isotopic
enrichment of $^{88}$Sr, 16 MeV protons, 30 μA beam current, 5 h irradiation time. Radioisotopic activity fraction (among Y radionuclides) rises from 52 % (EOB) to 88 % (3 h later). At EOB the high matrix activity is dominated by $^{14}$N produced by the $^{16}$O(p,α) reaction on target water. Some $^{18}$F is also generated by $^{15}$O(p,n) reaction. Further, nitrate generates $^{14}$C by $^{14}$N(p,α) and isomer $^{86m}$Y is formed simultaneously with the desired $^{86}$Y. These radionuclides become negligible, when the irradiated target solution (ITS) is allowed to decay for some hours before $^{86}$Y will be used for labelling. Formed Sr and Rb radionuclides can be chemically removed during workup of the ITS for $^{86}$Y purification and $^{88}$Sr recovery [5]. Since the used target (Figure 1) was not tight enough regarding cooling water, we recommend to use the “high yield F-18 target” from GE-MS instead with differently designed loading. Thus, demonstrated by the reported experiment, an opportunity is opened to produce radionuclides, which in the past were only accessible by solid target production technology. Several radionuclides (e.g. $^{11,12}$Mn, $^{57}$Co, $^{56,60}$Cu, $^{56,68}$Ga, or $^{94m,96}$Tc) may now have the potential to gain a broader application in nuclear medicine, provided that a suitable automatically operating chemistry module is present to fulfill both, extraction of the desired nuclide from the liquid target matrix and recovery of the expensive isotopically enriched target material for reuse in subsequent irradiations.

![Image](image_url)

Figure 1: Standard liquid target assembly (“Nitrogen-13 target”, Part No. P5230JF, General Electrics Medical Systems, Handbook of the cyclotron “PETtrace”) for irradiation with 16 MeV protons. (3) Target body of pure silver, (7) target foil of pure titanium. Target volume 0.8 nL, 30 μA maximum beam current in case of pure water filling.

References

ISOLATION OF LANTHANIDE AND HAFNIUM RADIOISOTOPEs FROM A MASSIVE Ta-TARGET


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Production of radioactive isotopes of rare earth elements (REE) is relevant for their application in systematic chemical, environmental and nuclear medical investigations. In particular, among the lanthanides the number of isotopes with different nuclear characteristics is very high, while their chemical properties are quite similar.

As a source of radiolanthanides, in this experiment a massive 195 g tantalum target was used, which has been irradiated with 1 GeV protons at CERN accelerator in 2002, totally receiving about 10^19 protons. A rough estimate of the overall REE mass in the target yielded 100 μg. Due to significant radiation dose (200 μSv at 100 cm distance), excess of the chemical matrix (Ta) and the complex radioelement distribution in the target, a sophisticated radiochemical separation procedure was developed. After the dissolution of the target in 1:1 of a HF(cons)+HNO₃ solution, the REE fraction was absorbed on 500 mg of finely dispersed charcoal. The charcoal was filtered from the solution, yielding 20% of the REE fraction. The REE fluorides were dissolved in a saturated solution of H₂BO₃ in 0.1 M HCl. The radiolanthanides were concentrated on a cation-exchange column (Dowex 50x8, V₀ = 8 ml). Final separation of individual REE was achieved at a small cation-exchange column (Aminex A6, V₀ = 0.2 ml) by gradient elution with α-HIB at pH = 4.6 (Fig.1). Various chemically high-purity radiolanthanide fractions in very small volumes of < 100 μl such as ¹⁷³,¹⁷⁵Lu, ¹⁶⁹Yb, ¹⁶⁸Tm, ¹⁶⁶Tb, ¹⁴⁶,¹⁵¹,¹⁵₄Gd, ¹⁴⁷,¹⁴₉,¹⁴₉Eu, ¹⁴³,¹⁴⁶Sm, ¹⁴₃,¹⁴₆Pm, ¹⁴⁷Ce (Table 1) have been isolated and can be used for systematic application. Isolation of the remaining REE was achieved by repeated sorption.

For the isolation of hafnium isotopes, the HF(cons)+HNO₃ solution remaining after the isolation of the REE fraction was passed through an anion-exchange column (Dowex 1x8, V₀ = 150 ml). While tantalum is not adsorbed, hafnium remains on the resin. Every eluate fraction was evaporated to dryness and subsequently transferred to the next, smaller column using 9 M HF + 1.2 M HNO₃ solutions. An average Ta / Hf separation factor of 50 was determined, thus resulting in an amount of < 1 μg of tantalum after fifth separation and the chemical yield of the procedures was >80%.

The hafnium fraction was used for a high-activity ¹⁷²Hf /¹⁷²Lu generator [1]. At the moment of generator loading, the activity of ¹⁷²Hf (T₁/₂=1.87 y) amounted to 85.1 MBq. The hafnium fraction also contained 35.2 MBq of ¹⁷⁵Hf (T₁/₂ = 70 d) and 2.2 MBq of ⁸⁸Zr (T₁/₂ = 83.4 d). The tungsten isotopes ¹⁷⁸W (T₁/₂ = 22 d) and ¹⁸₁W (T₁/₂ = 121 d) were not detected, because they have been separated in the course of the Ta / Hf anion exchange purification.
Fig. 1. Separation profile of individual lanthanides (30 µl volume per fraction)

Table 1. Activities of radiolanthanides.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>T_{1/2}</th>
<th>Activity, MBq</th>
<th>Radioisotope</th>
<th>T_{1/2}</th>
<th>Activity, MBq</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{173}$Lu</td>
<td>1.37 y</td>
<td>133</td>
<td>$^{127}$Eu</td>
<td>24.1 d</td>
<td>0.3</td>
</tr>
<tr>
<td>$^{174}$Lu</td>
<td>3.31 y</td>
<td>6.0</td>
<td>$^{138}$Eu</td>
<td>54.5 d</td>
<td>0.7</td>
</tr>
<tr>
<td>$^{169}$Yb</td>
<td>32.026 d</td>
<td>4.0</td>
<td>$^{129}$Eu</td>
<td>93.1 d</td>
<td>47.0</td>
</tr>
<tr>
<td>$^{169}$Tm</td>
<td>93.1 d</td>
<td>4.0</td>
<td>$^{145}$Sm</td>
<td>340 d</td>
<td>109.0</td>
</tr>
<tr>
<td>$^{169}$Dy</td>
<td>144.4 d</td>
<td>100</td>
<td>$^{145}$Pm</td>
<td>265 d</td>
<td>189</td>
</tr>
<tr>
<td>$^{166}$Tb</td>
<td>72.3 d</td>
<td>0.03</td>
<td>$^{149}$Pm</td>
<td>363 d</td>
<td>4.7</td>
</tr>
<tr>
<td>$^{154}$Gd</td>
<td>48.27 d</td>
<td>35.0</td>
<td>$^{150}$Pm</td>
<td>5.53 y</td>
<td>0.26</td>
</tr>
<tr>
<td>$^{153}$Gd</td>
<td>124 d</td>
<td>187</td>
<td>$^{139}$Ce</td>
<td>137.64 d</td>
<td>19.7</td>
</tr>
</tbody>
</table>

References

A NEW INTERNAL TARGET SYSTEM FOR PRODUCTION OF $^{211}$At ON THE CYCLOTRON U-120M

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The alpha emitter $^{211}$At (7.214 h) is considered to be a promising radionuclide for targeted cancer therapy due to its decay properties [1–3]. Among factors, which impede progress in this field, the availability of $^{211}$At in sufficient amount and purity plays the major role. This isotope is produced via the $^{209}$Bi($\alpha,2n$)$^{211}$At reaction on natural monoisotope $^{209}$Bi, which has threshold around 20 MeV and reaches the maximum cross section of ca 900 nb at 30 MeV [4,5]. However, one cannot use the full range of the beam energies suitable for production of $^{211}$At, since the following reaction, $^{209}$Bi($\alpha,3n$), resulting in $^{210}$At (8.1 h), which decays to the radiotoxic alpha emitter $^{206}$Po (138,38 d), has threshold at 28 MeV [5]. The goal is then to maximize $^{211}$At yield, while keeping the content of $^{210}$At at acceptable level [5,6]. Also design of the target has some importance for the effective use of the produced astatine, for it may influence the separation yield.

An ideal solution is to use a tangential (“grazing angle”) target that enables to use narrow interval of the beam energies close to 30 MeV. Theoretical saturation yield at this energy is equal to 420 MBq/μA [6]. The most efficient reported target system of this type reached the saturation yield 447±76 MBq/μA [7]. Nevertheless, the separation yield of $^{211}$At was for this target only 47±15 %, although usually the dry distillation technique used for $^{211}$At separation gives separation yields > 70 % [5, 8, 9]. The last reported separation procedure, which employs prompt evaporation of the quartz tube with volatilised astatine, resulted in ca 73 % separation yield (decay corrected activity of the solution of $^{211}$At in CHCl$_3$ vs. the activity of $^{211}$At inserted in the tube) [9]. However, in many cases, including [9], it is necessary to scrape the irradiated bismuth layer from the target holder before the separation. It makes the whole procedure longer, decreases overall yield (astatine loss during scraping) and is undesirable from the point of view of radiation safety.

Aim of this study was to develop a new, simple and reliable target system, which would keep favourable properties of the above mentioned systems, reducing their drawbacks as much as possible.

The target itself is created by a thin bismuth layer (3–5 μm) of 10×50 mm area evaporated on a light aluminium backing (7.5 g). The backing is fixed via an aluminium frame and o-ring sealing to the target holder with cooling water input and output. The system is tightened with a single screw and the backing can be, therefore, released within a few seconds. The target was irradiated at small angles (0.5–1.5°) for 1–2 h with beam currents 10–30 μA. Shortly after the EOB, the system was disassembled and the backing was inserted without any further processing into the pre-heated quartz tube, distilled according to [9] at 640 °C for 2 min and trapped in a Teflon capillary cooled in a bath of ethanol and dry ice. Astatine condensed on the wall of the Teflon capillary was eluted into 300 μl of methanol.
The saturation target yield of $^{211}$At in the target was found to be 400±25 Mbq/µA and the maximum activity prepared using the system was 1.8 GBq (EOB). The ratio of the activities of $^{210}$At and $^{211}$At at EOB was equal to ca 6×10⁻⁴, which corresponds to ca 1.5 kBq of $^{210}$Po resulting from the decay of $^{210}$At contained in 1 GBq of $^{211}$At. The overall separation yield of $^{211}$At was found to be 70–75 % (activity in 300 µl of methanol related to the activity in the target, decay corrected). Activity of $^{211}$At left in the target is less than 5 %. Separation was finished within 30 min after EOB.

Authors gratefully thank the Grant Agency of the Czech Academy of Science for financial support (grant no. B4048302).

References


INVESTIGATION OF THE PRODUCTION OF THE THERAPEUTIC RADIOISOTOPE $^{114m}$In THROUGH PROTON AND DEUTERON INDUCED NUCLEAR REACTIONS ON CADMIUM

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A rising trend in therapeutic use of radioisotopes is observed in recent years. For efficient internal radiotherapy it is essential that low energy beta radiation, Auger electrons, low energy x-rays or alpha particles are emitted by the radionuclides applied. The overwhelming part of the used therapeutic radionuclides is produced by reactor neutron induced reactions. Several of these radioactive species can, however, be produced efficiently by charged particle induced reactions too. One of the radionuclides used for radioimmunotherapy is $^{114m}$In that can be produced by both routes. The $^{113}$In(n,$\gamma$)$^{114m}$In reaction results in a non carrier free product. Alternatively in proton and deuteron induced reactions high specific activity, and carrier free $^{114m}$In products can be produced. A thorough search of the literature showed that the production of $^{114m}$In by charged particles was not investigated yet in detail. Only a few data were found for proton induced reaction but no experimental data were found for deuteron induced reactions. In the work plan of the co-ordinated research project started by the International Atomic Energy Agency on the most widely used therapeutic radioisotopes [1], the $^{114}$Cd(p,n)$^{114m}$In and the $^{114}$Cd(d,2n)$^{114m}$In reactions are included. This work describes new experimental results in comparison with critically analysed earlier results. Based on our data optimum production energies are presented. The target preparation, the chemical separation of the In radionuclides from the Cd target and the recovery of the enriched Cd target was already solved earlier in connection with the large-scale routine production via the $^{112}$Cd(p,2n) and the $^{113}$Cd(p,n) reactions of the widely used $^{111}$In medical radioisotope [2].

Experimental method and data evaluation

Highly enriched (99.01 %) electroplated $^{114}$Cd deposits on 12.5 μm copper foils and Cd foils with natural composition were used as targets. The targets from enriched material were prepared by constant current ac-electrolysis from slightly acidic (5<pH<6) 0.5M EDTA solutions, applying an asymmetric square wave plating voltage (i0/i0 = 2/1; cathodic duty cycle 80%) and a 15 mA net cathodic current. As plating setup a cylindrical PMMA plating vessel fitted with 4 plating windows (1.2x10 cm, rounded corners and surface area 11.69 cm²) and a single axial and grounded anode was used. To enhance the homogeneity of the cadmium layers, a cylindrical bi-directional perforated PEEK stirrer operating at 1300 rpm and a 8s/8s rotation cycle was used. Electrolysis was performed over a 15 hour period that results in a depletion ratio of the plating solution of more than 98%. Per plating batch four 12.8 ±1.9 μm target layers were produced. The cadmium deposits show an excellent surface area granulometry, an acceptable homogeneity and comply with a 250 °C
thermal shock test. From the deposits 8x8 mm cut-outs were prepared and irradiated in the stacks together with additional Ti, Fe, Cu monitor foils to follow the beam intensity and the energy degradation. The stacks were irradiated in a Faraday cup like target holder at 32 MeV and 15 MeV proton energies and at 20 MeV and 10 MeV deuteron energies. The gamma spectra emitted in the decay of the irradiated samples were counted non-destructively with HPGe detector. More details on the measuring technique and the data processing can be found in [3].

In the case of proton induced reactions the cross sections for the $^{114}$Cd(p,n)$^{114m}$In reaction were measured on the highly enriched targets up to 32 MeV and up to 20 MeV (threshold of the $^{116}$Cd(p,3n) reaction) on natural targets (by bombarding natural Cd with protons only the 2 mentioned reactions can contribute to the production of the $^{114m}$In). By subtracting the normalised excitation function of the $^{114}$Cd(p,n) reaction measured on enriched target from the excitation function of the $^{nat}$Cd(p,x) process above the threshold of the $^{116}$Cd(p,3n) process the cross-sections for the $^{116}$Cd(p,3n) reaction were deduced.

In the case of deuteron induced reactions on Cd targets with natural isotopic composition, the $^{113}$Cd(d,n) and $^{114}$Cd(d,2n) reactions contribute to the production of $^{114m}$In in the investigated energy range (the threshold of the $^{118}$Cd(d,4n) reaction is 19.63 MeV. In a similar way as above the excitation function of the $^{113}$Cd(d,n) reaction can be determined using separation based on the knowledge of the excitation function of the $^{114}$Cd(d,2n) reaction obtained from measurements on $^{nat}$Cd and results on $^{nat}$Cd targets.

Results and discussion

The experimental cross sections of the $^{114}$Cd(p,n)$^{114m}$In, $^{116}$Cd(p,3n)$^{114m}$In, $^{111}$Cd(d,n)$^{114m}$In, $^{114}$Cd(d,2n)$^{114m}$In, $^{nat}$Cd(p,xn)$^{114m}$In, $^{nat}$Cd(d,xn)$^{114m}$In reactions were determined. Integral yields as a function of the energy were calculated from the experimental cross-sections and are presented in the table below. It can be deduced, that at low energy PET cyclotrons the $^{114}$Cd(p,n) reaction can be used. The optimum energy range is 17 - 5 MeV for protons. For successful production with deuterons higher energy accelerators allowing exploitation of the $^{114}$Cd(d,2n) reaction are needed as the $^{113}$Cd(d,n) process does not contribute significantly to the production of $^{114m}$In. At higher energies, in the range of the commercial isotope production machines (proton energy around 35 MeV) the $^{114}$Cd(d,2n) and the $^{116}$Cd(p,3n) processes became energetically possible. The production yield for the (p,3n) reaction (40-20 MeV optimum range) is 5.6 GBq/C (547 μCi/μAh, 20 MBq/μAh) and the (d,2n) process (19-9 MeV optimum range) is 961 MBq/C (93.5 μCi/μAh, 3.46 MBq/μAh). When comparing the two processes we have to take into account that although the yield of the (p,3n) process is significantly higher than that of the (d,2n) process, the proton induced reaction requires enriched $^{116}$Cd, which has lower abundance and therefore more expensive than the enriched $^{114}$Cd. Additionally the new generation of commercial cyclotrons has only 30 MeV maximum proton energy, which results in lower yield by a factor of 1.9 when comparing to the achievable yield at a 40 MeV cyclotron. Data for the $^{113}$Cd(d,n)$^{114m}$In reaction are considered as preliminary, due to the well known separation problem of a small contributing part
\(^{113}\text{Cd}(d,n)\)\(^{114m}\text{In}\) from a larger main component \(^{114}\text{Cd}(d,2n)\)\(^{114m}\text{In}\) having about the same threshold energy as in the case of these two reactions.

Yields collected in Table 1 show that the \(^{116}\text{Cd}(p,3n)\) reaction can be considered as an important reaction for production of \(^{114m}\text{In}\). Therefore the list of the recommended reactions for the CRP probably will have to be extended with this process.

Using the \(^{114}\text{Cd}(d,2n)\) and \(^{116}\text{Cd}(p,3n)\) reactions two longer lived states of \(^{115}\text{In}\) are simultaneously produced via the \((d,n)\) and \((p,2n)\) reactions. The production cross-section for the \(^{115m}\text{In}\) (4.49 hour) was also investigated. This radionuclidic contamination however causes no problem due to the short half-life of the isomeric state while the very long half-life (5\(\times\)10\(^3\) y) ground state has no gamma emission.

We also investigated the production possibility of the \(^{114m}\text{In}\) by using targets with natural isotopic composition. In this case also the simultaneously produced contaminating radioisotopes of In can be kept below the required level by introducing a proper cooling time. Among them the radionuclide produced in high activity and with a long half-life is the \(^{111}\text{In}\) (\(T_{1/2} = 2.81\) d). The \(^{111}\text{In}\) is also a strong Auger emitter and is used both in medical diagnosis and therapy. By using a cooling time of one half-life of \(^{114m}\text{In}\), the \(^{111}\text{In}\) activity can be reduced by factor of 2\(\times\)10\(^3\).

Table 1. Thick target yields for production of \(^{114m}\text{In}\) using different targets

<table>
<thead>
<tr>
<th>Target</th>
<th>Reaction</th>
<th>Energy range (MeV)</th>
<th>Thick target yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{113}\text{Cd})</td>
<td>(d,n)</td>
<td>9 - 5</td>
<td>152 MBq/C</td>
<td>preliminary data</td>
</tr>
<tr>
<td>(^{114}\text{Cd})</td>
<td>(p,n)</td>
<td>17 - 5</td>
<td>399 MBq/C</td>
<td></td>
</tr>
<tr>
<td>(^{114}\text{Cd})</td>
<td>(d,2n)</td>
<td>19 - 9</td>
<td>961 MBq/C</td>
<td></td>
</tr>
<tr>
<td>(^{116}\text{Cd})</td>
<td>(p,3n)</td>
<td>40 - 20</td>
<td>5.6 GBq/C</td>
<td></td>
</tr>
<tr>
<td>(^{208}\text{Cd})</td>
<td>(p,xn)</td>
<td>40</td>
<td>219 MBq/C</td>
<td>after 50 day cooling</td>
</tr>
<tr>
<td>(^{208}\text{Cd})</td>
<td>(d,xn)</td>
<td>17</td>
<td>110 MBq/C</td>
<td>after 50 day cooling</td>
</tr>
</tbody>
</table>

References


THE PRODUCTION OF $^{111}$In FROM AN In/In$_2$O$_3$ TARGET

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The radionuclide $^{111}$In has particularly favourable characteristics for use in nuclear medicine. It decays with a half-life of 2.83 days by 100% electron capture, yielding two $\gamma$-rays of 171.3 keV and 245.4 keV [1-3]. Several routes for its production are performed, the most popular methods being $^3$He-bombardment of $^{114}$Ag and proton and deuteron bombardment of $^{116}$Cd or an enriched Cd isotope [4, 6].

At iThemba LABS radionuclide production is exclusively carried out with a primary 66 MeV external proton beam. The production of $^{111}$In is carried out by bombardment of a $^{114}$In/In$_2$O$_3$ target, the reaction being $^{114}$In(p, xn)$^{111}$Sn$\rightarrow^{111}$In. A $^{114}$In/In$_2$O$_3$ target was chosen because In has a too low melting point of 156.6 °C. The target was prepared as a disc pellet by cold pressing using a 55/45 ratio of In/In$_2$O$_3$ powdered mixture. The sintering of the two components resulted in the formation of indium suboxide, which has a much higher melting point and, thereby, making it a suitable target for bombardment.

The production of $^{111}$In via the production and separation of $^{111}$Sn has a distinct advantage over the $^{114}$Cd + p route in that $^{114}$Sn is a stable isotope and, therefore, no $^{114}$In will be present in the final product. $^{110}$In will not occur as a contaminant, as $^{110}$Sn has a half-life of 4 hours and decays to $^{110}$In, which has a half-life of only 69.1 minutes. Unfortunately, the short half-life of $^{111}$Sn (35.3 minutes) seriously limits the yield of $^{111}$In [5], which can be achieved in a batch production process. At least half of the potential yield of $^{111}$In is lost during the dissolution and separation processes. Profitable bombardment times are restricted to 1-2 hours, due to the saturation of $^{111}$Sn build-up in the target.

Concentrated HCl (50 ml) is heated in a reaction vessel at 80 °C before adding 30% H$_2$O$_2$ (5 ml). The target is introduced into the reaction vessel directly after the addition of the H$_2$O$_2$. As the reaction proceeds, more concentrated HCl and 30%
H₂O₂ are added to the reaction vessel at regular intervals until dissolution is complete. The resulting solution is then cooled, using a fan, for one minute.

The solution then is pumped through a 2.0 ml column containing AG1-X4 microporous anion exchange resin. The resin retains the tin radionuclides (formed during the proton bombardment) and ¹¹¹In (formed by decay of ¹¹¹Sn). The In is selectively eluted from the column using a 1 M HF/0.03% H₂O₂ mixture.

Subsequently, the remaining ¹¹¹Sn and ¹¹²Sn is eluted using 0.5 M HNO₃ and is pumped to a vessel containing 1 M HF/0.03% H₂O₂ mixture. This resultant solution is loaded on to a second column containing AG MP-1 macroporous anion exchange resin. Any remaining In is eluted from the resin using 1 M HF/0.03% H₂O₂ mixture and the ¹¹¹Sn on the resin is left for 2.5 hours to decay completely to ¹¹¹In.

The ¹¹¹In is finally eluted using 1 M HF/0.03% H₂O₂ and the solution is transferred to an evaporator and evaporated to dryness. The ¹¹¹In final product is dissolved in 0.1 M HCl and pumped into a product vial.

References

A VERTICAL THERMOCHROMATOGRAPHIC DEVICE
FOR VARIOUS RADIOCHEMICAL SEPARATIONS
INCLUDING RADIONUCLIDE GENERATORS

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The rapid development of thermochromatography in the 1960-1970's was stimulated first of all by the desire to discover new short-lived radionuclides and to investigate their nuclear-physical and chemical properties. Various methods for fast chemical separation in both liquid and gaseous phases were described in a review [1], allowing investigation of radionuclides with half-lives of about 1 s. New radionuclides produced at reactors (neutron-rich radionuclides) and at medium-energy particle accelerators (neutron-deficient radionuclides) have been discovered and investigated. For gas chemistry, chemically stable substances were utilized as targets, from which the produced radionuclides were transferred under controllable conditions into known volatile compounds for their subsequent thermochromatographic separation. For a recent review on thermochromatography cf. [2].

These separations were usually carried out in a horizontal apparatus, but recently the vertical arrangement of the TCC is believed to be more rational [3], cf. Fig. 1.

This vertical arrangement greatly decreases the carry-away of gaseous products against the direction of incoming reactant gas flow and allows the process to be easily automated. The target is loaded at the bottom of the open apparatus, the apparatus is closed using inserted smaller quartz tubes, the reactant gas is passed through the quartz tube system, and then the assembly is placed in the vertical oven with the required temperature distribution. After the termination of the separation process the assembly (or the inner TCC only) is taken out of the oven, cooled, and from the inner quartz tube surface the adsorbed product is washed off with a minimum volume of an appropriate solution.

This apparatus, first developed to separate the positron emitter $^{\text{94m}}\text{Tc}$ from the irradiated molybdenum oxide in 25 minutes [3], was subsequently used more universally for separations of the systems $^{\text{110}}\text{Sn}/^{\text{111}}\text{In}$ [4], $^{\text{188}}\text{W}/^{\text{188}}\text{Re}$, $^{\text{188}}\text{W}/^{\text{188}}\text{Re}$ [5], and $^{\text{72}}\text{Se}/^{\text{72}}\text{As}$ [6].

This type of thermochromatographic separation might in addition be used for construction of radionuclide generator systems. In this context, the parent-daughter radionuclide pairs $^{\text{188}}\text{W}/^{\text{188}}\text{Re}$ [5] and $^{\text{72}}\text{Se}/^{\text{72}}\text{As}$ [6,7] have been comprehensively studied.
Fig. 1. Vertical-type thermochromatographic apparatus for routine separation of $^{99m}$Tc from irradiated $^{99}$Mo targets: (1) TCC-inner quartz tube for adsorption of $^{99m}$Tc; (2) middle quartz tube for condensation of $^{99}$MoO$_3$; (3) outer quartz tube; (4) electric resistance oven [3]

The technical and radiochemical features of the vertical arrangement are discussed as well as its applications for various target / radionuclide or radionuclide generator systems.

According to radionuclide generators discussed earlier [8] and more recently [9], and the parameters of thermochromatographic separations [2], several radionuclide generator systems might be separated using the vertical thermochromatographic separation devise, cf. Table 1. Some of them are currently under investigation.
Table 1. Proposed processes for the utilization of the vertical thermochromatigraphic separation system in the case of radionuclide generators

<table>
<thead>
<tr>
<th>Generator</th>
<th>Chemical conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temperature, °C</td>
</tr>
<tr>
<td>$^{28}$Mg</td>
<td>(20.91 h) → $^{28}$Al</td>
</tr>
<tr>
<td>$^{68}$Ge</td>
<td>(270.8 d) → $^{68}$Ga</td>
</tr>
<tr>
<td>$^{81}$Rb</td>
<td>(4.576 h) → $^{81}$mKr</td>
</tr>
<tr>
<td>$^{83}$Rb</td>
<td>(86.2 d) → $^{83}$mKr</td>
</tr>
<tr>
<td>$^{109}$Pd</td>
<td>(13.70 h) → $^{109m}$Ag</td>
</tr>
<tr>
<td>$^{112}$Pd</td>
<td>(21.03 h) → $^{112}$Ag</td>
</tr>
<tr>
<td>$^{110}$Sn</td>
<td>(4.11 h) → $^{110m}$In</td>
</tr>
<tr>
<td>$^{113}$Sn</td>
<td>(115.1 d) → $^{113m}$In</td>
</tr>
<tr>
<td>$^{132}$Te</td>
<td>(3.204 d) → $^{132}$I</td>
</tr>
<tr>
<td>$^{189}$Ir</td>
<td>(13.2 d) → $^{189m}$Os</td>
</tr>
<tr>
<td>$^{208}$Pt</td>
<td>(12.5 h) → $^{208}$Au</td>
</tr>
<tr>
<td>$^{228}$Ra/Ac</td>
<td>(14.9 d)/ (10.0 d) → $^{213}$Bi</td>
</tr>
</tbody>
</table>

References


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DEVELOPMENT OF A GAS-JET-COUPL ED MULTITARGET SYSTEM FOR MULTITRACER PRODUCTION

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Since 1991 [1], the RIKEN multitracer technique has been successfully applied in investigations of the behavior of various elements in the fields of chemistry, biology, medicine, engineering, and environmental science. By using the falling ball system, radionuclides of a large number of elements were simultaneously produced from metallic targets such as Ti, Ag, and Au irradiated with a 135 MeV/nuc. $^{14}$N (or $^{12}$C, $^{16}$O) beam from the RIKEN Ring Cyclotron (RRC) [1]. After the irradiation, these radionuclides were chemically separated from the target material [1, 2], and then carrier-free and salt-free multitracer solutions were applied to various experiments.

Recently, we have installed a gas-jet-coupled multtarget system on the E3b beam line of RRC as an alternative to the falling ball system. A schematic of this system is shown in Fig. 1. In the first chamber, the 135 MeV/nuc. $^{14}$N (or $^{12}$C, $^{16}$O) beam from RRC passes through a HAVAR vacuum window of 6 μm thickness, and enters 30 multtarget of about 1 μm in thickness with 10 mm spacings. The recoiling multitracers are stopped in He gas, attached to aerosols such as NaCl, KCl, and C, and are continuously transported through a Teflon capillary to a hot laboratory, where the multitracers are collected on a glass filter. Then, the multitracer solutions are obtained simply by washing the filter with a suitable solution. Lastly, the $^{14}$N beam enters the thick metallic targets such as Ti, Ag, and Au, which are about 200 μm

Fig. 1. Schematics of the gas-jet-coupled multtarget system for multitracer production.
Advantages of the gas-jet coupled multitarget system are as follows. (1) The multitracers are separated from the target material without chemical separation and transported to the hot laboratory within a few seconds. Thus, radionuclides with short half-lives of less than 1 min are available for tracer experiments. (2) The targets with various chemical compositions are prepared by electrodeposition or vacuum-evaporation techniques. The composition of the radionuclides in the multitracers can be optimized by changing the target material and its array. (3) The radionuclides of interest can be easily concentrated by using a liquid chromatography apparatus based on ion exchange or solvent extraction. (4) All of the targets are continuously cooled with He gas during the irradiation. Thus, the beam intensity of ~1 pA is acceptable, though the maximum in the falling ball system was approximately 0.1 pA due to the irradiation in a vacuum chamber.

The performance of the gas-jet coupled multitarget system was investigated using the 30 multiple $^{64}$Cu targets of 2 μm in thickness irradiated with the 135 MeV/nuc. $^{14}$N beam of 50 pA in intensity. The multitracers recoiling out of the target were stopped in He gas (~80 kPa), attached to KCl aerosols generated by sublimation of the KCl powder at 640°C, and continuously transported through a Teflon capillary (2.0 mm i.d., 10 m long) to the hot laboratory just beneath the E3 irradiation room. The aerosols were collected on a glass filter ADVANTEC GB-100R for 15 min. The flow rate of the He carrier gas was 2.0 L min$^{-1}$. In the same irradiation, one Cu foil of 2 μm thickness and 15 x 15 mm$^2$ size sandwiched by one pair of Kapton foils of 50 μm thickness and 20 x 20 mm$^2$ size, which collected the recoiling nuclei from the target, was irradiated in the second chamber. After the irradiation, the glass filter, the Cu target, and the Kapton catchers were subjected to γ-ray spectrometry with a Ge detector.

The radioactivities of the 52 nuclides of 18 elements produced from $^{64}$Cu were identified in the glass filter. This number of nuclides is quite large as compared with the 11 nuclides of 10 elements produced from $^{68}$Cu by the falling ball system [3]. The radionuclides with short half-lives ($T_{½} \propto ~1$ min) such as $^{25}$Na (59.1 s), $^{32}$P (47.3 s), $^{32}$Cl (1.35 min), and $^{58}$Mn (65.3 s) were found to be applicable for tracer experiments. On the other hand, the 28 radionuclides varying from $^{61}$Cu to $^{25}$Na were identified in both the Cu target and the Kapton catchers. For these nuclides, the recoil efficiency $e_r$ and the gas-jet efficiency $e_g$ were calculated according to the equations $e_r = 100N_{\text{Kapton}}/(N_{\text{Kapton}} + N_{\text{Cu target}})$ and $e_g = 100N_{\text{Glass filter}}/30N_{\text{Kapton}}$, $N$ being the number of atoms, respectively. The $e_r$ and $e_g$ values are shown in Fig. 2 as a function of the mass difference ($\Delta M$) between a product and a target ($A = 65$), and are represented by open and closed circles, respectively. The $e_r$ values increase smoothly with an increase of $\Delta M$, reflecting both the increasing kinetic energy and the decreasing stopping power of Cu for the product nuclei. The $e_g$ values are about 30% for the product nuclei with $\Delta M = ~5$ and decrease to about 10% with an increase of $\Delta M$. It is interesting to note that the $e_g$ values of chlorine isotopes of $^{35}$Cl, $^{37}$Cl, and $^{38}$Cl appear to be smaller than the systematic trend from other products. The hot chlorine atom may interact with Cl atoms of the aerosol and form a gaseous C$_2$, which cannot be collected on the glass filter.

In separate experiments, the long-lived multitracers were produced from 200-μm-thick $^{109}$Ag and 300-μm-thick $^{197}$Au targets using the 135 MeV/nuc. $^{14}$N beam with the maximum intensity of 0.6 pA, which was more than six times the limit of the falling ball system. Thus,
the production efficiency of the multitracer was markedly enhanced. The entire target chamber was surrounded with 150-mm-thick iron and 300-mm-thick concrete blocks in order to shield the neutrons and γ-rays from the targets and the beam dump. The radiation dose in the E3 room during the multitracer production was decreased to about one fourth of that of the previous system.

![Graph](image)

Fig. 2. Variation of the recoil efficiency $e_r$ and the gas-jet efficiency $e_g$ as a function of the mass difference $\Delta A$.

References


\[ {}^{99m} \text{Tc} \] PRODUCTION ON THE

BASIS OF CENTRAL GENERATOR AND WASTELESS

REACTOR Zr-Mo GEL-TECHNOLOGY

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Currently, the principal methods of \[ {}^{99m} \text{Mo} \] production are reactor technologies based on neutron irradiation of targets from \[ {}^{235} \text{U} \] and \[ {}^{99m} \text{Mo} \]. Technology based on uranium irradiation results in production of \[ {}^{99m} \text{Mo} \] among other fission fragments of uranium. The most complicated problem arising in production of molybdenum by fission is the necessity of utilization of large amount of radioactive waste. At the end of irradiation the total activity of isotopes from uranium fission is higher than \[ {}^{99m} \text{Mo} \] activity by two orders of magnitude. The 24-hours stand-by of the one irradiated uranium targets results in decreasing of total activity of radioactive waste approximately by the order, while the activity of \[ {}^{99m} \text{Mo} \] decreases by 22%, only. The optimum stand-by period is equal to two days. However, in this case waste activity is still in six-seven times higher than the activity of \[ {}^{99m} \text{Mo} \]. According to the current needs in production of \[ {}^{99m} \text{Mo} \], the amount of radioactive waste from radiochemical processing of uranium targets can reach several tens millions GBq per year. The problem of management of long-lived radioactive wastes constrains the production of the radioisotope \[ {}^{99m} \text{Mo} \] by the uranium fission method. For developing countries, to which Belarus belongs too, such method of \[ {}^{99m} \text{Tc} \] production is inapplicable because of complexity, high costs and problems of utilization of high activity wastes.

Recently, a simpler and less expensive method of \[ {}^{99m} \text{Tc} \] production based on the irradiation of the target from stable \[ {}^{99m} \text{Mo} \] has been developed. Institute of Power Engineering Problems (National Academy of Sciences of Belarus) in cooperation with Research Institute of Oncology and Medical Radiology (Ministry of Health of Belarus) has finished the development of the original wasteless reactor Zr-Mo gel-technology for production of the \[ {}^{99m} \text{Tc} \] radiopharmaceutical preparation (RPhP) from irradiated \[ \text{MoO}_3 \] target in the central generator of \[ {}^{99m} \text{Tc} \] with \[ {}^{99m} \text{Mo} \] activity ranging from 100 to 400 GBq [1,2]. The central generator is designed for production of \[ {}^{99m} \text{Tc} \] solution with activity of 37 up to 100 GBq per day, ensuring use of the generator during 10-20 days. After the generator has been used up, the wastes are located in temporary storage facility where they are kept for approximately 30 days and then are disposed as usual chemical wastes. The specific activity of liquid radioactive waste (water after washing of gel and dissolution of generator matrix) is 25 kBq ml\(^{-1}\) for \[ {}^{99m} \text{Mo} \] and 1.1 kBq ml\(^{-1}\) for \[ {}^{99m} \text{Tc} \] [1, 2]. Total activity of wastes is 94 MBq at production volume 300 ml day\(^{-1}\) during 12 days.

Technological process of \[ {}^{99m} \text{Tc} \] sodium pertechnetate production is used in remote conditions and could be almost completely automated. The experimental (pilot) facility with the central generator had been designed. The pilot facility was constructed and mounted in the typical hot cell. Using this facility the working regimes of technological process were tested and verified.

With the use of the technology described above the pre-clinical and clinical tests of produced pertechnetate solution had been conducted in Research Institute of Oncology and Medical
Radiology and in a number of hospitals. The tests had shown, that on reproducibility of results, high stability of label, absence of side effects of pharmpreparations labeled by $^{99m}\text{Tc}$-pertechnetate produced using given technology, this pertechnetate is not different from currently used one and can be applied in diagnostic practices. The clinical tests were conducted on more than two thousand patients and have shown very good results. During the tests approximately 850 GBq of the given preparation was delivered to clinics. As a results of clinical tests the Ministry of Health of Belarus has allowed the clinical application of RPhP $^{99m}\text{Tc}$, produced by the given technology.

The appropriate patents of the Republic of Belarus [3,4] and Russian Federation [5,6] protect the central generator and technology of $^{99m}\text{Tc}$ production.

Within the framework of the given technology it is suggested to create a completely automated typical facility with the high-production central generators of $^{99m}\text{Tc}$ and to place such facilities in various clinics. This would allow to supply with $^{99m}\text{Tc}$ sodium pertechnetate the radioisotope laboratories in a radius of 100 km daily upon their requests. Such practice will allow clinics and hospitals to refuse from small single-use generators, to reduce considerably exposure doses to personnel, and to have the wasteless production of $^{99m}\text{Tc}$.

The distinctive advantages of the technology developed are:

- using of native molybdenum as start target (MoO$_3$);
- absence of deleterious and toxic impurities in the final product (nitrates, organics, etc.);
- the application of modified method of $^{99m}\text{Tc}$ extraction from $^{99}\text{Mo}$ with the help of Zr-Mo-gel that allows to shorten the number of process stages and simplify the technology. It is very important at its remote realization;
- the unit is readily automatized and remote-controlled;
- simplicity of design and compactness offers wide application of the unit.

The centralized generator design and the main technological steps are presented in Fig. 1 and Fig. 2.

![Fig. 1. Central generator of $^{99m}\text{Tc}$](image-url)
The facility for producing $^{99m}$Tc can be placed inside the shadow shielding in an ordinary room meeting the radiation protection and sanitary regulations. It is suggested to load such central generators with the special loading container with $^{99}$Mo activity 3-6 Ci. Such containers could be charged in a hot cell just after irradiation in the reactor. The loading container will be transported then in a location, where the central generator is placed, and irradiated MoO$_2$ will be loaded to the generator. Other equipment of the $^{99m}$Tc production site includes the generator column, a device for distribution of produced preparation, vacuum pump, technological capacities, operator's working place, and physical shielding.

TECHNETIUM GENERATOR WITH HYDROTALCITE AS 
SUPPORT OF $^{99m}$Mo

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Introduction

$^{99m}$Mo disintegrates through $\beta^-$ particle emission yielding $^{99m}$Tc. When $^{99m}$Mo is adsorbed on alumina packed in a column, the $^{99m}$Tc can be separated from the column by elution with a 0.9 % NaCl aqueous solution. This description corresponds to well known devices called technetium generators [1-3], which are widely used in nuclear medicine as a diagnosis tool. Looking for other materials to bear the $^{99m}$Mo, Serrano et al [4] recently investigated the use of hydrotalcite (HT) as $^{99}$Mo support to develop a new technetium generator.

Hydrotalcite (HT) is a mineral with a laminar structure whose chemical composition is given by the formula $\text{Mg}_6\text{Al}_2(\text{OH})_16\text{CO}_3\cdot 4\text{H}_2\text{O}$ (HT), where $\text{M}^{2+}$ and $\text{Al}^{3+}$ ions are randomly distributed in octahedral layers stacked on top of each other forming layered double hydroxides. HT bears a positive electrical charge which in nature is neutralized by carbonate ions located in the interlayer space together with water molecules. Hydrotalcite-like compounds are anionic clays whose chemical formula is $[\text{M}_{x\text{+}}^{2+}\text{M}_y^{3+}(\text{OH})_z]^+\text{[A}^{\text{2x+}}\text{]}m\text{H}_2\text{O}$, where $x$ is the molar ratio $\text{M}^{2+}/(\text{M}^{2+} + \text{M}^{3+})$. Usually $\text{M}^{2+}$ is $\text{Al}^{3+}$, $\text{Cr}^{3+}$, $\text{Fe}^{3+}$ or $\text{Co}^{2+}$ and $\text{M}^{3+}$ may be $\text{Mg}^{2+}$, $\text{Co}^{2+}$, $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, or $\text{Ni}^{2+}$. When HT-like compounds are calcined to 500 °C, they undergo dehydroxylation and decarbonation, the layer structure being destroyed. The calcined product, known as calcined hydrotalcite (CHT), is mainly $\text{MgO}$ with $\text{Al}$ dispersed in the oxide. CHT in the presence of water containing anions rehydrates and the laminar structure is recovered. If the anions in the solution are $^{99}$MoO$_4$$^-$$^-$ anions, they occupy the interlamellar space of the new hydrotalcite (HT-$^{99}$MoO$_4$), partially displacing the CO$_3$$^2$$-$ ions. From HT-$^{99}$MoO$_4$ packed columns, the generated $^{99m}$Tc can be separated by elution with 0.5 % NaCl as found by Serrano et al [4]. Since through batch experiments it was also found that HTC has a high retention capacity to molybdate ions (255.1 mg/ g), low specific activity $^{99m}$Mo can be used in this new technetium generator instead of high specific activity $^{99}$Mo utilized in an alumina technetium generator. In this work the sorption behavior of $^{99}$MoO$_4$$^-$$^-$ ions in hydrotalcite prepared with different molar ratios $\text{Al}^{3+}/(\text{Al}^{3+} + \text{Mg}^{2+})$ as well as the separation of $^{99m}$Tc from $^{99}$MoO$_4$$^-$$^-$ sorbed in hydrotalcite by means of dynamic experiments were studied.

Experimental

HT with $x = 0.25$ was synthesized in the laboratory according to the method of Sato et al [5]. Other hydrotalcites with $x = 0.30, 0.50$ and 0.70 were obtained from Sasol Germany, GmbH as PLURAL R MG 70, 50 and 30. All hydrotalcites were calcined to 500 °C in air for 24 hours. Low specific activity $^{99}$Mo (solution A) was prepared by mixing non-radioactive Na$_2$MoO$_4$ (250 mg dissolved in 250 ml of distilled water) and a few μCl of high specific activity $^{99}$Mo. Calcined
hydrotalcites were shaken with solution A for 70 h to determine the retention capacity of CHT’s. For column experiments, glass columns (10 cm height and 1.0 cm inside diameter) packed with 1.8 g of HTC were used. From the HT-239MoO4 packed column, 99mTc was eluted with 0.5 % NaCl aqueous. 99Mo and 99mTc radioactivities were determined by gamma spectroscopy, utilizing the 740 and 141 keV photopeaks, respectively. Hydrotalcites were characterized by x-ray diffraction and IR spectroscopy.

Results and discussion

Fig. 1 shows the time dependence of molybdate sorption by CHT (obtained by calcining HT with x = 0.30). As shown in the Figure, molybdate ion concentration decreased continuously with contact time of the solid phase with the 1.12x 10⁻⁵ M molybdate solution because of the sorption of molybdate ions by CHT during rehydration of HT-MoO4 which contains residual carbonate ions and water molecules, as revealed by IR spectroscopy. As can be seen, the equilibrium molybdate sorption is reached in about 20 h. The molybdate sorption capacity of CHT was calculated in this equilibrium zone.

Table 1 shows the molybdate equilibrium sorption capacity (meq/g) of calcined hydrotalcites, determined by batch experiments, as a function of Na2MoO4 molarity.

Table 1. Molybdate equilibrium sorption capacity of calcined hydrotalcites (meq/g). HT column shows the original content of Al³⁺ of hydrotalcites before calcination.

<table>
<thead>
<tr>
<th>HT Al³⁺/(Al³⁺+Mg²⁺) (x value)</th>
<th>Na₂MoO₄ molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>0.25</td>
<td>Meq/g</td>
</tr>
<tr>
<td>0.30</td>
<td>3.35</td>
</tr>
<tr>
<td>0.50</td>
<td>3.60</td>
</tr>
<tr>
<td>0.70</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>1.31</td>
</tr>
</tbody>
</table>

As expected, in equilibrium the amount of molybdate ions sorbed per gram of the various hydrotalcites increases as the molarity of the Na₂MoO₄ aqueous solution increases. On the other hand, when the content of Al in the hydrotalcites increases from 25 % to 70 %, one would expect an increase in the equilibrium sorption capacity, since the presence of Al³⁺ in hydrotalcites produces an excess of positive electric charges which have to be compensated for by molybdate anions. However, our results show that sorption capacities of CTH’s obtained by calcination of HT’s with x = 0.50 and 0.70 are lower than those of CTH’s obtained from HT’s with 0.25 and 0.30 (Table 1). According to Cavani et al [6] pure hydrotalcite can be obtained only when 0.17 ≤ x ≤ 0.33, thus, hydrotalcites with x = 0.5 and 0.7 can not be pure samples. In fact, their respective XRD patterns show the presence of a non-identified species mixed with hydrotalcites. CHT obtained by calcining HT with x = 0.30 showed the highest molybdate sorption capacity, the following experiments being carried out with this hydrotalcite.
Column experiments.

After calcining HT with $x = 0.30$, by means of dynamic experiments $^{99}$Mo (as $^{99}$MoO$_4^-$) was charged into a CHT packed column. Radioactive molybdate anions were sorbed by CHT and retained in the column. 24 hours later, the $^{99m}$Tc formed by $^{99}$Mo $\beta^-$ decay was eluted by using a 0.5 % NaCl solution. Figure 2 shows the corresponding elution profile. As seen, most of the $^{99m}$Tc is eluted with 30 mL of saline solution while $^{99}$Mo remains fixed in the hydrotalcite. One can conclude that because of their higher molybdate retention capacity, hydrotalcites with $x = 0.30$ and 0.25 are the adequate solids to obtain a new technetium generator. More concentrated saline solutions will subsequently be tested to get an optimal $^{99m}$Tc elution.

Fig. 1. Variation of MoO$_4^{2-}$ concentration vs time of contact between CHT and $^{99}$MoO$_4^{2-}$ solution.

Fig. 2. Percent of $^{99m}$Tc eluted with 0.5 % NaCl from HT-$^{99}$MoO$_4$ column.

References


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ESTIMATE OF IMPURITY PURIFICATION COEFFICIENTS FOR IRRADIATED SILVER TARGET PROCESSING AND PALLADIUM-103 EXTRACTION

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The development of the radiochemical method for extraction and purification of radioisotopes, including those for medical use, requires selecting a variant of radiochemical processing of irradiated target and purification of the aimed product. A selected method should satisfy some requirements, including:
- simple remote realization;
- the least number of consequent technological procedures;
- the efficiency of purification from macro- and micro-impurities and complete extraction of the finishing product.

This paper describes an important criterion for selecting the best method of the aimed product purification from impurity i, namely, a purification coefficient $K_{p,i}$. A procedure of $K_{p,i}$ estimation is illustrated by the example of palladium-103 extraction from irradiated silver targets.

Here we use the following designations: $E_{\gamma,i}$ – the energy of analytical $\gamma$-lines of isotope i; $\eta_{i}$ – the yield of the $E_{\gamma,i}$ energy $\gamma$-line; $\varepsilon_{i}$ – the effectiveness of registration of the $\gamma$-ray of energy $E_{\gamma,i}$; $A_{i} / A_{103\, Pd}$ – the radioactivity concentration of isotope i and $A_{i} / A_{103\, Pd}$ – the activities of isotope i and of the finishing palladium-103 sample; t – the decay time (or “cooling” time) of the irradiated target; $A_{\text{min,i}}$ – the minimum detected activity of isotope i; $L_{i}$ (pulse) – the registration limit (or detection limit) in the region of the analytical $\gamma$-line of isotope i, [1,2]; $L_{d,i}$ – the relative detection limit in the region of the analytical $\gamma$-line of isotope i;

$$L_{d,i} = \frac{L_{i} \cdot \varepsilon_{103\, Pd} \cdot \eta_{103\, Pd}}{A_{103\, Pd} \cdot \varepsilon_{i} \cdot \eta_{i}} = \frac{A_{\text{min,i}}}{A_{103\, Pd}}.$$ 

The requirements for the finishing product are as follows:
- the radioactivity concentration of palladium-100 impurity does not exceed 0.05%;
- the radioactivity concentration of the rhodium impurities does not exceed 0.01%;
- the radioactivity concentration of the impurities of other isotopes does not exceed 0.01%. So the radioisotopic purity of palladium-103 should not be lower than 99.93%.

The process of extraction and purification of palladium-103 consists of the following stages: “cooling” of the irradiated silver target during time t for decay of palladium-100 radioactivity concentration to 0.05%; dissolving of the silver target; purification from macro-impurities of the silver isotopes (silver-105 and silver-106m); purification from micro-impurities of rhodium-99, rhodium-101 and others.
One can evaluate the “cooling” time \( t \) of silver target in order that \( \left( A_{100\text{Pd}} / A_{103\text{Pd}} \right)_t = 0.05\% . \) This time is 35.5 days if \( \left( A_{100\text{Pd}} / A_{103\text{Pd}} \right)_{t=0} = 0.106 \).

The coefficient \( K_{ij} \) of purification from impurity \( i \) depends on the initial radioactivity concentration of impurity \( i \) in the irradiated target, complete palladium-103 extraction, the efficiency of purification from all impurities. It is evident that the upper limit of \( K_{ij} \) can be estimated if \( \left( A_i / A_{103\text{Pd}} \right)_t \) is divided by \( L_{\text{ir}} \) or by \( \left( A_{\text{min,j}} / A_{103\text{Pd}} \right)_t \) (which is the same), and the average apparatus background under \( E_{\text{Pd}} \) is used in the calculations \( \left( A_i / A_{103\text{Pd}} \right)_t \) since the contribution of palladium-103 \( \gamma \)-radiation in these regions is very small.

The Table summarizes the analytical \( \gamma \)-lines of basic isotopes, \( \left( A_i / A_{103\text{Pd}} \right)_{t=0} \) and the calculated values of \( L_{\text{ir}} \), \( A_{\text{min,j}} \), \( \left( A_i / A_{103\text{Pd}} \right)_t \) and \( K_{ij} \). (Measurement time of the apparatus background is 1 hour).

The highest estimates of \( K_{ij} \) for silver-105, rhodium-99 and rhodium-101 are \( \sim 7500 \), \( \sim 990 \) and 890 correspondingly.

### Table: Estimation of \( K_{ij} \) for radioisotopic impurities

<table>
<thead>
<tr>
<th>Radioisotope ( i )</th>
<th>( E_{\gamma} ), ( Bk )</th>
<th>( \left( A_i / A_{103\text{Pd}} \right)_t=0 )</th>
<th>( L_{\text{ir}} )</th>
<th>( A_{\text{min,j}} )</th>
<th>( \left( A_i / A_{103\text{Pd}} \right)_t )</th>
<th>( K_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{100}\text{Pd} )</td>
<td>74.8, 84.0</td>
<td>0.106</td>
<td>–</td>
<td>–</td>
<td>5.1 \times 10^{-4}</td>
<td>1</td>
</tr>
<tr>
<td>( ^{99}\text{Rh} )</td>
<td>89.4</td>
<td>6.8 \times 10^{-2}</td>
<td>6.3 \times 10^{-5}</td>
<td>4.2</td>
<td>6.2 \times 10^{-2}</td>
<td>990</td>
</tr>
<tr>
<td>( ^{101}\text{Rh} )</td>
<td>198</td>
<td>7.0 \times 10^{-3}</td>
<td>2.8 \times 10^{-5}</td>
<td>2.4</td>
<td>2.5 \times 10^{-2}</td>
<td>890</td>
</tr>
<tr>
<td>( ^{99}\text{Rh} + ^{101}\text{Rh} )</td>
<td>19.23</td>
<td>–</td>
<td>2.0 \times 10^{-5}</td>
<td>1.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( ^{101\text{m}}\text{Rh} )</td>
<td>306.8</td>
<td>0.12</td>
<td>4.71 \times 10^{-5}</td>
<td>3.2</td>
<td>1.8 \times 10^{-3}</td>
<td>60</td>
</tr>
<tr>
<td>( ^{105}\text{Ag} )</td>
<td>280.4</td>
<td>1.7 \times 10^{-2}</td>
<td>1.1 \times 10^{-4}</td>
<td>7</td>
<td>0.82</td>
<td>7500</td>
</tr>
<tr>
<td>( ^{96}\text{Ru} )</td>
<td>215.7</td>
<td>9.1 \times 10^{-2}</td>
<td>3.6 \times 10^{-5}</td>
<td>2.4</td>
<td>7.7 \times 10^{-5}</td>
<td>2.1</td>
</tr>
<tr>
<td>( ^{96}\text{Tc} )</td>
<td>778</td>
<td>0.13</td>
<td>9.5 \times 10^{-5}</td>
<td>6.3</td>
<td>1.8 \times 10^{-3}</td>
<td>1.9</td>
</tr>
</tbody>
</table>

According to the Table, the lowest \( A_{\text{min,j}} \) and \( L_{\text{ir}} \) are obtained by measuring the rhodium signal sum in the region of the X-ray radiation. However, it is better if the estimation uses gamma-lines with larger energy because a weak sum peak of the X-rays of rhodium isotopes (\( E_\gamma = 19.3 \text{ Kev} \)) is deformed by neighboring larger palladium-103 peak (\( E_\gamma = 20.2 \text{ Kev} \)).

The control of radioisotopic purity requires the use rhodium-99 and rhodium-101 radioisotopes. It is convenient to use rhodium-99 since \( \left( A_{99\text{Rh}} / A_{103\text{Pd}} \right)_{t=0} \) remains practically
unchanged when the activity of both isotopes change and, therefore, there is no need to introduce decay corrections.

The estimations of $K_{\phi\lambda}$ are approximate, since they depend on not only $(A_i / A_{i+3,\phi})_{t=0}$, but on the "cooling" time $t$ and on the process and measurement conditions. However, the order of the values and the method of calculations are the same.

References
PREPARATION AND QUALITY CONTROL OF CLINIC SCALE

\( ^{188}\text{W}-^{188}\text{Re} \) GENERATOR

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\(^{188}\text{Re} \) is an excellent candidate for the radionuclide therapy, since it is easily obtained as a "no-carrier-added" radioisotope from a \(^{188}\text{W}-^{188}\text{Re} \) generator. The half-life of 16.9 hours is suitable for tumor treatment and of benefit to minimize toxicity to whole body; Beta emissions with energies of 2.12 MeV (71.6%) and 1.97 MeV (25.1%) are suitable for therapy and the gamma emission of 155 keV (15%) allows imaging and dosimetry. The drug for tumor therapy has been a highlight of the new drug development in recent years. The radionuclide therapy has shown significant effectiveness in the treatment of various cancers. \(^{188}\text{W}-^{188}\text{Re} \) generator could conveniently provide high levels of carrier-free rhenium-188 at low cost for the treatment of a variety of cancers, cardiovascular diseases as well as the marrow transplantation\(^[1-3]\).

Experiments and results

Preparation of \(^{188}\text{W}-^{188}\text{Re} \) generator The 40.7 MBq \(^{188}\text{W}-^{188}\text{Re} \) generator was successfully prepared using home made Aluminum as absorbent and the \(^{188}\text{W}-\text{NaWO}_4 \) solution imported from ORNL, USA\(^[4,5]\). The pH value of \(^{188}\text{W}-\text{NaWO}_4 \) solution was adjusted to about 2 with the 2mol/L HCl solution and \(^{188}\text{W} \) was loaded on the generator at flow rate of 1mL/min. \(^{188}\text{Re} \) was eluted with 0.9% NaCl solution. The characteristics of the clinic-scale \(^{188}\text{W}-^{188}\text{Re} \) generators was shown in Table 1. The elution efficiency of \(^{188}\text{Re} \) was about 90% (10ml saline), breakthrough of \(^{188}\text{W} \) less than \(1 \times 10^{-6} \) nuclide purity over 99.9%, radiochemical purity over 95%, content of aluminum about 1mg/L, pyrogen free and sterile as well. The long term stability of elution yield for generator is shown in Fig.1; the elution efficiency of \(^{188}\text{Re} \) was always retained at 75% to 85% in about 11 months and during this time the breakthrough of \(^{188}\text{W} \) was less than \(3 \times 10^{-6} \) and the content of Al less than 1 mg/L.

Quality control of the \(^{188}\text{W}-^{188}\text{Re} \) generator The quality specifications of the chromatographic \(^{188}\text{W}-^{188}\text{Re} \) generator were thoroughly studied including the absorbent quality of alumina, breakthrough of \(^{188}\text{W} \), yield of \(^{188}\text{Re} \), stability of the generator and the radionuclide purity, radiochemical purity, pH value, specific
radioactivity concentration, content of aluminum, sterility and apyrogenicity of the eluate. According to the regulation of safe transportation of radioactive materials (GB 8703-88) the demands of protection and package for the generator were examined, the regulation of transportation, storage and operation of the generator was made, and the methods of quality assurance and quality control were also defined. In order to make the preparation of the $^{188}$W-$^{188}$Re generator more regular, to supply high quality $^{188}$Re to clinical medicine and scientific research, and to promote the industrialization of scientific results, we started preparing the industrial standard of the $^{188}$W-$^{188}$Re generator. The draft of the standard was finished and distributed for comments.

**Conclusion**

A clinical-scale $^{188}$W-$^{188}$Re generator loaded with more than one curie of $^{188}$W was successfully prepared. The yield of $^{188}$Re from generator eluted with 10mL isotonic saline was greater than 90%. Radionuclide purity was greater than 99.9% and radiochemical purity greater than 95% of the $^{188}$Re as perrhenate ion. Concentration of aluminum in eluate was about 1 mg/L. The generator provides a convenient supply of sterile $^{188}$Re as sodium perrhenate in injectable saline solution, ready for use in the preparation of $^{188}$Re labeled therapeutic reagents.

**References**


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![Graph](image.png)

**Fig 1** The long term stability of elution yield for generator
PRODUCTION OF NO-CARRIER ADDED $^{31}$Si FOR SILICON- UPTAKE
STUDIES IN YEAST CELLS

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Introduction

Silicon (Si) is the second most abundant element (25.7 % w/w) in the earth’s crust, being exceeded only by oxygen (49.2 %)[1]. The three stable isotopes, $^{28}$Si, $^{29}$Si and $^{30}$Si, have natural abundances of 92.23, 4.67 and 3.10 %, respectively. Silicon is undoubtedly important in many living organisms and it may have played a significant role in the origin of life [2]. It is regarded to be beneficial or essential higher animals and humans, although only a few clear-cut functions of silicon have been unravelled so far [3,4].

A convenient way for measuring interfacial transport rates is by means of radioactive tracers that are chemically and physically identical to the compound/substance of interest. To do so, two radionuclides of silicon are suitable, namely $^{30}$Si ($t_{1/2} = 2.62$ h) and $^{32}$Si ($t_{1/2} = 160$ y). Both radionuclides emit $\beta^-$ radiation with maximum energies of 0.225 MeV (0.07%) and 1.49 MeV (99.9%) for $^{30}$Si and of 0.213 MeV (100%) for $^{32}$Si. In addition, $^{31}$Si emits 1.27 MeV $\gamma$-rays (0.07%). Instead of Si radioisotopes, those of Ge have been used to study the behaviour of Si [5,6], but this is probably not representative under all circumstances.

$^{32}$Si can be produced by either the $^{31}$Cl(p,2$\alpha$)$^{32}$Si reaction or the reaction sequence $^{31}$P(n,$\gamma$)$^{32}$P(n,p)$^{32}$Si using an accelerator or a high neutron flux reactor [7]. It has been used for example in studies of silicon in marine food webs and for human uptake kinetics [8,9]. However, the use of $^{31}$Si is advantageous in short-term experiments, because (a) it is easy to produce in high yields using a low neutron flux reactor, (b) it doesn’t decay to $^{32}$P which can interfere with radioactivity measurements and (c) it results in much less radioactive waste. In addition, double tracer experiments using both $^{31}$Si and $^{32}$Si would become possible.

$^{31}$Si can be produced by thermal neutron irradiation of silicon by the $^{28}$Si(n,$\gamma$)$^{29}$Si nuclear reaction with a cross section ($\sigma$) of 0.108 barn. It can also be produced by fast neutron irradiation of phosphorus by the $^{31}$P(n,p)$^{32}$Si nuclear reaction having a threshold energy of 0.731 MeV and a $\sigma$ for fast neutrons of 0.0312 barn. As there is no information available on the concentration of silicon impurities in phosphorus targets the final specific activity of $^{31}$Si in the no-carrier-added product is not yet known. However, one may assume that it will exceed that of (n,$\gamma$) product.

Production of $^{31}$Si from phosphorus using the (n,p) route is accompanied by the simultaneous production of $^{22}$P ($t_{1/2} = 14.26$ d) due to the presence of thermal neutrons. The involved nuclear reaction $^{31}$P(n,$\gamma$)$^{32}$P has a $\sigma$ of 0.16 barn. Note that $^{32}$P emits $\beta^-$ radiation with maximum energy of 1.710 MeV.

Our present study aims at producing $^{32}$P-free $^{31}$Si in high specific activities via the $^{31}$P(n,p)$^{31}$Si reaction and its subsequent use in uptake studies of silicon in baker’s yeast, a model organism for eukaryotic cells [10].
Materials and Methods
The target material, 100 mg orthophosphoric acid (H₃PO₄) was solid packed in small sealed polyethylene tubes. These tubes were placed in polyethylene “rabbits” and pneumatically transported to a position close to the core of the 2MW swimming pool research reactor of the IRI in Delft. The targets were irradiated with thermal and fast neutrons for 5.0 h. The neutron fluxes at the target position were about $3.0 \times 10^{12}$ cm$^{-2}$ s$^{-1}$ for thermal and $3.7 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ for fast neutrons.

The irradiated H₃PO₄ was dissolved in 1.5 ml deionized water and transferred to a plastic centrifuge tube. About 3.3 mmol solid silver acetate was added to the radioactive solution causing a yellow precipitate, probably silver orthophosphate (Ag₃PO₄, $K_s = 8.9 \times 10^{17}$). The suspension was centrifuged, the supernatant removed and 0.5 mmol NaCl (solid) was admixed to precipitate the remaining silver ions as AgCl ($K_s = 1.8 \times 10^{-10}$). A final centrifugation led to a supernatant free of precipitate particles and silver ions.

$^{31}$Si and $^{32}$P were measured using a LKB liquid scintillation counter ($\beta^+$) with a detection efficiency of 98%. Moreover, $^{31}$Si was determined in a well-type Ge-detector ($\gamma$). All samples were counted repeatedly in time in order to calculate the original $^{31}$Si and $^{32}$P ratio at the end of the target bombardment. Moreover, half-lives were checked to ascertain for the absence of contaminations.

Results and Discussion
The $^{31}$P(n, p)$^{31}$Si and $^{31}$P(n, $\gamma$)$^{32}$P reactions resulted in the production of $^{31}$Si and $^{32}$P as determined using both a liquid scintillation counter ($^{31}$Si and $^{32}$P) and a well-type Ge-detector ($^{31}$Si). An amount of 3.6 MBq$^{31}$Si per mmol P was produced, accompanied by 3.5 MBq $^{32}$P. The amounts were approximately 70% of the expected values which is probably due to discrepancies between estimated and real neutron fluxes and spectra, and the accuracy of the cross sections.

Removal of $^{32}$P(PO$_4^{3-}$) was successful by precipitation with silver acetate, although 0.3 % remained in the solution, calculated as percentage of $^{32}$P at the end of bombardment. Sequential precipitation with fresh AgNO₃ did not lead to higher recoveries of $^{32}$P. No straightforward explanation can be given as yet for the remaining $^{32}$P in the solution, but it probably concerns a chemical form alternation of phosphorus during the irradiation. No $^{31}$Si co-precipitation with $^{32}$P was observed.

Correction of the $^{31}$Si signal for $^{32}$P background was performed by subtracting the fitted $^{32}$P count rate at time 0 from the fitted $^{31}$Si count rate as shown in Fig. 1. The half-lives of $^{31}$Si and $^{32}$P were calculated from these fits. The values, 2.62 and 14.23 days, respectively, agreed well with the literature. This indicates the absence of major radionuclide contaminations.

The small contamination of $^{31}$Si with $^{32}$P appeared to be no problem in yeast uptake experiments. Currently, more yeast experiments and liquid-liquid extractions are in progress. The latter is performed to get more information about the chemical form of $^{31}$Si as it might be not only silicate ($^{31}$SiO$_4$).
The $^{31}$Si/$^{32}$P ratio's can be modified by using neutrons with different characteristics or when the beam used is modified. The $^{31}$P$(n,\gamma)^{32}$P reaction is due to the thermal neutron flux, in contrast to the fast neutrons for the $^{31}$P$(n,p)^{30}$Si reaction. This means that shielding material with a high thermal neutron capture cross-section (e.g. cadmium or boron) during the irradiations would increase this $^{31}$Si/$^{32}$P ratio. However, this is only required when $^{32}$P interferes with the experiments.

References
$^{89}\text{Sr}$ SEPARATION FROM IRRADIATED YTTRIUM USING VINYLPIRIDINE CHELATING RESIN VPC

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$^{89}\text{Sr}$ preparations are used in nuclear medicine for some oncological disease palliative treatment. The commercial scale production process based on the $^{90}\text{Y} (n,p)\ ^{89}\text{Sr}$ reaction, occurring in fast neutron fluxes has been realized at RIAR. Use of above mentioned nuclear reaction allows producing $^{89}\text{Sr}$ preparations with radionuclide specific activity higher than 1000 Ci/g.

Because of extremely low content of the final nuclide in the irradiated material ($\text{Sr}$ to $\text{Y}$ mass ratio does not exceed 0.001 %) the most difficult radiochemical procedure is the separation of strontium from the bulk of yttrium. Novel procedures based on $^{89}\text{Sr}$ ion-exchange sorption both from filtrates after yttrium oxalate precipitation [1], and from yttrium concentrated solutions [2] have been developed at RIAR. Some characteristics of VPC chelating resin used for $^{89}\text{Sr}$ isolation are listed below.

Method of synthesis: oxidation of copolymerisation product of 2,5-methylvinylpyridyne and divinyl benzene

Type of matrix: macroporous

Functional groups:

If the bulk of yttrium is separated by precipitation of its oxalate, the mother solution containing $^{89}\text{Sr}$ should be stabilized by adding sodium citrate before strontium sorption on VPC. Sorption of $^{89}\text{Sr}$ from mixed oxalate- citrate solutions is sufficiently complete even in presence of significant amounts of yttrium (Fig. 1).

In presence of reagents forming stable, readily soluble complexes with yttrium, selective sorption of strontium is possible even from concentrated yttrium solutions. $^{89}\text{Sr}$ distribution between VPC and concentrated solutions of yttrium complex compounds with carbonic, citric and ethylenediaminetraacetic (EDTA) acid anions has been studied in detail. Fig.2 shows strontium distribution coefficient depending both on pH and sodium citrate to yttrium molar ratio.

Experimental results of static sorption as well as column separation of strontium and yttrium using VPC are reported.

References
Fig. 1. $^{89}$Sr distribution coefficients in yttrium mixed oxalate - citrate solutions.

Fig. 2. $^{89}$Sr distribution coefficients in yttrium citrate solutions ([Y] = 10 g/l).
EXTRACTION AND HIGH PURIFICATION OF ACTINIUM-225 ISOTOPE FOR MEDICAL APPLICATION


State Scientific Center of the Russian Federation – Institute for Physics and Power Engineering (SSC RF IPPE), 249033, Obninsk, Russian Federation

Radionuclide therapy applying short-lived alpha-emitters seems to be the most promising for curing such malignant diseases as acute and chronic leukemia, melanoma, etc. The Actinium-225 isotope is one of the most available alpha-emitters now, which can be extracted from fission products of Uranium-233.

The presentation contains research results of extraction of the Thorium-229 isotope from nitric acid solution of uranium. The irradiation of Radium-225 in a high-flux reactor or Thorium-230 in reactors or accelerators is an alternative method of Actinium-225 production. A Thorium-229 accumulation in case of uranium decay for 10 years and 50 years (that is 42.9mg/kgU and 214.5mg/kgU, correspondingly) was calculated and evaluated experimentally.

A method of joint extraction of uranium and thorium from the nitric acid solution in a multi-phase extraction device with application of washing of the extractant with weak-acid media was investigated. This washing provides for transfer of thorium and the other fission products of Uranium-233 into the raffinate solution. The produced Thorium-229 is aged for accumulation of Actinium-225 after the purification from the uranium fission products and traces.

Uranium and Thorium separation using solid extractants was investigated. Solid extractants on the basis of multiradical phosphine oxide and tributylphosphate were used. The results of this separation from nitric acid solutions were positive, too.

In the "precursor" generator the raffinate solutions of all the listed processes went to anion-exchange column with Dowex1×4-100 resin, in which thorium was almost completely extracted with 8-10M HNO₃, and the fission products remained in the raffinate and the washing solution. The stripped thorium in the form of nitric acid solution was a mother solution of the "precursor" generator and was held in this form for a certain period till subsequent extraction of Actinium-225.

In the developed Thorium-229/Actinium-225 generator system actinium is extracted on Dowex50×4-100 cationite from the corrected 1M HNO₃ solution; then Radium-225 is extracted from the affinate and the washing solution, and the actinium sorbate is washed additionally with 1M HCl and stripped with 3.5-4M HCl.

A combination of anion and cation exchange, application of different acid concentrations enabled us to develop a design of a sorption generator intended for production of the Actinium-225 isotope and to prove it experimentally. The developed design makes it possible to produce Actinium-225, whose technical specifications meet the medical requirements.

Alpha- and gamma-spectra of the Actinium-225 product are given in the presentation. They prove a high radionuclide purity of the obtained product.
Alpha- and gamma-activities of samples of various solutions were measured during investigations of the isotope extraction procedures and the generator systems development. The measurements aimed at identification of radionuclides, determination of their purity and quantities. A semi-conducting alpha-spectrometer with the resolution of ~30 keV and an alpha-spectrometer with the resolution of 17 keV as well were applied for measuring the alpha-activities.

The alpha-spectrometric method of determination of radionuclide compositions and their activities is based on measurements of alpha-emission spectra of the radionuclides contained in the samples, identification of the radionuclides by alpha-emission peaks and activity calculations taking into account the spectrometer efficiency and a yield of alpha-particles per a radionuclide decay event.

A gamma-spectrometer with semi-conducting germanium-lithium detector was used for γ-emission measurements during the investigations performed. A detector made of pure germanium with thin beryllium window was used for interpreting gamma-spectra in the “soft” gamma-emission range (25-150 keV). The radionuclides identification and their activity calculations when analyzing process solutions were performed on the basis of the gamma-emission energies and their intensities.

Thus, one may state as a whole that the application of α- and γ-spectrometric measurements at all research phases makes it possible to control efficiently completeness and quality of the applied methods and radionuclide purity levels of the extracted radionuclides.

The results have been obtained when implementing the ISTC Project #962.
PRODUCTION AND SEPARATION OF $^{236}\text{Pu}$ AND $^{237}\text{Pu}$ FOR LABORATORY USE

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$^1$ Interdisciplinary Scientific and Technical Center “Shelter”, 07270, Chernobyl, Ukraine
$^2$ Institute for Nuclear Research, 03028, Kiev, Ukraine

Both $^{236}\text{Pu}$ and $^{237}\text{Pu}$ provide convenient yield tracers for determination of Pu in environmental samples. Previous reports have described the preparation of $^{236}\text{Pu}$ by irradiating U (95 % $^{235}\text{U}$) with $^4\text{He}$ ions and $^{237}\text{Pu}$ by the reaction $^{235}\text{U}(^4\text{He}, 2n) ^{237}\text{Pu}$ with U target 99.993 % enriched in $^{235}\text{U}$ [1, 2].

The experimental production of gamma ray emitting isotopically pure $^{237}\text{Pu}$ with alpha bombardment of $\text{U}_3\text{O}_8$ in the energy range up to 100 MeV is presented. Irradiation of $^{238}\text{U}_3\text{O}_8$ was done on cyclotron U-240 Institute for Nuclear Research NAS Ukraine (Kiev) and $^{237}\text{Pu}$ produced by reaction $^{238}\text{U}(\alpha, 5n) ^{237}\text{Pu}$. The $\text{U}_3\text{O}_8$ pellets were mounted on Al block (Fig.1) and cooled from the underside with running water during the irradiation. The target assembly was installed at the periphery of U-240 cyclotron and irradiated with an internal beam of 100 MeV alpha particles.

Tracer of $^{237}\text{Pu}$ containing impurity of $^{236}\text{Pu}$ (2.5 %) and $^{238}\text{Pu}$ (1.0 %) at the moment of the ending of irradiation is turned out and allocated without the carrier.

![Fig. 1: Target assembly for production of $^{237}\text{Pu}$ in U-240 cyclotron](image)

For routine determination of plutonium in the environmental samples, pure $^{236}\text{Pu}$ was obtained by the reaction $^{239}\text{Pu}(p, 3n) ^{236}\text{Np} \rightarrow ^{236}\text{Pu}$ by irradiation of $\text{U}_3\text{O}_8$ with protons at energy range up to 40 MeV. Content of $^{238}\text{Pu}$ was less than 1.5 % by activity. Alpha emissions corresponding to $^{239}\text{Pu}$ were found as less than 0.01 % in an alpha spectrum of $^{239}\text{Np}$ (Fig.2).
After cooling for 12 days, the target was processed to prepare sources of $^{236}\text{Pu}$ or $^{237}\text{Pu}$. No carrier added $^{236}\text{Pu}$ and $^{237}\text{Pu}$ were separated from $\text{U}_3\text{O}_8$ cyclotron-targets by a procedure based on co-precipitation with LaF$_3$ and ion exchange chromatography on the column with Dowex 50x8 resin. Passing of 0.16 M 2– hydroxy – iso - butyric acid pH 4.75 stripped Pu, it was checked out that 85 — 90 % of plutonium was stripped out with the first 1.0 ml of the solution.

Fig. 2: Alpha spectrum of $^{236}\text{Pu}$ produced by irradiation of $^{238}\text{U}$ with protons

$^{237}\text{Pu}$ has been applied for the analysis of chemical yield of plutonium during development of separation procedure of $^{238}\text{Pu}$ and $^{239+240}\text{Pu}$ from environmental samples. The technique of definition of plutonium in objects of an environment is developed (soils, sediments), allowing radiochemical concentration and allocation of plutonium on cation-exchange resin Dowex 50x8. Further developments in the production of $^{236}\text{Pu}$ and $^{237}\text{Pu}$ are under discussion.

References
PRODUCTION OF HIGHLY PURE EINSTEINIUM AND FERMIUM PREPARATIONS

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Highly pure einsteinium and fermium preparations are in increased demand due to the progress of the following fields of modern sciences:

- **Fundamental and applied nuclear physics.** Heavy actinides are necessary for detailed study of structure and decay of a nucleus, as well as initial material both for nuclear synthesis of new superheavy elements and for manufacturing radioactive radiation sources.

- **Fundamental and applied radiochemistry.** Einsteinium and fermium preparations are required to investigate chemical properties of these hard-to-obtain elements and to improve technology of their recovery and purification.

- **Nuclear medicine.** Biologically active compounds labeled with alpha-emitting einsteinium and fermium may be applied in prospect for a radioimmunotherapy of oncological diseases.

The principal method of einsteinium and fermium production is irradiation of curium or californium isotopes in a high-flux nuclear reactor. Large-scale production of transplutonium elements at RIAR enables also to produce regularly significant quantities of einsteinium and fermium.

Irradiated curium reprocessing procedure provides simultaneous extraction purification of californium, einsteinium and fermium from fission products and non-radioactive impurities. Subsequent separation of Cf-Es-Fm mixture is carried out by cation exchange chromatography using α- hydroxyisobutyric acid (α-OHIBA) as eluant. Disposable and relatively short (41-45 cms) chromatographic columns filled with strong acidic cation exchanger AG50Wx8 (200-400 mesh) are used to simplify chromatographic process in hot cells. Columns used provide effective separation of einsteinium and fermium even at high resin loading with californium-252. The HETP and distribution coefficient of einsteinium values as a function of the mass loading of the column with californium are shown in Fig. 1.

Two following purification steps of Es-Fm mixture from californium are usually needed before cation exchange separation and subsequent purification of the obtained Es and Fm preparations are carried out:

- Anion-exchange separation from iron impurity in 8 mol/l HCl medium;

- Extraction-chromatographic separation from wide range of nonradioactive (alkaline and alkaline-earth elements, nickel, chromium etc.) and radioactive (\(^{90}Zr, ^{93}Nb, ^{103}Ru\)) impurities in HNO\(_3\) medium using teflon powder impregnated with HDEHP as stationary phase;
• Separation from rare-earth radionuclides by cation exchange (in presence of DTPA) or extraction (HDEHP - HNO₃) chromatography methods;
• Final cation-exchange purification of fermium from einsteinium in α-OHIBA medium.

The purification procedure used allows to reduce the activity of ²³⁵Cf and fission products in einsteinium preparations to a value less than 0.05%. Depending on duration of the span between the end of irradiation (EOI) and isolation of einsteinium, the preparations with relative alpha activity of ²⁵³Es or ²⁵⁴Es above 99% can be obtained.

To obtain einsteinium preparation with increased ²⁵⁵Es content, trial irradiation of ²⁵³Es and ²⁵⁴Es mixture in the SM reactor was carried out. Einsteinium sample characteristics prior and after its irradiation are shown in the table below.

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<th>Radionuclidic composition of Es sample (at EOI)</th>
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<th>after the irradiation</th>
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<td>Alpha-emitters activity, MBq</td>
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<td></td>
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<tr>
<td>²⁵³Es</td>
<td>0.09</td>
<td>0.34</td>
</tr>
<tr>
<td>²⁵⁴Es</td>
<td>7.2</td>
<td>0.52</td>
</tr>
<tr>
<td>²⁵⁵Es⁺²⁵⁵Fm</td>
<td>0.003</td>
<td>0.13</td>
</tr>
<tr>
<td>²⁵³Cf</td>
<td>0.014</td>
<td>1.5</td>
</tr>
<tr>
<td>Gamma-emitters activity, MBq</td>
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</tr>
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<td>²⁵⁶Tb</td>
<td>0.32</td>
<td>40</td>
</tr>
<tr>
<td>²⁵⁶Eu</td>
<td>-</td>
<td>3700</td>
</tr>
</tbody>
</table>

The availability of einsteinium preparation with high ²⁵⁵Es content allows realizing periodical chromatographic isolation of its daughter ²⁵⁵Fm (radionuclide generator). This generator pair has longer half-lives (²⁵³Es – 39.8 days; ²⁵⁴Fm – 20.1 hours) than the radionuclidic pair ²⁵⁴Es⁺²⁵⁵Fm (39.3 hours) → ²⁵⁴Fm (3.2 hours) commonly used in chemical practice. Thus use of ²⁵⁵Es provides both longer generator exploitation period and greater convenience when working with its daughter radionuclide.

Possibility of regularly obtaining ²⁵⁴Fm preparations with radionuclidic purity not less than 99%, suitable for radiochemical research, was demonstrated experimentally. The cation-exchange isolation of ²⁵⁴Fm was carried out by passing α-OHIBA solution through 46.5 cm height column containing 5 cm² of the resin. The elution curves of fermium, einsteinium and californium from the generator column are shown in Fig. 2.

Laboratory research results as well as radiochemical procedures of irradiated targets processing and characteristics of obtained ²⁵³,²⁵⁴,²⁵⁵Es, ²⁵⁵Fm, ²⁵⁷Fm preparations are described in the report.
Fig. 1. HETP and dynamic distribution coefficient of einsteinium as a function of the column loading with californium.

Fig. 2. Ion exchange elution of $^{255}$Fm from einsteinium preparation.
A COMPARISON OF THE ADSORPTION BEHAVIOUR OF RADIOISOTOPES FROM THEIR ORGANIC SOLUTIONS ON SOLID SORBENTS

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Compared to other radioactive wastes, the volume of organic wastes generated is small; nevertheless they require a waste management strategy for safe handling, processing and final disposal [1].

Radioactive liquid organic wastes include oils [2], reprocessing solvents [3] such as tributyl phosphate (TBP) and amines, scintillation liquids which are used in radiochemical analysis and consist of a three component mixture: a solute, a solvent, e.g., steroids, lipids etc. or non-polar solvents (e.g., toluene, p-xylene, 1,2,4-trimethyl benzene, dioxane etc.) and the sample under investigation [4,5]. Sludge and decontamination liquids such as toluene, CCl₄, acetone, alcohols and trichloroethane [6]. The treatment of organic liquid wastes with absorbents such as natural fibres (sawdust, cotton), synthetic fibre (polypropylene), vermiculite (mica), clays, diatomaceous earth and imibiber beads (alkyl styrene polymer) has been studied at Brookhaven National Laboratory, Upton, NY [7].

It was found in 1986 [8] that the distribution of metallic species between a nonpolar organic solvent and a filter paper could be useful for separation and preparation of radioactive tracers. Thus ²³⁴Th (UXI) was prepared by dissolving uranyl nitrate hexahydrate in diethyl ether in a beaker containing at its bottom a filter paper with the same diameter as the beaker. The ether solution was then removed and the filter paper was washed many times with smaller portions of ether until the yellow colour of the uranyl ion disappears, indicating that all uranium is extracted from the paper. The UXI could easily be desorbed from the filter paper by dilute acid. El-Sourougy and Hooper [9] used this procedure for preparing UXI in a study of the use of seeded ultrafiltration for the treatment of thorium-uranium mining waste streams. It seems that the extraction/adsorption method can be generalized to involve other isotopes and solvents. Covalent halides of some elements such as arsenic, antimony, germanium, tin, selenium and tellurium are extractable from strong sulphuric acid solution by nonpolar solvents such as benzene, toluene, xylene, nitrobenzene, cyclohexane, kerosene, chloroform and carbon tetrachloride [10-13]. The distribution of these halides between the solvents and various solid sorbents represents an interesting area of research. Thus the distribution of Sb(III) chloride between the nonpolar solvents benzene, toluene, xylene, nitrobenzene, cyclohexane, chloroform and carbon tetrachloride and a filter paper was reported [14]. In case of benzene the Sb(III) activity (given in counts-s⁻¹. ml⁻¹) decreases from 51500 to 200 after 24 hours. The corresponding values are about 1200 and 540 for toluene, 1330 and 50 for xylene, 1050 and 700 for nitrobenzene, 1080 and 22 for cyclohexane, 330 and 30 for chloroform and 130 and 40 for carbon tetrachloride. More than 95% of the adsorbed Sb(III) is desorbed by 1M HNO₃, 1M HCl or 0.5M H₂SO₄ by contacting the loaded filter paper with any of these acids for 27 hours.

The sorption of ¹²⁴Sb (III) from benzene, toluene, o-xylene and nitrobenzene on treated fly ash, pyrolysis residue and bentonite clay was also studied [15]. The results were compared with those for the Sb(V) sorption from the same organic media on the above sorbents [16].
The results revealed relatively higher sorption of the trivalent state than the pentavalent one. According to the type of the nonpolar solvent used, the order of uptake of the radioactive isotopes was often o-xylene ≥ toluene > benzene. The sorption tendency of the sorbents used towards the radionuclides was: bentonite ≥ pyrolysis residue > treated fly ash. Sorption from aqueous medium on the same sorbents has also been investigated for $^{124}\text{Sb(III)}$ compared to $^{124}\text{Sb(V)}$, $^{152}\text{Eu(III)}$ and their mixtures. The obtained results showed that the order of uptake of the different radionuclides was: $\text{Eu(III)} >> \text{Sb(III)} > \text{mixture}$. The investigation was extended to the desorption studies of these radionuclides in the acidic and the neutral media from the dried radioactivity loaded sorbents.

Work on Se(IV) sorption from its solutions in nonpolar solvents on the same sorbents is now underway. As a tracer of Se(IV) $^{75}\text{Se}$ (t $^1/2 = 127$d) prepared from the irradiation of hydrated selenium dioxide (selenious acid) has been used. In fact very high extraction of Se(IV) is obtained from 0.05 M HCl in about 10M H$_2$SO$_4$ by benzene, o-xylene and cyclohexane [12].

References
RADIOCHEMICAL REPROCESSING OF ACTIVATED V-CR-TI ALLOY AS STRUCTURAL MATERIAL FOR FUSION REACTOR

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Vanadium-chromium-titanium (V-Cr-Ti) alloy is considered as a potential structural material for the first wall, blanket and divertor of the Russian Demonstration fusion reactor (DEMO-S). Base of this alloy (up to 90 wt.%) is expensive vanadium.

Activated structural materials of nuclear reactors after decommissioning, in principle, can be purified radiochemically from activation products and then refabricated. We developed a schematic diagram of the radiochemical reprocessing of such an alloy with the purpose of its subsequent refabrication. Figure 1 presents the general diagram of the V, Cr, Ti extraction and separation.

The suggested schematic diagram includes V-Cr-Ti alloy dissolution in nitric acid and its following extraction reprocessing which results in refining of V, Cr and Ti from activation products. Solutions of (V-Cr-Ti) alloy, that contained 90% V, 5% Cr and 5% Ti, were used in experiments. The solution of di-2-ethyl-hexyl-phosphoric acid (D2EHPA) in a hydrocarbon solvent (dodecane) was opted as an extractant. According to our calculations, an extraction cascade of 50 stages should ensure the purity of the alloy components, allowing their refabrication without biological shielding from ionizing radiation, i.e. at an effective dose rate of 12 mSv/h.

Practical realization of the radiochemical alloy reprocessing should include the following steps:
- alloy comminution,
- alloy dissolution in nitric acid with argon bubbling,
- solution clarification,
- extraction separation of V, Cr and Ti and their purification from the activation products,
- production of metal oxides using plasma denitration,
- cementation of radioactive waste containing activation products,
- containerization of cement blocks.

To determine the economic expediency of the radiochemical V-Cr-Ti alloy reprocessing, its cost was compared with that of the alloy disposal (long-term storage). The disposal scheme included:
- alloy comminution,
- crushed alloy housing into special reservoirs and their hermetic encapsulation,
- housing of the reservoirs with the alloy into containers.

Calculations were made assuming that 400 t/year of the alloy would be reprocessed or disposed and that cost of vanadium would be in the range from 10.5 to 250 $/kg. The construction and operation costs for the reprocessing plant and for the activated alloy storage are given in the paper. The technical and economic assessment has shown that the alloy reprocessing is appreciably more profitable than its disposal under assumed plant capacity and vanadium cost.

Thus, the pay-back period of the plant will be ~0.2 years at vanadium cost of 250 $/kg and ~4 years at V-cost of $ 10.5 $/kg, whereas the alloy disposal pay-back period will be ~13 years independently of the vanadium cost.

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INVESTIGATION ON THE CHEMICAL BEHAVIOUR OF A CROWN ETHER IRRADIATED IN HIGH GAMMA RADIATION FIELDS

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One of the basic requirements involved in most radiochemical separations is the achievement of a very good selectivity. In order to fulfill this premise and to improve the known methods, a variety of new reagents were tested in the last decades. Among them, crown ethers have been successfully employed, because of their excellent complexing properties. These compounds are cyclic polyethers with a cavity in which metallic ions can be lodged. The oxygen atoms are usually distributed inside the ring oriented to the centre and following a regular configuration, this spatial arrangement being a determining factor on their complexing capacity.

Crown ethers, dissolved in adequate organic solvents, are employed in current solvent extraction processes; alternatively, they can be retained in inert supports, thus allowing their use in columns [1]. Sometimes, the ion of interest is directly determined in the organic phase where it is extracted.

Several radiochemical applications of crown ethers, in connection with analytical methods or waste management, have been published [2-5]. Because of their nature as organic compounds, the evaluation of the radiation damage and the eventual modification of the behaviour are matters that should be specially taken into account.

Some investigations tending to assess the radiation damages of crown ethers in solution have been carried out; it was found that the solvent could modify the process of radiolysis [6-9]. Use of crown ethers for purposes other than analytical applications, e.g. for separations at industrial scale, involve higher doses, which subsequently imply the need to accomplish a thorough and systematic study about the changes that could affect their extractive properties [10]. However, the nowadays known possibility of preparation of fixed phases, based on the retention of crown ethers in inert supports, opens a new aspect for the study. In that sense, it is necessary to consider the components of the chromatographic columns, i.e. supporting material plus crown ether, as an entity.

As part of a project destined to explore the feasibility of using crown ethers for isolation of some fission products at industrial scale, the authors have characterised the performance, after irradiation at high gamma radiation doses, of the material known under the commercial name SrResin, from Eichrom Industries (U.S.A.). It consists of a crown ether, 4, 4’ (5’’ – bis (t – butyl – cyclohexane) – 18 – crown – 6, in a solution of 1 – octanol absorbed in a polymeric support [11]. All the experiments were performed with the matrix disposed in columns of the same brand; the characteristics of these columns were: 100 μm – 150 μm particle granularity, 0.7 cm internal diameter, 3.8 cm extractive phase height, and 1.5 cm³ extractive volume.

The irradiations were carried out with the 60Co radiation field of the Semi-Industrial Irradiation Plant, belonging to Centro Atómico Ezeiza, at growing doses, starting from 2 kGy, which corresponds to the actual situation of an industrial production process. The dose rate, about 0.17 kGy.min⁻¹, was higher than that estimated for the conditions of the radiochemical
separation; this fact probably led to an overestimation of the radiation effects. L.D. (low dose, 1 kGy – 10 kGy) and H.D. (high dose, 5 kGy – 50 kGy) potassium dichromate dosimeters were used for dose measurements.

The columns were irradiated either moistened with dilute HNO₃, such as they are delivered by the fabricant, or imbibed with 8 M HNO₃, medium currently employed for radiochemical separations that could influence the radiolytic process. No physical damages were observed in the irradiated columns, although at high doses (20 kGy) a yellow tonality was apparent, especially in the presence of HNO₃.

After irradiation, the separative properties of the columns were measured, using ¹³¹Ba and ⁸⁵Sr tracers, through the well characterised barium – strontium separation. Briefly, it comprises the initial retention of strontium in concentrated nitric acid, medium in which barium is eluted, and its subsequent elution with very dilute nitric acid.

Some illustrative results for barium separation are indicated in figures 1 and 2. Except for a slight tailing in the elution curve, the elution of barium is not affected by irradiation at 2 kGy (The evolution of the elution for untreated columns is not included, for the sake of an easier visualisation). Higher elution volumes are necessary in order to assure its complete removal, thus implying eventual losses of strontium. The effects of irradiation at 20 kGy are more noticeable, especially in the columns imbied with HNO₃, where the elution peak is widened and shifted to higher volumes.

![Figure 1. Elution curves of barium for columns irradiated at 2 kGy.](image)

![Figure 2. Elution curves of barium for columns irradiated at 20 kGy.](image)

Irradiation of the columns represents a diminution of the strontium recovery. While 75% of the total activity is collected for an initial elution fraction in untreated columns, this figure is only 60% for a column moistened with dilute HNO₃ and irradiated at 2 kGy. Losses due to strontium retention are higher for columns irradiated with greater doses, particularly in the presence of 8N HNO₃. As in the case of barium, the elution peaks widen and shift to higher volumes for growing doses and in presence of HNO₃. This effect is shown in figure 3.
Figure 3. Influence of the dose on the strontium elution, in the presence of 8N HNO₃.

Irradiation, even at high doses, does not represent any retardation in the elution flux of the columns. In spite of the displacement of the elution volumes and the increment of the losses, the quantitative separation of barium and strontium is still viable.

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References


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EFFECT OF METAL NITRATES ON STRONTIUM EXTRACTION
WITH 4',4''-DI-TERT-BUTYL-DICYCLOHEXANO-18-CROWN-6

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Extraction with crown ether, in particular – with 4',4''-di-tert butyl-dicyclohexano-18-crown-6 (D8C8H18C6) is one of the most efficient methods of strontium extraction from nitrate-solutions, that is practically used for isolation of strontium-90 from spent fuel reprocessing solutions, for determination of $^{90}$Sr in environmental samples, etc. [1-4].

The model, considering a formation of strontium and nitric acid complexes with crown ether can be used to describe the extraction process [5]

$$\text{Sr}^{2+} (\text{aq}) + 2\text{NO}_3^- (\text{aq}) + \text{Crown}_{\text{org}} \leftrightarrow \text{SrCrown}^{2+} \cdot 2(\text{NO}_3^-)_{\text{org}}$$

$$\text{Crown}_{\text{org}} + \text{HNO}_3 \leftrightarrow \text{Crown} \cdot \text{HNO}_3_{\text{org}}$$

$$\text{Crown}_{\text{org}} + 2\text{HNO}_3 \leftrightarrow \text{Crown} \cdot 2\text{HNO}_3_{\text{org}}$$

Main factors influencing efficiency of strontium extraction are the concentration of extracting agent in the organic phase ($C_{\text{Crown}}$) as well as the concentration of nitrate-ions ([NO$_3^-$]) and nitric acid ([HNO$_3$]) in aqueous phase. At a low binding of the extracting agent it can be described with the following expression

$$D_{D2} = K_{D2} \cdot C_{\text{Crown}} \frac{[\text{NO}_3^-]^2}{1 + K_{\text{n1}}[\text{HNO}_3] + K_{\text{n2}}[\text{HNO}_3]^2}$$

where $K_{D2}$, $K_{n1}$, $K_{n2}$ - conditional extraction constants for strontium, $\text{Crown} \cdot \text{HNO}_3$ and $\text{Crown} \cdot 2\text{HNO}_3$, respectively.

In case of extraction from the nitric acid solutions at a fixed concentration of extracting agent expression (1) can be transformed as follows

$$D_{D2} = \text{Const} \frac{[\text{HNO}_3]^3}{1 + K_{\text{n1}}[\text{HNO}_3] + K_{\text{n2}}[\text{HNO}_3]^2}$$

For practical purposes extraction of strontium from solutions containing other metal nitrates is more important. Some metal ions, like K$^+$, NH$_4^+$, Pb$^{2+}$, Ca$^{2+}$ [6,7], are able to form strong complexes with 18-crown-6 thus suppressing extraction of strontium. At the same time metal nitrates are known to increase concentration of nitrate-ion in the system thus facilitatign effective extraction of strontium. This effect can be described with the following expression

$$D_{D2} = K_{D2} \cdot C_{\text{Crown}} \frac{([\text{HNO}_3] + [\text{NO}_3^-])^2}{1 + K_{\text{n1}}[\text{HNO}_3] + K_{\text{n2}}[\text{HNO}_3]^2}$$

where $[\text{NO}_3^-]$ is the nitrate-ion concentration, provided by the salt presence in the solution.
Unfortunately, detailed information describing the effect of foreign ions on the strontium extraction with crown-ethers is not available in literature. A formal analysis of expression (3), describing an asymptotic dependence \( D_g = f([HNO_3],[NO_3^-]) \), shows that at a certain concentration of the nitric acid and nitrate-ion extraction of strontium from neutral solutions can be more efficient than that from the strongly acidic ones ([HNO_3] ≥ 3 mol/l), which are traditionally used for strontium extraction. Results of our experiments presented in the figure below have confirmed this assumption. The effect of lithium, magnesium, aluminum and yttrium nitrates has been studied. These metals do not form strong complexes with 18-crown-6 but they supply nitrate-ions. At a low concentration of nitric acid the increased concentration of metal nitrate gives monotonic increase of \( D_g \). At a higher acid concentration the \( D_g = f([NO_3^-]) \) dependency turns to the asymptotic one. A position of asymptote depends on the nature of metal. The effect is most pronounced for aluminum and yttrium nitrates. It can be explained by the fact that lithium nitrate produces three times less of nitrate ion then aluminum or yttrium nitrates produce. We think that the most interesting and practically valuable is the fact that at a foreign nitrate concentration exceeding 1.2 - 1.5 mol/l strontium distribution ratio is higher for extraction from aqueous solution than that for the nitric acid solution, independently of the metal nature.

Based on the effect described above the method of \(^{89}\text{Sr} \) isolation from yttrium oxide irradiated by fast neutrons was developed [8]. That allows for development of a highly effective process for production of non-carrier added strontium-89 of high radionuclidic and chemical purity. In this process low concentration of nitric acid allows one to increase concentration of yttrium nitrate up to ~2 mol/l (solubility of yttrium nitrate strongly depends on concentration of nitric acid and is lower than 1 mol/l for [HNO_3] ≥ 3 mol/l), thus increasing a production capacity of the process. At the same time, it gives considerable rise of \( D_g \) that is important for separation of yttrium and strontium in a chromatographic mode.

References

Extraction of strontium with 0.4 mol/l solution of DtBCH18C6 in n-octanol in the presence of lithium (a), magnesium (b), aluminum (c) and yttrium (d) from water (1), 1 M HNO₃ (2), 3 M HNO₃ (3) and 5 M HNO₃ (4)
SAFETY RELEVANT NUCLIDES
IN ADVANCED SPALLATION NEUTRON SOURCES

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Advanced spallation sources for generation of short neutron pulses (∼ 1 µs) are under construction in USA (SNS) and Japan (J-PARC); a decision about the European project ESS is expected not earlier than 2006. Spallation sources consist mainly of an accelerator (1 – 10 MW beam power, 0.8 – 3 GeV proton energy), a compressor ring and one or more target stations, where neutrons are formed by spallation [1]. A liquid mercury target is favoured by most concepts, but (liquid) lead bismuth eutectic (LBE) and solid state targets (tungsten) are in discussion, too. An advantage of liquid targets lies in the fact that the heat removal is easier, because no direct target cooling is required; this avoids H-3 formation as in the direct target cooling by water. On the other hand, cavitation problems associated with microsecond pressure pulses in liquid targets are not yet completely solved for power values > 1 MW. Further on, the absence of a crystal lattice as activity release barrier has to be taken into account in the safety design of liquid target systems. This paper describes accumulated activities for an ESS liquid mercury target station as well as dose/emission values for the most radiotoxic nuclides. Comments are made about the final waste disposal, including the necessary solidification process for liquid mercury. More details are found in the ESS Project Volume III Update Report [2].

Nuclides formed in the spallation target cover the whole range of atomic numbers between 1 and values slightly higher than the target material. The number of nuclides to be taken into account is in the range of 1500 - 2000. The nuclide formation is calculated by code systems like MCNP; their experimental validation related to spallation source has still to be extended. Unfortunately, a large fraction of these nuclides generated in spallation sources are not yet as well examined as those, being relevant in fission systems. This also holds for dose factors, free handling limits etc. Further on, formation yields for most nuclides in spallation sources are associated with higher uncertainties than in fission systems, although at least for about 70 % of the nuclides these uncertainties were estimated to remain within of a factor of 2 [3]. Due to the high power of advanced spallation sources and due to the fact, that the target is not changed during the lifetime of the spallation source, the total target nuclide inventory is comparable to that of neutron generating research reactors and, accordingly forces careful safety examinations. It has to be taken into account, however, that spallation is an energy consuming process, and for that criticality cannot occur; failure of the proton beam shutdown system, internal fires and external hazards are the main events to be considered within safety studies for spallation sources [2,4].

Fig. 1 compares the total inventories of each 5 MW mercury target (ESS) with those of one core of a typical medium sized (20 MWth) research reactor, depending on time after shutdown. The slow decay of research reactor fuel at decay times > 1000 y is mainly due to actinide formation in LEU (low enriched uranium) fuel, and does not occur for HEU (high enriched uranium) fuel. As a general rule it may be taken that the activity in a mercury target is the same order of magnitude as in a fission system with similar thermal power.
The inventory of a single reactor core is the correct basis for comparison, as long as safety considerations for accidents are the main focus. However, if final waste handling is the main point of concern, the long-lived activities of a research reactor summed up for the whole reactor life have to be compared with the inventory of both ESS-targets.

![Graph showing activity over time after shut-down for ESS and research reactor targets.](image)

**Fig. 1:** Comparison of activities in an ESS target and in a research reactor core

The most relevant nuclides in the ESS target are given in Table 1 together with their estimated inventories, their half-lives, their radiation type and their boiling points. The accumulated activity is scaled in power from the SNS (1 MW) results [4]; for Hg-194 additional, validating MCNP calculations were performed. These most relevant nuclides present in the ESS target are identified by criteria like formation yield, lifetime, dose factors and volatility. Concerning volatility, nuclides were divided into 3 volatility categories [4]: High volatile nuclides (tritium, iodine, noble gases), mercury isotopes (having an average volatility) and low volatile nuclides (most metals other than Hg).

Most dominating nuclides for the different pathways are given in full-tone. Dose calculations for source terms of ESS design basis accidents indicate that the dominating dose contribution will result from long-lived Hg-194, due to its short-lived daughter nuclide Au-194 (high energetic γ-emitter), by its groundshine. These particularly radiotoxic nuclides will be also found in LBE targets (which in addition contain α-emitting and therefore pronounced radiotoxic, volatile Po-210 in substantial quantities), but not in solid tungsten ones. Thermochemical examinations on the chemical status of iodine in a mercury target indicate that mostly solid HgI₂ and FeI₂ (the latter by interaction with the metallic target hull) are formed [3]; these compounds are far less volatile than elemental iodine and, accordingly, their formation reduces the iodine source term (influencing strongly the doses of the ingestion pathway) in certain accident scenarios.
Concerning the total radiotoxicity of a mercury target already the inventory of α-emitting Gd-148 in a 5 MW target exceeds the EU free handling limit by a factor of 10⁶, which means, that - within German practice - a nuclear emergency plan is probably required. A comparison of the radiotoxicity of mercury with its chemical toxicity indicates that the radiotoxicity dominates within the conservative licensing framework due to the ground-shine of Hg-194, but that the chemical toxicity cannot be neglected. In case of realistic consequence estimations the role of the chemotoxicity of mercury increases.

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1) German directives for design basis accidents. Infants (70 cm height) and ground shine. Effective doses except for iodine (thyroid). Minimum distance 250 m. Emission height 2.5 m. 2) Preliminary ingestion model of German rules. 3) HTO oxidation by skin (preliminary model). 4) Ingestation to HTO in soil considered.

Volatility classes: a = high volatile, b = mercury (intermediate volatility), c = low volatile.

Table I: Overview on radiological most relevant nuclides in an ESS-target (5 MW, 40 y operation with 5000 h/y)

Liquids are not allowed within a repository and - because Hg-194 cannot be separated from the target - solidification is required prior to disposal of the mercury, e.g. to HgS or amalgams. Due to the comparatively high specific activity this is a major task and respective R&D work has to be started; the total amount of mercury in ESS is at about 30 t. A very long lived nuclide occurring in mercury targets is Ho-163 (t₁/₂ = 4750 y, 1900 Gbq in one ESS target). This nuclide is not yet part of most radiation protection regulations; however, because it is known to emit X-rays from electron capture only, it is not expected to be highly radiotoxic. The problems concerning disposal of ultra long lived, fissile and highly radiotoxic actinides as in LEU fission systems do not exist in advanced spallation sources.

EVALUATION OF CROSS SECTION DATA FOR APPLICATIONS IN ACCELERATOR DRIVEN ENERGY SYSTEMS AND IN PRODUCTION OF MEDICAL RADIOISOTOPES

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Investigations aimed at the development of neutron and charged particle cross section evaluations at intermediate energies performed in IPPE during the last years are discussed. Evaluated nuclear data both for neutron and charged particle cross sections are needed for various applications. The main efforts up to now were devoted to the evaluations of neutron induced reactions in the energy range up to 20 MeV, which meet requirements of nuclear power production in thermal and fast reactors. Another problem has been widely discussed over the last decades: the problem of long-lived nuclear waste. Huge amount of long-lived radioactive waste have been accumulated, including long-lived fission products and actinides, mainly minor actinides. These wastes can be incinerated, in principle, in fast reactors. However, the criticality conditions create strong limitations to the quantity of radioactive materials, which can be loaded to the reactor. As alternative to nuclear reactors, to avoid criticality conditions, it was suggested to create and use ADS-accelerator driven systems, consisting of high-energy accelerator with intense beam, special target where this beam creates high intensity neutron flux, which is multiplied in the sub-critical blanket and can incinerate LLW.

Recent development of accelerator-driven transmutation systems (ADS) and their relevance for nuclear waste management has created a new interest in high quality nuclear data for fissile isotopes, structural materials and fission products. In practice, the energy interval from thermal energies to a few thousand MeV should be covered in order to properly model ADS [1]. The status of available nuclear data differs strongly for the energy regions below and above 20 MeV. In the energy region below 20 MeV several versions of national and international libraries have been created. In contrast, for energies higher than 20 MeV data are rather scarce and are not yet systematized.

Both neutrons and protons in the energy range between 20 MeV and a few hundreds of MeV play non-negligible role in accelerator-driven systems and transport of these particles should be simulated with a better precision than allowed by available data today. Therefore it was decided that special attention should be put to this energy region, and the evaluated data files for energies from 20 to 150 MeV should be prepared in the same manner as for the energy region below 20 MeV [1] for the most important structural and fissile materials. Valuable efforts have been already made by the Los Alamos group [2] and the evaluated data files for more than 40 of the most important structural and shielding materials were extended up to 150 MeV in the ENDF/B-VI library. Similar evaluations for the most important fissile isotopes Th-232, U-238, Pu-239 and Pu-240 have been performed at the Institute of Physics and Power Engineering [3-5]. Some results of experimental data analysis and evaluations for the intermediate energy neutron data file for $^{237}$Np are presented below.
During the past twenty years, many laboratories reported a large number of experimental data for medical radioisotope production and nuclear data centers compiled most of those data. However, no systematic efforts was devoted to standardization of those data. So the IAEA initiated in 1995 the Research Coordinated Project on “Development of Reference Charged-Particle Cross Section Database for Medical Radioisotope Production”. The project focused on radioisotopes for diagnostic purposes and the related beam monitor reactions [cf. 6]. Last year another IAEA CRP on “Nuclear Data for the Production of Therapeutic Radionuclides” was started. Many laboratories are participating in the collection, initial screening and systematic treatment of data. However the methods of analysis, calculations and evaluations of nuclear data were mainly developed in IPPE. In particular, the methods of statistical optimization of experimental data based on approximation of cross sections with rational functions were used [6]. The ALICE-IPPE code was developed and used also in those evaluations of excitation functions for the reactions producing medical radioisotopes. Some example of these evaluations for the reactions induced by alpha-particles is shown in Fig. 1.

Creation of complete data files for actinides in the range up to 150 MeV is more complicated task than evaluation of excitation functions only. The more wide scope of methods, models and codes is applied to solve this task, including those, which were used in evaluations of excitation functions for the production of medical radionuclides. As an example the evaluation of fission cross section for $^{237}$Np in the neutron energy range up to 200 MeV is given in Fig. 2.

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![Graph](image)

**Fig. 1.** Excitation function for $^{209}$Bi(alpha,2n)$^{211}$At. Dashed line –calculation with ALICE-IPPE, solid line–approximation of experimental data with rational functions.
Fig. 2. Fission cross section $^{237}$Np(n,f). Solid line is approximation of experimental data with rational functions.

References
Oscillatory extraction of Eu-152

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Processes of extraction of macroconcentrations of cerium and microconcentrations of europium by three-n-butyl-phosphate (TBP) in various diluents from a nitric solution where periodic Belousov-Zhabotinsky (BZ) reaction takes place has been investigated. Introduction of nitric acid or/and nitrate of lithium or sodium, as well as contact of the aqueous phase with an organic phase, results in a change of amplitude and the oscillation frequency of the potential of a platinum electrode $E(t)$, and because of this phenomenon the change of the period and duration of oscillations in comparison with a classical BZ reaction has been observed.

The partition coefficients of cerium were measured by chelatometry method and the partition coefficients of europium-152 by radiometric method. The consecutive set of samples of aqueous and organic phases was taken while BZ reaction takes place in aqueous phase. The experimental technique is described elsewhere [1, 2].

It was found that the extraction of cerium and europium is coordinated to a periodic BZ reaction, which is taking place in an aqueous phase. Synchronous behavior of the distribution coefficient of cerium with $E(t)$ conforms that process of Ce extraction / stripping is rather fast. The concentration of $Ce^{3+}$ in organic phase during BZ reaction is in phase with $E(t)$. This can be explained by high lability of extractible complexes of Ce. The oscillations of $D_{ew}$ are asynchronous with the oscillations of $E(t)$ and $D_{x}$. This fact is explainable by a competition of metals for the extractant and the fact that europium is not involved into an oxidation-reduction cycle of BZ periodic reaction. The synchronous oscillations of partition coefficients of cerium macroconcentration and the asynchronous oscillations of partition of europium microconcentration with $E(t)$ specify the mutual influence of the periodic reaction and the extraction process. This mutual influence can be used to separate chemically similar elements. It can be used also in new developed methods of kinetic investigation of extraction of various elements. Such researches have great potential for a wide range of elements capable to form the oxidation / reduction pairs and to participate in periodic reactions.

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References

PROGRESS IN THE METHOD FOR PREPARING STANDARD LOW ENERGY X-RAY POINT SOURCE SET

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The key to raise the accuracy of standard low energy x-ray source set lies in preparing thin, uniform and fine crystal sources as much as possible. Up to present, there is still no satisfactory source-making method meeting the requirement. For this reason we propose a new method for preparing the source set using new process and technologies such as (1) the process for preparing radionuclides with high radionuclidic purity and high specific radioactivity in order to decrease the mass thickness of the source set; (2) the improved method for increasing the weighing accuracy of radioactive standard solution microdrops; (3) the technology for preparing a new surfactant to precisely control the size and location of the source spots; (4) the method and technologies for accurately determining the source self-absorption and radioactivities using the instruments made by ourselves.

We have investigated the effects of the related factors systematically and have recommended the optimum conditions to prepare the source set. By the method a set of standard low energy x-ray point source set consisting of 8 radionuclides at 370 KBq (each radionuclide) covering energy range from 0.5 to 5 kev was obtained. The radionuclides are homogeneously deposited on a 2mm diameter spot in the geometric center of the film with 2mg/cm² thickness. The results show that the method can satisfactorily meet the needs of preparing standard low energy x-ray source set, for instance the source set obtained by the method is much more homogeneous, thinner and more accurate than the source set prepared by using general source-preparing methods and have been successfully applied to the accurate calibration of low energy x-ray measurement devices.

Several factors, which affect the accuracy of the source set, are also discussed in this paper.
IRRADIATION FACILITIES AT THE NEW RESEARCH REACTOR FRM-II MUNICH

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The new reactor FRM-II is equipped with various irradiation facilities. Due to the different tolerable sample volumes, neutron flux densities and obtainable neutron fluences, they allow in their entirety a broad scope of possible applications in basic and applied science.

On 2nd March 2004, the FRM-II became critical for the first time. During the nuclear start-up phase of the reactor the following facilities will be tested and optimised:

- a pneumatic rabbit system (RPA),
- a hydraulic rabbit system (KPA),
- a test-rig for a silicon doping facility (SDA),
- a pneumatic rabbit system (TRP) for prompt transport of irradiated samples into the neighbouring institute for radiochemistry.

In addition, a high speed pneumatic rabbit system with a transfer time shorter than 300 ms is already planned and will be built in the near future.

All of the irradiation positions are located within the heavy water moderator tank and can be loaded and unloaded during reactor operation. A major advantage of these irradiation positions is the availability of a very pure thermal neutron field. Thus, parasitic threshold reactions by fast neutrons and the production of large clusters of irradiation defects are suppressed effectively.

The pneumatic rabbit system (RPA) serves typically for the activation of samples for neutron activation analysis. The pneumatic devices are operated by CO₂ gas in order to avoid production of radioactive ⁴¹Ar during the irradiation of air. The facility is composed of 6 identical independent irradiation channels, except for the vertical position within the moderator tank. Consequently the neutron flux densities in the positions vary between 5·10⁻¹² cm⁻²s⁻¹ and 2·10⁻¹⁴ cm⁻²s⁻¹ and the appropriate irradiation position can be chosen to fit the individual task. For radiation protection reasons the entire handling takes place in a room used exclusively for this facility. Irradiation times can be chosen between about 20 s, i.e. a significantly longer time compared to the transport time of the rabbits of a few seconds, and 5 hours. The maximum irradiation time is limited by the use of polyethylene rabbits as outer irradiation package. After irradiation the sample is first transported into a shielded cooling position where the induced gamma dose rate is measured. Finally it is transported back into a handling room where it is either removed from the irradiation facility by remote handling tools or alternatively sent directly to the institute for radiochemistry via a connected rabbit system (TRP).

In contrast to the pneumatic system the hydraulic rabbit system (KPA) will be used for long term exposure or for irradiation of larger sample volumes up to approximately 35 cm². Consequently the samples are contained in Al rabbits during irradiation, which however are
perforated in order to guarantee the cooling of the samples by pool water during irradiation. If necessary the direct contact between sample and pool water is avoided by the use of sealed quartz ampoules or small welded inner Al containers. The facility offers 2 independent identical irradiation channels each of which can be loaded by up to 5 rabbits at the same time. The driving medium of the facility is reactor pool water. The neutron flux densities have been calculated to be about $4 \cdot 10^{15}$ cm$^{-2}$s$^{-1}$. Since rather high activities will have to be handled in the hydraulic rabbit system, most of the handling procedure, in particular the receipt of irradiated samples and the measurement of the induced gamma dose rate, is done remotely under water about 3.5 m below the reactor pool level. In addition, also the loading of the samples into lead shielded transport containers takes place under water.

Both the rabbit systems are controlled automatically by the Siemens-SPS control system through a PC with WindowsNT/2000 operating system. The current situation of each transfer system, including the position of the irradiation capsules and the status of all control valves and other important parameters such as system pressure and gamma dose rate at the sample cooling positions can be directly displayed on the screen of the control PC. If necessary, a semi automatic control through direct operation of single components by mouse click is also possible.

The silicon doping facility (SDA) will serve for the P doping of the semiconductor Si by means of the nuclear reaction $^{28}\text{Si}(n,\gamma)^{30}\text{Si} \rightarrow ^{30}\text{P}$. This so called neutron transmutation doping offers the most homogeneous doping profile, necessary particularly in high power electronic components. In order to fulfill the requirement of homogeneity, however, it is of crucial importance to guarantee a constant neutron flux density over the entire volume of the Si ingot. Therefore the ingot is rotated during irradiation and the irradiation position has to be equipped with a specially shaped absorber. During the nuclear start-up phase the neutron flux distribution in the Si ingot will be determined experimentally by using a simplified test rig. Then, based on this flux distribution the exact shape of this absorber made from Ni can be calculated and constructed. Once the absorber profile will be known the final Si doping facility offering a semi automatic operation will be completed. It will be suitable for Si ingots with diameters of up to 200 mm and a capacity of ca. 10 tons per year.

Samples with different weight and irradiation time are loaded and transferred during the start-up test of the rabbit systems under all possible conditions in order to simulate the real situations. Tests of several irradiation tasks in the same time and same transfer system are also performed. Flux monitors (Au, Zr etc.) will be placed and irradiated at 18 positions within one test Si ingot during the nuclear start-up to determine the neutron flux distribution inside the Si ingot.
6. Radiotracers in Life Sciences
RADIOTRACERS IN LIFE SCIENCES

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Introduction

Radiopharmaceuticals in combination with Single Photon Emission Computer Tomography (SPECT) and Positron Emission Tomography (PET) have been used extensively in clinical diagnosis, pathophysiology and drug research [1]. These scintigraphic techniques are delivering in vivo metabolic information and are often more sensitive than other imaging modalities such as X-ray Computer Tomography (CT) and Magnetic Resonance Imaging (MRI). A prerequisite for SPECT or PET studies is the availability of suitable radiopharmaceuticals. The selection, preparation and pre-clinical evaluation of new radiopharmaceuticals are addressed by the fields of radiochemistry and radiopharmaceutical chemistry.

The most widely applied radionuclides in diagnostic imaging decay primarily by $\gamma$-emission. Corner stones for SPECT are the radionuclides $^{99m}$Tc and $^{123}$I. Of the two modalities SPECT is still the most widely applied. However, a strong advantage of PET over SPECT is the possibility to use $^{11}$C, $^{13}$N and $^{15}$O, radionuclides of the elements of life. These positron-emitting radionuclides allow the preparation of radiopharmaceuticals with the same biochemical properties as the natural analogues in the living human body. This makes the methodology extremely useful for the in vivo assessment of the metabolic and functional consequences of, for example, gene expression: imaging of functional genomics. Another interesting application is in the field of drug research. Almost all drugs contain carbon atoms. Labeling with $^{11}$C results in radioactive compounds with the same pharmacokinetic properties as the parent drug. Another advantage of PET over SPECT is the quantitative capability to measure the radioactivity distribution with high resolution and sensitivity. A disadvantage of PET is the short half-life of $^{15}$O, $^{13}$N or $^{11}$C (2-20 min). It requires access to an on site cyclotron. It also limits the data acquisition time available for performing a PET study. For this reason there is much interest in the development of positron emitting radiopharmaceuticals with longer half-lives, e.g. $^{64}$Cu, $^{86}$Ga, $^{82}$Br, $^{86}$Br, $^{94m}$Tc, $^{124}$I [2,3].

Fluorine-18 is applied to produce analogues of compounds in which a C-H or C-OH bond has been replaced with a C-$^{18}$F bond. [$^{18}$F]-Fluorodeoxyglucose ($^{18}$FDG), the most widely applied radiopharmaceutical in PET measuring glucose metabolism, is based on this principle. Fluorine-18 has a half-life of 110 min which allows distribution to nearby hospitals (satellite concept).

The molecular mechanisms on which radiopharmaceuticals are based are receptor binding (either peripheral or cerebral, intracellular or at the membrane surface), metabolism (enzyme activity or measurement of the resulting trapping or clearance of the radioactivity), transport across the cell membrane (carrier systems, efflux pumps), and binding to several kinds of macromolecules (DNA, RNA, proteins). In the ideal case, the radiopharmaceutical interacts only with the molecules of interest and no nonspecific accumulation is observed. The selection criteria for a new radiotracer have been extensively reviewed elsewhere [4,5].

Many synthetic routes to prepare PET radiopharmaceuticals have been developed during the last decades. The great majority of the PET tracers are labeled with $^{11}$C and $^{18}$F. The half-lives of $^{13}$N and $^{15}$O are too short to perform radiochemical syntheses of more than one reaction
step. In most cases $^{125}$O-labeled radiopharmaceuticals are limited to radiolabeled water, butanol, and gases for inhalation studies (CO, CO$_2$). In the case of $^{15}$N, this radionuclide is incorporated into nitrite/nitrate and ammonia. $^{15}$N-ammonia has been used to prepare $^{15}$N-cisplatin and some amino acids [6].

Among the many possible radiochemical preparation methods, a few have been extensively developed and are used by many PET-centers. With these preparation methods, i.e., nucleophilic substitution with $^{18}$F-fluoride, electrophilic fluorination, and $^{13}$C-methylation, a large variety of biologically active compounds can be prepared. Widespread use of these specific methods has been encouraged by the appearance of commercially available synthesis modules. Some general aspects of PET radiochemistry have to be considered. First the preparation of a radiopharmaceutical is a fight against time, because of the short half-lives of the radionuclides. A second aspect is the amount of reagents used. Most often the non-radioactive precursor compound is present in an excess of a few orders of magnitude as compared with the radioactive precursor. Therefore the reaction kinetics are first order. Another important aspect is isotopic dilution of the produced radioisotopes. Stable $^{12}$C or $^{19}$F isotopes are introduced in the target or during work-up of the radioactivity prior to the actual synthesis.

**Carbon–11 labeling methods**

In carbon-11 radiochemistry a wide variety of small $^{11}$C-labeled precursors have been developed, e.g. $^{11}$CH$_4$, $^{11}$CH$_3$OSO$_2$CF$_3$, $^{11}$CN, $^{11}$COCl$_2$, and $^{11}$CH$_3$MgBr. Carbon-11 can be produced in the target system as $^{11}$CO$_2$ or $^{11}$CH$_4$, both via the $^{14}$N(p,α)$^{11}$C nuclear reaction.

The majority of the $^{11}$C-preparations uses $^{11}$CH$_3$ or $^{11}$C-methyl triflate. Methylation reactions are simple and yield many biologically interesting compounds. There are two common ways to prepare $^{11}$C-methyl iodide: the wet method via reduction of $^{11}$CO$_2$ to $^{11}$C-methanol by LiAlH$_4$ followed by treatment with HI, and the gas phase method using iodine vapor and $^{11}$CH$_4$. The use of $^{11}$C-methyl triflate has several advantages over the use of $^{11}$CH$_3$I. Because methyl triflate is far more reactive, methylation reactions can be conducted using lower reaction times. $^{11}$C-methyl triflate can easily be prepared by passing $^{11}$CH$_3$I through a column containing silver triflate heated at 200 °C.

**Radiofluorination reactions**

Radiofluorination reactions can be nucleophilic as well as electrophilic. Advantages of nucleophilic preparation methods are that a wide variety of radiopharmaceuticals can be prepared with high radiochemical yields and high specific activities. The precursor $^{18}$F$^-$ is produced by the irradiation of $^{18}$O-enriched water using the (p,n) nuclear reaction. $^{18}$F$^-$ can be produced in high quantities (35-70 GBq). Since $^{18}$F$^-$ is not soluble in organic solvents suitable for Sr,2 react.ons a phase transfer catalyst is needed. To this purpose tetraalkylammonium salts or aminopolymethers (Kryptofix 2.2.2) are used. After the work-up of the $^{18}$F$^-$ several options are possible. First the direct substitution of an appropriate leaving group $^{18}$F$^-$ followed by hydrolysis of protective groups. An example of this method is the preparation of [3-$^{18}$F]-fluoro-3-deoxythymidine ($^{18}$FLT). The second option is the preparation of a reactive $^{18}$F$^-$ fluorinated intermediate by nucleophilic substitution, followed by a second reaction, such as an alklylation.
For electrolytic fluorinations elemental $^{18}$F$_2$ is used. $^{18}$F$_2$ is produced by irradiating Neon-20 containing 0.1-0.3% F$_2$. Because F$_2$ is very reactive, it is necessary to add non-radioactive F$_2$ to the target to prevent adsorption of $^{18}$F to the target wall and transporting tubing. The fluorination can be performed directly with $^{18}$F$_2$ but often $^{18}$F$_2$ is converted into [$^{18}$F]acetilhypofluorite prior to the reaction. Also conversion to N-$^{18}$F[fluoropyridinium salts has been described. Another approach based on $^{18}$F$_2$ is the addition to double bonds or an aromatic substitution. A common reaction nowadays is an electrophilic aromatic substitution of a trialkyl tin or mercury group. A well-known example is the preparation of L-$^{18}$F[fluoroDOPA.

Applications

The clinical value of PET is appreciated in many different areas such as neurology, psychiatry, cardiology and especially oncology. In oncology patients $^{18}$FDG/PET is often the method of choice to detect tumors and metastases.

In malignant tumors amino acid metabolism is increased due to a high protein synthesis rate in the tumor. Carbon-11 labeled amino acids are frequently used oncology tracers. For the satellite concept a longer half-life is necessary. For this reason much effort is directed to the development of $^{18}$F-labeled amino acids [7].

Recently a new radiopharmaceutical reflecting DNA-synthesis has emerged: $^{18}$F-labeled fluoroodeoxythymidine (FLT). Imaging and quantification of the DNA-synthesis rate with FLT is a direct measure of cell proliferation and tumor growth [8].

So far the clinical efficacy PET/FDG in prostate and bladder cancer is limited. Recently $^{11}$C-choline has been reported [9]. Choline is one of the components of phosphatidylycholine, an essential element of phospholipids in the cell membrane. This tracer may also be useful for other tumors, e.g. in the brain and the lungs.

References

RADIOMETAL-LABELED SOMATOSTATIN ANALOGS FOR CANCER THERAPY

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The delivery of radiopharmaceuticals to tumors for cancer therapy is a growing area of research. In the United States, the first clinically approved agent for radioimmunotherapy of cancer was $^{90}$Y-ibritumomab tiuxetan (Zevalin; IDEC Pharmaceuticals Corp., San Diego, CA).[1] This agent, for the treatment of non-Hodgkin’s lymphoma, consists of a therapeutic metal radionuclide, $^{90}$Y ($t_{1/2} = 2.7$ d; 100% $\beta^-$), which is radiolabeled to an anti-CD20 monoclonal antibody using an analog of diethylenetriaminepentaacetic acid (DTPA) called MX-DTPA. This agent is likely to be the first of many more therapeutic radiopharmaceuticals that consist of radionuclides attached to biological molecules. Another near-success story of a class of therapeutic radiopharmaceuticals is that of the radiolabeled somatostatin analogs, of which there are several ongoing clinical trials. The focus of this presentation will be the chemistry and biology of the development of radiometal-labeled somatostatin analogs.

The targeting of somatostatin receptors (SSRs) in tumors has been a goal in cancer treatment and diagnosis since the 1980’s. Somatostatin is a receptor that plays an inhibitory role in the regulation of many organ systems, and somatostatin receptors (SSTR) are upregulated in many tumor types, including those of the neuroendocrine system.[2] Somatostatin analogs labeled with $^{111}$In, $^{90}$Y, and $^{177}$Lu (Figure 1) have been evaluated as cancer therapy agents in patients with somatostatin receptor (SSTR) positive tumors.[3-8] Overall, these agents have shown success, with responses ranging from palliation of pain, stable disease, to partial and complete responses. Other radiolabeled somatostatin analogs have shown to be effective cancer therapy agents in animal models, including those labeled with $^{64}$Cu.[9, 10] Table 1 shows the modes of production and decay characteristics of therapeutic radionuclides that have been used to label somatostatin analogs.

In the development of radiolabeled somatostatin analogs, multi-disciplinary research involving many aspects of chemistry and biology is necessary. For example, research in peptide chemistry has been required for developing optimal methods for forming the cyclic peptides and the C-terminal threoninol for octreotide.[11] An understanding of metal complexation and metal complex stability under biological conditions is essential for stably binding the radiometals to the peptides.[12-14] Biodistribution studies in SSTR-tumor bearing animal models have been traditionally performed to determine the uptake in the tumors and clearance through the normal tissues. [15, 16] Pre-clinical therapy studies, as well as determining the dosimetry and maximum tolerated dose are performed in tumor-bearing rodent models prior to human studies.[17, 18] Imaging studies in humans, either by gamma scintigraphy or positron emission tomography.
Aspects of the development of radiometal-labeled somatostatin analogs for cancer therapy will be highlighted to demonstrate the importance of chemistry, radiochemistry and biological evaluation that is required prior to clinical studies.

**Figure 1:** Structures of somatostatin analogs labeled with radiometals for cancer therapy.

**Table 1.** Radiometals for labeling somatostatin analogs for cancer therapy.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>T1/2</th>
<th>Method of production</th>
<th>Decay mode</th>
<th>Eₚ, (max, MeV)</th>
</tr>
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</table>
| ^64Cu   | 12.7 h | Cyclotron, ^64Ni(p,n)^64Cu | β⁻ (19%)  
EC (41%)  
β (40%) | 0.57 |
| ^111In  | 2.8 d | Cyclotron  
^111Cd(p,n)^111In | EC(100%)  
γ (183%) | 0.173 (89%)  
0.247 (94%) |
| ^90Y    | 2.7 d | ^90Sr generator | β⁻ (100%) | 2.27 |
| ^177Lu  | 6.7 d | Reactor  
^176Lu(n,γ)^177Lu | β⁻ (100%)  
γ (17.4%) | 0.49  
0.113 (2.8%)  
0.208 (6.1%) |
SINGLE-STEP SYNTHESIS OF NO CARRIER ADDED $[^{18}F]$FLUOROANISOLS VIA ARYL-HETEROARYL-IODONIUM SALTS

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Iodonium salts are very interesting precursors for labelling arenes with n.c.a. $[^{18}F]$fluoride ($t_{1/2} = 109.7$ min), especially since they make direct radiofluorination of electron rich arenes possible [1, 2]. On the basis of their stability and their easy preparation, iodonium salts have been employed for the preparation of a variety of $[^{18}F]$fluoroarenes [1-5]. The introduction of $[^{18}F]$fluoride via the $S_{N}Ar$-mechanism leads to $[^{18}F]$fluoroarenes and the corresponding iodoarenes (Scheme 1).

\[
\begin{align*}
&\begin{array}{c}
\text{X} = \text{Hal, OTos, OTf}...
\end{array}
\end{align*}
\]

The nucleophilic attack on the diaryliodonium salts occurs preferably at the electron deficient arene, but steric influence of substituents is also observed, especially by ortho-substituents [6].

In cases of iodonium salts with aromatic rings of different electron density and/or steric structure, the regioselectivity of the substitution can be determined. Hence the use of highly electron rich heteroarenes should offer the possibility of nucleophile $^{18}F$-labelling of electron rich arenes without the need of further activating groups.

So far, reactions of symmetric and asymmetric diaryliodonium salts with n.c.a. $[^{18}F]$fluoride were only studied with non-heteroaromatic groups. However, various reactions of non-radioactive nucleophiles with aryl-heteroaryl-iodonium salts are described and show a very high regioselectivity [7, 8].

In this study, the high regioselectivity of the nucleophile attack on asymmetric iodonium salts containing the 2-thienyl group was used for preparing $[^{18}F]$fluoroanisoles as model compounds (Scheme 2). The precursor ortho-, meta- and para-methoxyphenyl-2-thienyl-iodonium salts were synthesized as their bromides and iodides according to literature [7, 9]. These iodonium salts were treated with n.c.a. $[^{18}F]$fluoride under various conditions and the desired $[^{18}F]$fluoroanisoles were obtained in moderate radiochemical yields (RCY = 18 - 42 %).
Hereby, all methoxyphenyl-2-thienylidonium iodides give higher RCY than their corresponding bromides. Furthermore, the RCY of the ortho- and para-methoxyphenyl-2-thienylidonium salts are nearly the same, but both are higher than the RCY with the meta-precursor. A so-called “ortho-effect” could not be confirmed [6].

The best results were obtained with 2-methoxyphenyl-2-thienylidonium iodide as precursor, with a RCY of up to 45%. Figure 1 shows the time dependent RCY of n.c.a. 2-[\textsuperscript{18}F]fluoroanisole in the reaction of 2-methoxyphenyl-2-thienylidonium iodide and n.c.a. [\textsuperscript{18}F]fluoride under optimised conditions. The reaction runs fast and reaches a maximum at about 20 min. The RCY of [\textsuperscript{18}F]fluoroanisoles were determined by radio-HPLC.

![Figure 1: Synthesis of 2-[\textsuperscript{18}F]fluoroanisol via 2-methoxyphenyl-2-thienylidonium iodides: RCY as a function of the reaction time](image)

In summary, the methoxyphenyl-2-thienylidonium salts represent useful precursors for n.c.a. \textsuperscript{18}F-labelling of [\textsuperscript{18}F]fluoroanisoles. Their advantage is the very high regioselectivity and the one-step preparation, leading only to the desired n.c.a. [\textsuperscript{18}F]fluoroanisoles without any radioactive side-product, which simplifies the isolation. Present studies concentrate on the use of triflate and tosylate iodonium salts as precursors.
References


SYNTHESIS OF 2′-DEOXY-2′-[\textsuperscript{18}F]-FLUORO-5-IOODO-1-\textbeta-D-ARABINOFURANOSYLURACIL (\textsuperscript{18}F]-FIAU) AND MICRO-PET IMAGING OF SUICIDE GENE EXPRESSION IN TUMOR-BEARING NUDE MICE

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Introduction: Herpes simplex virus type-1 thymidine kinase (HSV1-tk) is being used as a suicide gene for gene therapy of cancer [1,2]. An in vivo method to assess the HSV1-tk enzyme activity after gene transfer is desirable to monitor gene expression as an indicator of gene delivery. Imaging of the HSV1-tk reporter gene along with various reporter probes is of current interest [3-6]. We originally developed \textsuperscript{18}F]-FHPG and \textsuperscript{18}F]-FHBG for PET imaging of HSV1-tk gene expression [5-7] and demonstrated that \textsuperscript{18}F]-FHBG is more useful than \textsuperscript{18}F]-FHPG for this purpose [7]. \textsuperscript{125}I]-FIAU has been shown to be a potential PET imaging agent for HSV1-tk gene expression [8], and is superior to \textsuperscript{18}F]-FHPG and \textsuperscript{18}F]-FHBG. We also demonstrated that radiolabeled \textsuperscript{18}FMAU can be used as a marker for HSV-tk gene expression, and is superior to \textsuperscript{18}F]-FHPG and \textsuperscript{18}F]-FHBG [9]. Earlier we reported a synthesis for 2′-deoxy-2′-[\textsuperscript{18}F]-fluoro-5-methyl-1-\textbeta-D-arabinofuranosyluracil (\textsuperscript{18}F]-FMAU) and some other \textbeta-5-substituted nucleosides [10,11]. We have synthesized now \textsuperscript{18}F]-FIAU, used the tracer for micro-PET imaging of suicide gene expression in tumor-bearing nude mice, and compared the results with earlier studies using \textsuperscript{14}C]-FMAU.

Methods: Synthesis of \textsuperscript{18}F]-FIAU was performed following our earlier general method [11]. Briefly, 2′-deoxy-2′-trifluoromethanesulfonyl-1,3,5-tri-O-benzoyl-\textbeta-D-ribofuranose was reacted with tetraethylammonium\textsuperscript{18}F]-fluoride to produce 2′-[\textsuperscript{18}F]-fluoro-1,3,5-tri-O-benzoyl-\textbeta-D-arabinofuranose, which was converted to its 1-bromo-derivative by treatment with hydrogen bromide in acetic acid (HBr/AcOH). The \textsuperscript{18}F]-labeled bromosugar was coupled with the protected 5-iodouracil, and the product was hydrolyzed in base. The crude material was purified by HPLC to obtain the desired product \textsuperscript{18}F]-FIAU. In vitro studies were performed in HT-29 cells (human colon cancer) by incubation of \textsuperscript{18}F]-FIAU at 30 min, 1h and 2h. Uptake in cells was normalized to dpm/million cells. In vivo studies were performed on tumor-bearing nude mice. Tumors were grown using HT-29 cells, wild type on the left flank and transduced with HSV1-tk on the right flank. When tumor size was approximately 1 cm in diameter animals were used for PET imaging studies. \textsuperscript{18}F]-FIAU (0.2 mL, 0.2 mCi) was injected (iv) through the tail and micro-PET imaging studies were performed at 30 min, 1h and 2h post-injection. Biodistribution was performed at 2h post-injection using \textsuperscript{14}C]-FIAU on a different group of animals. The biodistribution result was compared with that of \textsuperscript{14}C]-FMAU.

Results: The radiochemical yield of \textsuperscript{18}F]-FIAU was 15-24% decay corrected (d. c.) with an average of 19% in 3 runs, and specific activity > 2 GBq/\mu mol at the end of synthesis. In vitro uptake of \textsuperscript{14}C]-FIAU was 20-fold to 26-fold higher in transduced cells compared to that in wild

392
type cells (Fig. 1). In vivo uptake of $[^{14}\text{C}]-\text{FIAU}$ in transduced cells was 6.8-fold higher than in non-transduced cells (Fig 2). There was a slight higher uptake of activity in kidney due to renal clearance.

![FIAU uptake in HT-29 cells](image1)
![Biodistribution of FIAU](image2)

**Fig. 1:** FIAU uptake in cells  **Fig. 2:** Biodistribution of FIAU

Micro-PET images also demonstrated selective uptake of $[^{18}\text{F}]-\text{FIAU}$ in HSV1-tk expressing tumor without any significant uptake in control tumor and organs, consistent with the biodistribution results (Fig. 3).

![30 min coronal](image3)
![2h coronal](image4)
![2h projection](image5)

**Fig. 3:** Micro-PET images

Total uptake in transduced tumors was comparable to that of FMAU, however uptake ratio (tk/w) was 1.8-fold higher due to relatively high non-specific trapping of FMAU by the host kinase (Fig. 4).
Conclusion: Synthesis of [18F]-FIAU has been accomplished. In vivo results suggest that [18F]-FIAU may be superior to [18F]-FMAU for imaging suicide gene expression in human colon cancer. [18F]-FIAU also may be superior to [124I]-FIAU due to lack of deiodination.

References

Neuronal nicotinic acetylcholine receptors (nAChR) belong to the superfamily of ligand-gated ion channels and are assembled by five protein subunits which form a barrel like structure in the cell membrane. Homomeric receptors such as the α7 subtype (an important nAChR subtype in the brain) are assembled by 5 identical subunits. The heteromeric receptor subtypes such as the α4β2 subtype (the most frequent nAChR subtype in the brain) or the α3β4 subtype (the ganglionic type nAChR, autonomic ganglia, brain) are assembled by 2 α subunits and 3 β subunits. NACHR receptors play a fundamental role in brain development and maintenance of brain function. Therefore tracers for nicotinic receptors labelled with positron emitters are of high interest for diagnosis and therapy control with PET (positron emission tomography) for instance in neurodegenerative diseases such as Morbus Alzheimer.

In this abstract we describe synthesis, radiosynthesis and biological evaluation of both stereoisomers of NCFHEB (norchlorofluorohomoepibatidine, 4) and compare the biodistribution data with 2-\[^{18}\text{F}\]fluoro-A-85380, a tracer currently used for imaging nicotinic receptors with PET [1-3].

Figure 1: Synthesis scheme of standard compounds, radiolabelling precursor and radiosynthesis of norchlorofluorohomoepibatidine.

Organic synthesis of precursors and standard compounds was performed according the reaction scheme presented in figure 1. The racemate of NCFHEB (4) was resolved on a
A solution of kryptofix 222/potassium carbonate complex containing the \(^{18}\text{F}\)fluoride in acetonitrile was reacted with 0.4 mg of \(7\) in a chemistry microwave system (CEM-discover). The reaction mixture was filtered through an Alumina N cartridge and deprotection was achieved by addition of iodo(trimethyl)silane and thermal heating. The product was injected onto a radio-HPLC system (Chirobiotik T) column. Radiochemical yield of \(^{18}\text{F}\)NCFHEB (9) was 2% for each enantiomer. 2-\(^{18}\text{F}\)Fluoro-A-85380 was prepared as described elsewhere[1]. (+)-\(^{18}\text{F}\)NCFHEB, (-)-\(^{18}\text{F}\)NCFHEB and 2-\(^{18}\text{F}\)Fluoro-A-85380 were purified on a second semipreparative HPLC-system (Mutsosphere 100 RP18-AQ, 5 % Ethanol, 95 % 20 mM NaH\(_2\)PO\(_4\) pH 4 or 3 % Ethanol, 97 % 20 mM NaH\(_2\)PO\(_4\) pH 4 respectively). The appropriate fractions were collected and diluted with buffer.

First biological evaluation of these compounds was performed by the determination of affinity to nicotinic receptors in rat thalamus homogenate by (±)-\(^{3}\text{H}\)epibatidine competition assays. In summary, the 8-N-ethylated derivatives of NCFHEB (6) show a low affinity for nAChR in rat thalamus preparation (> 100 nM) and therefore prove not to be suitable as PET tracers, while the stereoisomers of the 8-N-methylated derivatives (5) display large differences in affinity (K\(_d\)(8-N-methyl-(+)-NCFHEB) = 14.9 ± 0.4 nM, K\(_d\)(8-N-methyl-(−)-NCFHEB) = 0.11 ± 0.02 nM). These data are in good agreement with earlier results obtained by other methylated epibatidine and homoepibatidine derivatives [4, 5]. The high-affinity stereoisomer binds to the nAChR with an affinity comparable to (-)-epibatidine (K\(_d\) = 0.07 ± 0.01 nM), which is a disadvantage with respect to putative toxicity and slow pharmacokinetic behaviour. Probably long scanning times would be necessary to reach a steady state in the brain, which is disadvantageous for the application as a PET tracer. Therefore we selected both stereoisomers of NCFHEB (K\(_d\)((+)-NCFHEB) = 0.51 ± 0.16 nM, K\(_d\)((−)-NCFHEB) = 0.94 ± 0.06 nM) for further evaluation. The results of the \(^{3}\text{H}\)epibatidine competition assays performed to determine the subtype-specific affinity to human \(\alpha_4\beta_2\), \(\alpha_3\beta_4\) and \(\alpha_7\) expressed in HEK293 cells (\(\alpha_4\beta_2\) and \(\alpha_3\beta_4\)) or SH-SY5Y cells (\(\alpha_7\)) are shown in table 1. Both enantiomers of NCFHEB show a higher selectivity for \(\alpha_4\beta_2\) compared to \(\alpha_3\beta_4\) than epibatidine. The affinity to the \(\alpha_7\) subtype is too low to cause considerable changes in tissue uptake in vivo.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>HEK293-(\alpha_4\beta_2)</th>
<th>HEK293-(\alpha_3\beta_4)</th>
<th>SH-SY5Y-(\alpha_7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)-Epibatidine</td>
<td>0.014 ± 0.003</td>
<td>0.06 ± 0.02</td>
<td>67 ± 1</td>
</tr>
<tr>
<td>(+)-NCFHEB</td>
<td>0.064 ± 0.003</td>
<td>3.8 ± 0.9</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>(-)-NCFHEB</td>
<td>0.112 ± 0.035</td>
<td>2.6 ± 0.9</td>
<td>20 ± 6</td>
</tr>
</tbody>
</table>

The biodistribution of (+)-\(^{18}\text{F}\)NCFHEB, (-)-\(^{18}\text{F}\)NCFHEB and 2-\(^{18}\text{F}\)Fluoro-A-85380 was determined in awake mice at 5 min, 20 min and 60 min post injection. The highest brain uptake was found at 20 min post injection for all three tracers. The biodistribution data at this time is given in figure 2. Both stereoisomers of \(^{18}\text{F}\)NCFHEB showed a considerably higher brain uptake than 2-\(^{18}\text{F}\)Fluoro-A-85380 at 20 min, the (+)-isomer exceeding the uptake of 2-
[18F]fluoro-A-85380 by more than a factor of 2. Injection of carrier-added (+)-[18F]NCFHEB or (-)-[18F]NCFHEB at a pharmacological dose of 25 μg/kg bodyweight significantly reduced the brain uptake of (+)-[18F]NCFHEB and (-)-[18F]NCFHEB by respectively 76 % and 75 % and proved the naturability of the radiotracer binding. Because no toxic or pharmacological effects were observed at the dose of 25 μg/kg, both stereoisomers of NCFHEB display a considerably lower toxicity than other epitaxilide derivatives [4-6]. These promising results encourage us to continue with the development of these tracers for future use in PET investigations.

Figure 2: Biodistribution data of both stereoisomers of [18F]NCFHEB and 2-[18F]fluoro-A-85380 in mice after 20 min.

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ACCUMULATION AND PERSISTENCE OF NICOTINE DERIVED DNA AND HEMOGLOBIN ADDUCTS IN MICE AFTER MULTIPLE ADMINISTRATION OF 14C-NICOTINE AT LOW DOSE LEVEL

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The hypothetic role of nicotine in causing smoking related diseases has not been well established. Based on our early finding of the genotoxicity of nicotine[1], a sub-chronic study on the accumulation and persistence of nicotine derived DNA and hemoglobin (Hb) adducts in mice following multiple low dose exposures was carried out by accelerator mass spectrometry (AMS). AMS is a sophisticated ultrasensitive nuclear method, which facilitates the detection of adduction of DNA and other bio-macromolecules with xenobiotics at human relevant environmental dose levels.

Briefly, in this study [N-14CH₃]-nicotine (s.a. 16.2 μCi/μmol) was administered to mice by gavage once daily at 3.0 μg/kg b.w., which is equivalent to an estimated nicotine dose inhaled by a 70 kg person smoking 5 cigarettes, for 14 consecutive days. Lung DNA, liver DNA and Hb were isolated from tissues and blood samples which were collected at 1, 3, 5, 7, 10, 14, 15, 17, 21 and 25 days time point, respectively.

The results (Fig.1a and 1b) show that the adducts number in lung DNA, liver DNA as well as Hb increases rapidly during the first 7 days of nicotine exposure, then the increasing rate slows down. After the 14th day exposure, the adduct number in lung DNA is about twofold of that in liver DNA, whereas the adducts in Hb only count for 2.9% of that in lung DNA. In the time course study after the cessation of nicotine exposure, the decay half-life of lung DNA and liver DNA adducts is 9.5 and 5.8 days respectively (P<0.05). The longer half-life of lung DNA adducts indicates that lung tissue has lower efficiency of eliminating nicotine-derived DNA adducts. Therefore, during the long-term smoking, nicotine may cause more damages to lung DNA than that to liver DNA. That is compatible to the epidemiologic data that smoking causes lung cancer mostly [2].

Meanwhile, Fig. 1b shows the nicotine-Hb adducts remain much longer than DNA adducts do and have a decay half-life of 30.9 days, which is close to the lifespan of mouse erythrocytes (≈ 40 days). This indicates that the nicotine-Hb adducts are quite stable in vivo. Since the Hb adducts have no repair system towards modification, it is more suitable than the DNA adducts for use as a biomarker for the internal dosimetry of nicotine.

Concerning the mechanism of nicotine adduction with DNA and Hb, the possible paths were discussed. The path of demethylation of the N-methyl group of nicotine yielding its metabolite formaldehyde may play an important role in the formation of nicotine-derived DNA/Hb adducts. To clarify whether there existed 14C incorporation into DNA/Hb molecules
from the one carbon pool, further study combined with the HPLC technique is ongoing in this lab.

Fig.1. Accumulation and persistence of nicotine derived DNA/Hb adducts in mice. Mice were administrated [N-\(^{14}\text{CH}_3\)]-nicotine 3.0 µg/kg/day for certain consecutive days. The samples were collected and isolated at 1, 3, 5, 7, 10, 14, 15, 17, 21 and 25 days as described. Most data are means ± SD of three parallel samples, except n=2 at 25 days time point for lung, at 7, 21, 25 days time points for liver, and n=1 for 3, 14, 17 days time point for liver.

References
ASTATINATION OF NANOPARTICLES CONTAINING SILVER AS POSSIBLE CARRIERS OF $^{211}$AT FOR CANCER THERAPY

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Alpha emitter $^{211}$At (7.214 h) is considered to be a promising radionuclide for targeted cancer therapy due to its decay properties, for it may deliver large radiation doses into small volumes of cancer tissue, not affecting much the surrounding healthy tissue [1–3]. Different carrier systems were proposed for transport of $^{211}$At to tumours: monoclonal antibodies and their fragments, steroid hormones, epidermal growth factor, smaller molecules preferentially metabolized by cancer cells (methylene blue) or colloids and microspheres [1,2]. From the last group of carriers, tellurium colloids with attached $^{211}$At showed encouraging results in the curing of mice with malignant ascites [4], but the low stability of the colloid excluded any clinical testing [4,5]. Due to this stability problem, the monodisperse 1.8μm polymeric microspheres were prepared and proposed for the same purposes, and their in vitro stability seemed to be sufficient [6].

Concerning drug delivery systems of colloidal character in general, much attention has been recently paid to nanoparticles of well-defined chemical composition and molecular weight [7,8]. These systems themselves concentrate in tumour tissues via so-called “enhanced permeability and retention effect” (EPR effect), or they can be modified by attachment of any tumour recognizing molecule (e.g. MABs) in order to increase the specific uptake in the cancer tissue. In addition, a surface modification of nanoparticles by hydrophilic polymers, e.g. poly(ethylene glycol), PEG, which repel plasma proteins, together with the proper choice of their size may protect them from being quickly opsonized and then absorbed by macrophages [7].

We studied the possibility to label colloidal systems containing silver, which can be used as a good linker of astatine to nanoparticles. Remarkable affinity of astatine towards metallic silver is known for a long time [9].

In the beginning, commercially available colloidal silver (silver protein) was used to get preliminary data. It was found that it is labelled with high yields (> 94 %) within 10 min in the pH range 5–8. The label was found to be stable after separation on size exclusion chromatography after 5 h even in the presence of high surplus of chloride ions. Labelling take place spontaneously, and the presence of oxidizing (Chloramine-T) or reducing (ascorbic acid) agents does not practically change the yield.

Based on these results, a new nanoparticle system was developed, containing colloidal silver covered by non-immunoreactive PEG of defined size and weight. Two groups of particles of
ca 120 and 160 nm diameter and respective weights 2000 and 5000 were prepared and
labelled under the similar conditions like silver protein. The system was successfully asta-
inated with high yields (> 90%) in very short time (10 min) in neutral pH and does show high
stability even in the presence of competing chloride ions. We are currently continuing work in
this field.

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TUMOR TARGETED LIPOSOMES FOR NEUTRON CAPTURE THERAPY

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Introduction

The concept of neutron capture therapy (NCT) was introduced as early as 1926, only four years after the discovery of neutrons [1]. It is based on the delivery of an appropriate stable isotope, usually \(^{10}\)B, to the tumor and the subsequent induction of radioactivity by local irradiation with a neutron beam. \(^{10}\)B is irradiated with low energy neutrons to yield \(^{4}\)He (α particles) and \(^{4}\)Li nuclei. These nuclei deposit their energy within a relatively short range (10 μm), representing approximately one cell diameter. This process induces DNA strand breaks and arrests tumor cell growth. Moreover, a gammaphoton of 0.48 MeV is emitted which can be used to image the ongoing neutron capture.

Clinical trials have been performed with patients who have brain cancer (glioblastoma) or melanoma using two boron-containing compounds: an amino acid derivatized boronophenylalanine (BPA) and a polyhedral borane structure disodium mercapto-dodecaboronate (BSH). However, the success of these trials has been limited, mainly due to the relatively poor tumor targeting characteristics of the compounds used [2,3].

The neutron capture therapy field is now awaiting approaches that allow for specific targeting to tumors of large quantities of the NCT compounds. For this purpose, we are using recently developed liposomal targeting devices to improve tumor specificity and to deposit much higher amounts of \(^{10}\)B into the tumors than can normally be obtained with free compounds [4]. Liposomes are small vesicles (typically 100 nm) composed of a phospholipid bilayer enclosing an aqueous phase (Fig. 1). They are promising carriers for tumor delivery of NCT compounds as they: (1) can encapsulate or incorporate both hydrophilic and hydrophobic compounds in high quantities in their aqueous interior or in the lipid bilayer, respectively, (2) protect their contents from degradation, (3) efficiently localize in tumors due to their size, favorable pharmacokinetics and the leaky characteristics of tumor vasculature, (4) can be modified at their surface with targeting ligands such as antibodies or peptides.

Figure 1. Schematic representation of a liposome vesicle composed of a bilayer containing phospholipid and cholesterol in which water soluble and lipophilic drugs can be incorporated. The liposome surface can be modified with polymers (e.g. to shield from recognition by the immune system) and proteins and peptides which can be used for cell specific targeting.
The most important advantage of the use of NCT over more conventional liposomal drug delivery approaches e.g. in chemotherapy, is that the neutron beam can be used to irradiate a small area where a tumor is present. This local production of radioactivity after delivery of the drug will prevent toxicity caused by undesired liposomal homing, usually to liver, spleen and skin.

The aim of our work was to develop $^{10}$B-loaded liposomes as a platform for the coupling of targeting ligands that allow for tumor specific targeting and NCT. Two approaches for tumor targeting were adopted; first, direct targeting to tumor cells using a tumor cell specific monoclonal antibody attached to the liposomes [5] and second, targeting to tumor vasculature using liposomes equipped with a RGD-sequence containing peptide [6].

Methods

Liposomes composed of dipalmitoylphosphatidylethanolamine (DPPC), cholesterol (Chol), Polyethylene glycol (PEG)2000-distearylphosphatidylethanolamine (DSPE) and maleimide-PEG-DSPE (molar ratio 1.85:1.0.075:0.075) were prepared by the lipid film hydration method [5,6] in a HEPES-buffer containing 30 mg/ml disodium dodecahydrododecaborate (DHDB). Non-encapsulated DHDB was removed by ultracentrifugation. Antibodies and peptides were covalently coupled to the liposomes using sulphydryl-maleimide coupling chemistry [5,6]. Liposomes were analyzed for phosphate content, size and protein content, all as described before [5,6]. Liposomal DHDB content was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). Cellular association and localization of fluorescently labeled liposomes with human ovarian cancer OVCAR3 cells or human umbilical vein endothelial cells (HUVEC) was assessed by confocal laser scanning microscopy using a Leica TCS-SP system.

Results and discussion

Liposome preparation and characterization

Liposomes were sized to 100 nm as this meets the requirements of the leaky tumor vasculature. We were able to encapsulate DHDB into these liposomes up to concentrations of 30 μg per μmol of lipid, equating an encapsulation efficiency of 3 to 5%. These levels are to be expected for passive loading of hydrophilic compounds into small liposomes [7]. Experiments assessing the stability of the liposomes revealed that when incubated at 4°C liposomes retained their content for the study period of 3 weeks. Incubations of the liposomes at 37 °C showed no leakage of DHDB for a period of up to two days. In both experiments no increases in size of the liposomes was observed. These observations are relevant in view of storage of the liposomes after preparation and shows that they can be used for at least a period of 3 weeks after preparation. Incubations at 37 °C suggest stable encapsulation of the boron compound during incubations with cells and when used in vivo in the near future. Premature leakage of liposome contents in circulation would lower the efficiency of delivery to the tumor site and could result in unwanted toxicities by distributing to normal cells in the body.

Cellular uptake of liposomes

Liposomes should retain their content until arrival at the tumor site. There, cell-specific and intracellular delivery of the DHDB should be facilitated by the targeting ligand attached to the liposomes. To achieve tumor cell targeting, a monoclonal antibody that recognizes the epidermal growth factor receptor (EGFR) was coupled to the liposomes. The EGFR is overexpressed on a variety of tumor cells, including the OVCAR3 human ovarian cancer cell line [5]. These tumor cell targeted liposomes showed enhanced interaction with human ovarian cancer cells and cellular uptake of the liposomes as proven by the presence of intense
punctuated fluorescence intracellularly as observed by confocal laser scanning microscopy (Fig. 2).

In addition, we aim to target the tumor vasculature, because damage there can strongly inhibit tumor activity [6]. Moreover, it was recently reported that endothelial cells have considerable radiosensitivity [8,9], suggesting that tumor vasculature-targeted NCT may offer a promising approach in radiotherapy. Specific targeting to tumor vasculature may be achieved by targeting liposomes to integrin αv-receptors, which are overexpressed on angiogenic endothelial cells [6]. We used liposomes with an RGD-peptide coupled to specifically target this receptor. Binding and internalization of RGD-liposomes by proliferating endothelial cells (HUVEC) in culture was also evident from the punctuate intracellular fluorescence pattern observed by confocal microscopy (Fig. 2).

Internalization and localization of NCT compounds in close proximity of the nucleus as was observed for both types of targeted liposomes, is of major importance in view of the short range of the produced radioactivity and the importance of DNA damage in killing of tumor cells and cells of the tumor vasculature. Cellular uptake of boron-loaded liposomes by both OVCAR3 and HUVEC cells was assessed by ICP-OES after incubating cells with different liposome formulations and confirmed the microscopy findings (data not shown).

Studies in the near future will address the therapeutic activity of tumor cell as well as tumor vasculature targeted liposomes encapsulating NCT compounds towards different types of tumors in vitro and in vivo.

Conclusion

We have available several tumor targeted liposomal systems that can efficiently retain a hydrophilic boron compound. Internalization of these targeted liposomes by tumor cells and endothelial cells was proven and allows for efficient delivery of the NCT compounds intracellularly. Targeted liposomal delivery of NCT compounds to tumor cells as well as to tumor vasculature represents an attractive approach in the treatment of cancer, combining the advantages of liposomal drug delivery with those of neutron capture therapy.

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A NEW $^{72}\text{Se}/^{72}\text{As}$ RADIONUCLIDE GENERATOR BASED ON SOLID PHASE EXTRACTION

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Radionuclide generator systems play an important role in providing both diagnostic and therapeutic radioisotopes for various applications in nuclear medicine. The most commonly used radionuclide in nuclear medicine, namely $^{99m}\text{Tc}$, is produced via the $^{99}\text{Mo}/^{99m}\text{Tc}$ generator system. Similarly, the application of positron emission tomography (PET) at centres not possessing a cyclotron to produce the necessary radioisotopes depends on the availability of biomedical PET radionuclide generators.

The radionuclide generator $^{72}\text{Se}/^{72}\text{As}$ consists of the long-lived mother, $^{72}\text{Se}$ ($T_{1/2} = 8.5\text{ d}$, 100% e) and the short-lived daughter, $^{72}\text{As}$ ($T_{1/2} = 26\text{ h}$, 88% β$^\text{+}$). The aim of this study was to develop a $^{72}\text{Se}/^{72}\text{As}$ generator relevant to the routine separation of $^{72}\text{As}$ to provide a reliable source for the future use of $^{72}\text{As}$ in radiopharmaceutical labelling chemistry.

Different radiochemical no-carrier-added (nca) generator procedures have been published, based on either:
- distillation of nca $^{72}\text{AsCl}_3$ from nca $^{72}\text{Se}$ solutions under HCl flow [1];
- filtration after addition of selenium carrier in form of selenic acid and cyclic reduction of selenium to $\text{Se}^{(0)}$, with $^{72}\text{As}$ separated by filtration with subsequent oxidative dissolution of $\text{Se}^{(0)}$ using $\text{H}_2\text{O}_2$ prior to each cycle [2];
- elution of $^{72}\text{As}$ from a coagulated form of carrier-added $^{72}\text{Se}$ on a Dowex 50 column in 15 ml of water [3].

However, in each case, complexity, separation quality or operating expenses are too high to allow their use for any practical application. Therefore the development of a new and more reliable $^{72}\text{Se}/^{72}\text{As}$ radionuclide generator was necessary prior to the development of a new $^{72}\text{As}$-labelling chemistry.

The $^{72}\text{Se}$ was produced at the Forschungszentrum Jülich via the $(^1\text{He},3n)$-reaction on natural germanium at a beam current of 5 $\mu\text{A}$ for 12 h, giving a yield of 5 mCi. To simulate the behaviour of $^{72}\text{Se}$, $^{72}\text{Se}$ was used in some cases, which was produced via the $(n,\gamma)$-reaction at the nuclear research reactor at the HMI Berlin.

100 mg of irradiated natural germanium were dissolved in 5 ml $\text{HF}_{\text{conc}}$ and 500 µl $\text{HNO}_3$ at $T = 25\text{ }^\circ\text{C}$ within 3 hours. Aliquots of 100 µl were added to 5 mg of hydrazine dihydrochloride in 900 µl $\text{HF}_{\text{conc}}$ and the mixture was stirred for 30 min. The concept of the new generator is based on the reduction of $^{72}\text{Se}$ to $^{72}\text{Se}^{(0)}$ with hydrazine dihydrochloride without addition of any carrier. This metallic nca selenium can be fixed up to 99% by a standard solid phase extraction system based on a polystyrol matrix. An ENV-solid phase extraction cartridge was preconditioned with 5 ml of MeOH, 5 ml H$_2$O and 5 ml $\text{HF}_{\text{conc}}$. $^{72}\text{Se}^{(0)}$ is fixed to the solid phase, while macroscopic Ge is eluted with the mobile phase as [GeF$_3$]$^-$, cf. Fig. 1
Fig. 1:
Scheme of a $^{72}$Se/$^{72}$As-Radionuclide generator based on solid phase extraction

1. Nitrogen
2. Acetonitrile
3. Aqu 
4. HF with KI
5. HF with hydrazine hydrochloride
6. Chloroform
7. Target
8. Reactor I
9. Reactor II
10. Generator cartridge
11. Solid phase extraction
12. Drying cartridge
13. Waste
14. Product, nca $^{72}$AsI$_3$

The produced $^{72}$As daughter can be subsequently eluted using 1 ml HF$_{con}$ giving $\geq 50\%$ yield already in the first 200 $\mu$l, cf. Fig. 2. The amount of selenium occurring in the product fraction is less than 0.01%. The radiochemical purity is demonstrated in Fig. 3.

Fig. 2: Typical elution profile of a 100 $\mu$Ci $^{72}$Se/$^{72}$As radionuclide generator (eluted with HF$_{con}$)
Fig. 3: a) γ-ray spectrum of the $^{72}\text{Se}/^{72}\text{As}$ radionuclide generator before elution (characteristic emissions of $^{75}\text{Se}$, a side-product of cyclotron production of $^{72}\text{Se}$, are used as an indicator for radioselenium) b) γ-ray spectrum of nca $^{72}\text{As}$ after elution, characteristic γ-lines: 511 keV (176 %), 834 keV (80 %), 1023 keV (sum-peak)

For subsequent radiopharmaceutical synthesis the arsenic has to be transformed into a suitable chemical form. Consequently, to the eluent obtained, 10 mg KI are added, forming nca $^{72}\text{AsI}_3$. The mixture is stirred for 10 min at room temperature. Then it is transferred to a second solid phase extraction cartridge, where $^{72}\text{AsI}_3$ is fixed to the solid phase. It is eluted with chloroform and dried with CaCl$_2$. With KI, nca $^{72}\text{AsI}_3$ is formed quantitatively. As this compound is soluble in organic solvents, the product fraction of the new generator can be used directly for organic synthesis.

References
QUANTITATIVE PET-IMAGING WITH THE NON-PURE POSITRON EMITTERS $^{124}$I AND $^{86}$Y

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The commonly used radionuclides in positron emission tomography (PET) are the short-lived positron emitters $^{11}$C, $^{13}$N, $^{15}$O, and $^{18}$F. If slow biological processes are to be observed with PET, longer-lived non-pure positron emitters such as $^{124}$I or $^{86}$Br are useful. Furthermore, the non-pure positron emitter $^{86}$Y has often been chosen to quantify the biodistribution and dosimetry of radiotherapeutics labelled with the purely β-emitting analogue isotope $^{90}$Y. The quantitation of the radioactivity of non-pure positron emitters is, however, hampered by the existence of prompt gamma coincidences which are recorded within the coincidence time window of, e.g. 12 ns, in addition to the commonly registered true, random and scattered coincidences. A gamma coincidence occurs, if one annihilation photon is recorded simultaneously with a single photon which is emitted in cascade with the positrons and fits into the energy window of the detector directly or after Compton scattering. The amount of gamma coincidences especially increases in the 3D acquisition mode for which the septa are not extended. Although different correction procedures are available for random and scattered coincidences, they do not apply to gamma coincidences. As a result gamma coincidences cause a background in sinograms and lead to errors both in qualitative and quantitative respects. Here we report on our experience with the non-pure positron emitters $^{124}$I and $^{86}$Y which were investigated with different phantoms, PET scanners, and acquisition modes.

High-purity $^{124}$I was produced via the $^{124}$Te(p,n) nuclear reaction [1] on 99.8% enriched $^{124}$TeO$_2$ using the proton energy range of 13.5 → 9 MeV. $^{124}$I was evaluated by comparative phantom measurements using the 2D-PET-scanner GE/Scanditronix PC4096+ and the Siemens/CTI ECAT Exact HR+ scanner operated in 2D and 3D modes. The phantom studies utilised a line source placed in water and air, the 3D-Hoffman brain phantom, and a phantom consisting of two chambers (2C-phantom) which simulates the grey/white matter (GM/WM) distribution at the level of the basal ganglia. In this 2C-phantom, the region of interest (ROI) could be defined without partial volume effect.
$^{86}$Y was obtained via the $^{86}$Y(p,n) nuclear reaction [2] on 96.3% enriched $^{86}$SrCO$_3$ over the proton energy of 14 $\to$ 10 MeV. The measurements with $^{86}$Y were done with a water-filled cylindrical phantom of 22 cm diameter containing three cold rods, i.e. a solid rod of teflon (density of bone) and two rods, one filled with air, the other with water, each with a diameter of 5 cm. The water outside the rods had a radioactivity concentration of about 5 kBq/ml $^{86}$Y, as determined by $\gamma$-ray spectroscopy. The phantom was positioned in the centre of the field of view. PET acquisitions were done with the PC4096+ scanner in 2D and the HR+ scanner in 2D- and 3D-mode. Furthermore, different percentages of background were subtracted in the case of 3D acquisition with the HR+. These were 25%, 50%, 75% and 100% of the background counts measured in the random corrected sinograms outside the phantom. All sinograms including the background corrected ones were scatter and attenuation corrected and reconstructed by filtered backprojection with the common settings.

The reconstructed image resolution (FWHM) for $^{124}$I was 0.5 to 1 mm inferior to that for $^{18}$F. Analysis of sinograms showed an increased background (Fig.1) caused by gamma-coincidences (data obtained in air) and scattered coincidences (data obtained in water). Imaging of the 3D-Hoffman brain phantom revealed a loss of resolution and contrast when $^{124}$I was used in comparison to $^{18}$F (Fig.2). The tests with the 2C-phantom demonstrated the increase of gamma-coincidences in the 3D mode by a higher GM/WM ratio compared to the 2D-acquisitions. Compared to the PC4096+ the radioactivity distribution reconstructed with the HR+ either in 2D or 3D mode was lower, e.g., when the radioactivity found with the PC4096+ was underestimated by -4%, the corresponding numbers of the HR+ ranged between -16% and -24%. Some results on these measurements have been published [3]; more detailed studies are continuing.

![Fig.1 Profiles across a sinogram of a line source filled with $^{18}$F or $^{124}$I and measured in water with the 3D-acquisition mode.](image1)

![Fig.2. Reconstructed images of a 3D Hoffman phantom filled with $^{18}$F (left) or $^{124}$I (right) and recorded with the 3D-acquisition mode.](image2)
When the reconstructed ratios of the measured radioactivity concentration of $^{86}$Y was related to the true ones, overestimations became obvious, i.e. a measured/true ratio of 1.17 was found for the HR+ in 2D, 1.51 for the HR+ in 3D and 1.09 for the PC4096. Considerable amounts of reconstructed $^{86}$Y radioactivity were found within the teflon and water rods, especially in the 3D-mode (Fig.3). The overestimations of the $^{86}$Y radioactivity in the teflon and water rods could be reduced by background subtraction applied to the sinograms, whereas this procedure led to increased values within the air-filled rod.

![Fig 3 Images of the 3 rod phantom filled with $^{86}$Y before (left) and after (right) subtraction of background applied to the sinograms (a: rod consisting of teflon; b: rod filled with water; c: rod filled with air).](image)

Our study demonstrates that quantitation of the radioactivity of non-pure positron emitters must take into account the specific decay characteristics. An isotope like $^{124}$I which emits only a minor part of its gamma radiation in cascade with the positron emission and within the energy window of the PET scanners may be quantified without the need of additional corrections. Such corrections, however, are necessary for $^{86}$Y due to its high amount of gamma coincidences. Especially in the case of 3D recording, there is a need for correction procedures which combine the elimination of scattered and gamma coincidences.

References


BIODISTRIBUTION AND TUMOR UPTAKE OF IODINE-125-LABELLED FULLEROLS IN MICE

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Ever since the bulk preparation of fullerene is established, lots of interests arise for its biological applications. Since the proposed photodynamic therapeutic property of fullerene has been reported [1] and fullerols are the most easily available water-soluble fullerene derivatives, thus we prepared ¹²⁵I-C₆₀(OH)ₓ, studied its biodistribution in mice and tested its accumulation in two tumor models.

The C₆₀(OH)ₓ used herein was synthesized following a reported method [2]. Radioiodination was carried out by in situ oxidation of sodium iodine-125 using chloramine-T. In brief, a mixture of 100 µg C₆₀(OH)ₓ, 10 µl of carrier-free Na¹²⁵I (Perkin-Elmer, USA) and 20 µl of 5 mg/ml chloramine-T was reacted in deionized water for 30 min at room temperature. Then the reaction was terminated with 40 µl of 5 mg/ml Na₂S₂O₅. A Sephadex G-15 column (8x180 mm) was used to separate the ¹²⁵I-C₆₀(OH)ₓ from ¹²⁵I⁻. The radioactivity was detected by a γ counter (E 5002, Packard, USA). The radiochemical purity and the stability of ¹²⁵I-C₆₀(OH)ₓ were examined by TLC.

Two tumor models were employed in the study of distribution of ¹²⁵I-C₆₀(OH)ₓ. The first one is mouse H₂₂ hepatocarcinoma implanted on the hind legs of 30 Kunming mice (6 mice per group). Each mouse was intravenously injected with 100 µl of the ¹²⁵I-C₆₀(OH)ₓ solution (ca. 1x10⁶ cpm). They were sacrificed at 1h, 6h, 24h and 72h post dosing, respectively. Skin, muscle (leg), bone (shank), brain, heart, lungs, liver, kidneys, spleen, stomach (emptied) and large/small intestines (emptied), as well as tumor were immediately dissected, and the blood was collected. Each organ was wrapped in an aluminium foil, weighed and counted. The distribution was expressed as % I.D./g tissue. Urine and feces were also collected for the fifth group of mice over the 72h period. The second one is human OS732 osteosarcoma implanted on the hind legs of 5 nude mice. The distribution study was done only at 24 h time point post-dosing.

Fig. 1 clearly shows that ¹²⁵I-C₆₀(OH)ₓ was distributed in all tissues. Liver, bone, kidney and spleen are the major organs retaining ¹²⁵I-C₆₀(OH)ₓ. As time elapsed, the distribution in most tissues decreased gradually, except the activity in bone remains within the experimental span. This result is similar to a previous biodistribution study of ⁹⁹mTc-C₆₀(OH)ₓ in rabbit [3]. In the excretion study, about 56% of the total activity was excreted till 72 h post dosing. Among which, 92% was in the urine and only 8% in the feces. The distribution in nude mice is similar to that of Kunming mice at 24 h time point. However, the accumulations in two kinds of tumor are rather different. The T/N ratio (tumor to normal muscle tissue) for H₂₂ hepatocarcinoma is 3.4 ± 0.8, whereas for OS732 osteosarcoma is 1.2 ± 0.3 only that indicates no accumulation in OS732 osteosarcoma. Although there is slight accumulation in H₂₂ hepatocarcinoma, it is not suitable for the proposed further study of the photodynamic therapy.
Fig.1. The biodistribution of $^{125}$I-C$_{60}$(OH)$_x$ in H$_2$2 hepatocarcinoma bearing mice at different time points post dosing.

References
SYNTHESES OF $^{18}$F-LAabeled ACYCLIC PURINE AND PYRIMIDINE NUCLEOSIDES INTENDED FOR MONITORING GENE EXPRESSION

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Gene therapy is a rapidly evolving experimental modality for the treatment of numerous human diseases. Amongst other things, suicide gene therapy with herpes simplex virus 1 thymidine kinase gene (HSV-1 tk) gives a strategy to treat malignancies. Positron emission tomography (PET) shows a promise for a non-invasive monitoring of location, duration and magnitude of the viral kinase enzyme expression [1]. HSV-1 tk can not only be used as ‘marker gene’ in a direct gene therapy approach but also as reporter gene for ‘indirect’ imaging of other therapeutic transgenes. [$^{18}$F]FHBG 1 has been used as PET marker in a HSV-1 tk based approach of cardiac gene expression [2]. Several nucleoside analogs labeled with fluorine-18 used as reporter probes have been developed. They are often derivatives of acyclonucleosides, among them the well-known 9-[(3-$^{18}$F]-fluoro-1-hydroxy-2-propoxy)methyl]guanine ([$^{18}$F]FHPG) 2, and 9-[(4-$^{18}$F]-fluoro-3-hydroxymethyl]butyl]guanine ([$^{18}$F]FHBG) I [3, 4]. Phosphorylation of these radioactive labeled nucleoside analogs by virus-encoded thymidine kinase leads to metabolites trapped within the infected tumor cells, and the ensuing accumulation of radioactivity allows monitoring of the enzyme activity with PET.

To search improved PET radiotracers for gene therapy monitoring in addition to [$^{18}$F]FHBG 1 and [$^{18}$F]FHPG 2 a series of novel acyclic nucleosides were synthesized (Fig. 1).

![Figure 1: Synthesized $^{18}$F-labeled acyclonucleosides](image)

The tracers were produced by nucleophilic substitution of the corresponding precursors with a K[$^{18}$F]F/kryptofix 2.2.2™ complex and subsequent cleavage of methoxytrityl protecting groups under acidic conditions followed by HPLC separation (scheme I, considering [$^{18}$F]FHBG 1 as example). The radiochemical yield of the $^{18}$F-tracers amount to 5-15% (decay
corrected) after a synthesis time of 85-95 min, the radiochemical purity was > 98% and the average specific activity was 19 GBq/μmol at the end of synthesis. The labeling procedures of \([^{18}F]FHBG\) 1, \([^{18}F]FHPG\) 2 and of the new tracers 3 - 8 were studied in detail. Synthesis of the precursors and the reference substances was an extensive multistep procedure [5].

![Scheme 1: Labeling procedure](image)

To evaluate the behavior of the new fluorinated compounds 3-5 and their related hydroxylated analogs against the viral thymidine kinase, screening tests with the isolated enzyme HSV-1 TK were performed. Cell uptake studies in transfected (HT-29 tk + and MC38 tk +) and non-transfected cells (HT-29, MC38) with 3-5 were also carried out and the results were compared with the cell uptake of 1 and 2, pointing out that the uptake is depending on the cell types used.

The antiviral activity of several nucleoside analogs is often limited by a fast degradation caused by human thymidine phosphorylases (TP). Because acyclic derivatives are generally more stable against TP, the behavior of the new compounds against this enzyme will be tested. The synthesis of inhibitors for TP will be an alternative approach in gene therapy experiments.

References


CARBON SOURCES WHICH DECREASE THE SPECIFIC ACTIVITY OF $[^{13}C]CH_3$I SYNTHESIZED BY THE SINGLE-PASS $I_2$ METHOD

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Introduction
Using the single pass $I_2$ method, Suzuki et al. have developed an automated synthesis system for producing $[^{13}C]CH_3$I and synthesizing several PET ligands with specific activities of $4700\pm/2500$ GBq$\mu$mol (1,2). However, during the production of the PET ligands, significant decrease ($<30$ GBq$\mu$mol) of the specific activity of $[^{13}C]CH_3$I was occasionally encountered. The sudden decrease of the specific activity took place only after the used $I_2$ and Ascarite in the quartz tube were replaced, while the other parts including the target system, transferring gas and Porapak Q trap remained unchanged. Therefore, we assumed that some organic reagents serving as sources of contaminants in the synthetic line may react with $I_2$ to form CH$_3$I in the heated quartz tube, resulting in a decrease of the specific activity of $[^{13}C]CH_3$I. In this study, we attempted to determine the putative carbon sources decreasing the specific activity of $[^{13}C]CH_3$I synthesized by the $I_2$ method.

Results and Discussion
1. Heating organic reagents with $I_2$ in the quartz tube
Some organic solvents and oils were heated with $I_2$ in the quartz tube to determine whether carrier CH$_3$I was formed during the process (Figure 1).

Figure 1. Schematic diagram for producing the carrier CH$_3$I and $[^{13}C]CH_3$I

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After the organic solvent (100 μL) in vessel A was passed into the heated quartz tube with He gas, the gas reactants were collected for 10 min in vessel B containing CH₃CN. As shown in Table 1, these reagents reacted at 630°C with I₂ to yield CH₃I at different efficiencies. Even when only 1 μL of acetone was used, 80 nmol of CH₃I was formed, an amount sufficient to decrease the specific activity of [¹¹C]CH₃I significantly. Then, the non-volatile silicone oil or paraffin (500 mg) was inserted into the inner surface of the quartz tube, and the quartz tube was set in the device and heated, and the formation of CH₃I was determined for at least 40 min in the solution for collecting the gas reactants from the tube, although the amount of CH₃I trapped in the CH₃CN solution was found to decrease with the passage of time.

Table 1. Amount of carrier CH₃I in the trapping solution by heating organic reagents with I₂ in the quartz tube at 630°C

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction time</th>
<th>CH₃I trapped in 500 μL CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COCH₃</td>
<td>1.4 mmol</td>
<td>81.8 ± 5.3 μmol</td>
</tr>
<tr>
<td>CH₃COCH₃</td>
<td>13.6 μmol</td>
<td>80.7 ± 5.5 nmol</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>2.5 mmol</td>
<td>507.5 ± 7.4 μmol</td>
</tr>
<tr>
<td>DMF</td>
<td>1.3 mmol</td>
<td>1.4 ± 0.2 μmol</td>
</tr>
<tr>
<td>CH₃COOEt</td>
<td>1.0 mmol</td>
<td>3.1 ± 0.1 μmol</td>
</tr>
<tr>
<td>THF</td>
<td>1.2 mmol</td>
<td>5.1 ± 0.9 mmol</td>
</tr>
<tr>
<td>(CH₃)₂CO₂O</td>
<td>1.0 mmol</td>
<td>2.2 ± 0.2 mmol</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>1.9 mmol</td>
<td>2.0 ± 0.8 mmol</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>500 mg</td>
<td>165.4 ± 5.8 mmol</td>
</tr>
<tr>
<td></td>
<td>1 st 10 min</td>
<td>165.4 ± 5.8 mmol</td>
</tr>
<tr>
<td></td>
<td>2 nd 10 min</td>
<td>107.5 ± 3.1 mmol</td>
</tr>
<tr>
<td></td>
<td>3 rd 10 min</td>
<td>46.8 ± 2.9 mmol</td>
</tr>
<tr>
<td></td>
<td>4 th 10 min</td>
<td>2.3 ± 0.3 mmol</td>
</tr>
<tr>
<td>Paraffin,</td>
<td>500 mg</td>
<td>390.6 ± 8.2 mmol</td>
</tr>
<tr>
<td></td>
<td>1 st 10 min</td>
<td>390.6 ± 8.2 mmol</td>
</tr>
<tr>
<td></td>
<td>2 nd 10 min</td>
<td>99.2 ± 9.0 mmol</td>
</tr>
<tr>
<td></td>
<td>3 rd 10 min</td>
<td>46.4 ± 4.8 mmol</td>
</tr>
<tr>
<td></td>
<td>4 th 10 min</td>
<td>7.2 ± 0.6 mmol</td>
</tr>
</tbody>
</table>

a) Amount of CH₃I (mean ± SE, n = 3) as determined by analytic HPLC from a sample withdrawn from the CH₃CN solution.

The mechanism of formation of CH₃I by these treatments was considered to be as follows. At high temperatures, I₂ is easily cleaved into iodine radicals which may attack the organic reagents to produce CH₃I or iodinated compounds, which may further undergo pyrolysis to yield CH₃I. On the other hand, many organic solvents were found to decompose into methyl radicals as the initiation product during pyrolysis at high temperatures (3); the methyl radicals could then bind with the iodine radicals to form CH₃I.

2. Radiosynthesis of [¹¹C]Flumazenil

To ascertain whether the above organic reagents were the sources of contaminants during
[\textsuperscript{11}C]CH\textsubscript{3}I production, we synthesized [\textsuperscript{11}C]flumazenil under the above conditions and determined whether the specific activity of [\textsuperscript{11}C]flumazenil was decreased. After [\textsuperscript{11}C]CH\textsubscript{4} was allowed to leave the pompek Q trap and mix with acetone or hexane (10 \textmu L), the mixture was introduced into the heated quartz tube to form a mixture of [\textsuperscript{11}C]CH\textsubscript{3}I and putative CH\textsubscript{3}I for the synthesis of [\textsuperscript{11}C]flumazenil. In the presence of acetone or hexane, the specific activity of [\textsuperscript{11}C]flumazenil was reduced to about 1 GBq/\textmu mol, whereas the control level was 2000 GBq/\textmu mol. After the quartz tube was replaced, [\textsuperscript{11}C]flumazenil was synthesized again according to the routine production procedure and its specific activity had recovered to 2440 GBq/\textmu mol. These results suggest that the decrease of the specific activity of [\textsuperscript{11}C]flumazenil was mainly due to the carrier CH\textsubscript{3}I resulting by the reaction of acetone or hexane with I\textsubscript{2} in the heated quartz tube.

Through our experiments, we found that traces of organic reagents, such as CH\textsubscript{2}OH, acetone, silicone oil and paraffin, reacted with I\textsubscript{2} to form CH\textsubscript{3}I in the heated quartz tube, resulting in a significant decrease in the specific activity of [\textsuperscript{11}C]CH\textsubscript{3}I. These sources of contaminants may arise from the atmosphere of the chemical laboratory or humans, or arise from the washing of device components or operation of vacuum pumps. Thus, if a sudden decrease in the specific activity of [\textsuperscript{11}C]CH\textsubscript{3}I is encountered, timely replacement of I\textsubscript{2} and Ascarite, as well as of the quartz tube, is recommended in addition to routine maintenance of the synthesis system. When these materials are changed, their careful handling is necessary. The tube must be carefully washed, dried under a vacuum and returned to the atmospheric pressure with an inert gas before I\textsubscript{2} and Ascarite with high qualities are re-inserted into the quartz tube. Moreover, direct touching of these reagents or of the inner surface of the quartz tube by the handler must also be avoided. To achieve extra high specific activity of [\textsuperscript{11}C]CH\textsubscript{3}I using the single pass I\textsubscript{2} method, the present findings should be taken into consideration when using the [\textsuperscript{11}C]CH\textsubscript{4} production, pre-irradiation and target systems described by Suzuki et al. (1).

Conclusion
In this study, we determined that some organic reagents may serve as sources of contaminants decreasing the specific activity of [\textsuperscript{11}C]CH\textsubscript{3}I synthesized by the single-pass I\textsubscript{2} method. These findings may be helpful and advisable for producing [\textsuperscript{11}C]radioligands with extra high specific activity using the single-pass I\textsubscript{2} method as well as the recirculating I\textsubscript{2} method.

References
STABILITY OF $^{11}$C-RADIOPHARMACEUTICALS AGAINST RADIOLYSIS AND THEIR SYNTHESIS AT HIGH RADIOCHEMICAL PURITY

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Introduction
The radiochemical purity of radiopharmaceuticals is important for maintaining the quality of PET studies. However, it has been recognized that radio labeled compounds tend to decompose via radiolysis caused by their own radioactivity [1]. The degree of radiolysis depends on the radioactivity level and specific activity of the compound, and type of radiation emitted from the radionuclide. Because PET radiopharmaceuticals are labeled with positron emitters and posses a high radioactivity level and specific activity, they tend to decompose by radiolysis [2 - 4]. In the present study, we report on the stability of a wide variety of $^{11}$C-radiopharmaceuticals against radiolysis, as well as a method to prepare these radiopharmaceuticals at high radiochemical purity.

Method
The carbon-11 labeled radiopharmaceuticals listed in Figure 1 were prepared by including reactions of $[^{11}\text{C}]$CH$_3$I or $[^{11}\text{C}]$methyl triflate as $[^{11}\text{C}]$-methylating agent with their corresponding desmethyl precursors. The stability of these $^{11}$C-radiopharmaceutical solutions was investigated by determination of their radiochemical purity using radio HPLC at appropriate intervals for up to 60-80 min after EOS (end of synthesis). The effects of radical scavengers on the radiolysis were investigated using EtOH, HCOONa (OH radical scavenger), NaNO$_3$ (hydrated electron scavenger) and sodium ascorbate (AsNa).

Results
Compounds 1 - 3 showed excellent stability with high radiochemical purity (>98%) at EOS and the radiochemical purity was maintained even after 60 min. However, the other $^{11}$C-radiopharmaceuticals (4 - 14) showed poor radiochemical purity at the EOS, and furthermore, their radiochemical purity decreased with time. The degree of decomposition increased with the level of radioactivity and specific activity of the compounds. These results suggested that the decrease in the radiochemical purity of radiolabeled compounds is attributed to radiolysis caused by their own radioactivity. The results of the examination of the effects of radical scavengers revealed that radiopharmaceuticals could
Fig. 1. A series of $^{11}$C-radiopharmaceuticals examined in the present study. 1 $[^{11}]$C]MP4A (R$_1$ = OCOCH$_3$, 2 $[^{11}]$C]MP4P (R$_1$ = OCOCH$_2$CH$_3$), 3 $[^{11}]$C]Flumazenil (R$_1$ = F, R$_2$ = H), 4 $[^{11}]$C]NMSP, 5 $[^{11}]$C]raclopride (R$_1$ = OH, R$_2$ = Cl), 6 $[^{11}]$C]FLB 457 (R$_1$ = H, R$_2$ = Br, R$_3$ = OH), 7 $[^{11}]$C]SCH 23390 (X = Ph), 8 $[^{11}]$C][(+)] NNC 112 (X = benzofuran), 9 $[^{11}]$C]methionine, 10 $[^{11}]$C]DASB, 11 $[^{11}]$C]verapamil, 12 $[^{11}]$C]Ro 15-4513 (R$_1$ = N$_3$, R$_2$ = H), 13 $[^{11}]$C]iomazenil (R$_1$ = H, R$_2$ = I), 14 $[^{11}]$C]PE2I be classified into 4 groups based on their resistance to radiolysis. Table 1 shows the categories: Group 1 (1 - 3 in Fig 1) showing excellent stability; Group 2 (4 - 11 in Fig 1) showing suppressed radiolysis in the presence of a selective scavenger of hydroxyl radicals (OH radicals); Group 3 (12 and 13 in Fig 1) showing suppression of radiolysis in the presence of a selective scavenger of hydrated electrons ($e_{aq}^{-}$); Group 4 (14 in Fig 1) showing little suppression of radiolysis in the presence of ether the OH radical scavenger alone or the $e_{aq}^{-}$ scavenger alone, but marked suppression in the presence of both OH radicals and $e_{aq}^{-}$ scavengers. It was suggested that the primary radicals of the OH radical and $e_{aq}^{-}$ generated in water play an important role in the radiolysis of $^{11}$C-radiopharmaceuticals. Ethanol,
known as a scavenger of OH radicals, and nitrate ions, known as a scavenger of e\textsubscript{aq}, had an
excellent stabilizing effect in the case of the Group 2 and Group 3 radiopharmaceuticals,
respectively, but not in the case of Group 4. On the other hand, ascorbate ions with their
high rate of reaction with both OH radicals and e\textsubscript{aq} suppressed radiolysis in all the groups.
Taking into consideration these results, radiolytically unstable radiopharmaceuticals could be
prepared with excellent radiochemical purity (> 99%) even with high levels of radioactivity
and specific activity.

<table>
<thead>
<tr>
<th>Category</th>
<th>Compound</th>
<th>Effective radical scavengers for the suppression of radiolysis</th>
<th>Participating primary radicals in radiolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>1-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Group 2</td>
<td>4-11</td>
<td>EtOH, HCOO', AsNa</td>
<td>OH radicals</td>
</tr>
<tr>
<td>Group 3</td>
<td>12,13</td>
<td>NO\textsubscript{3}⁻AsNa</td>
<td>e\textsubscript{aq}</td>
</tr>
<tr>
<td>Group 4</td>
<td>14</td>
<td>EtOH+NaNO\textsubscript{3}, AsNa</td>
<td>OH radical, e\textsubscript{aq}</td>
</tr>
</tbody>
</table>

**Conclusion**

In the present study, tolerance of \(^{11}\text{C}\) radiopharmaceuticals to radiolysis was classified into 4
types according to the radicals participation in the radiolysis. Additionally, effective
methods for the suppression of radiolysis are shown. The findings of the present study are
expected to be useful for the production of other \(^{11}\text{C}\)-radiopharmaceuticals at high
radiochemical purity, even with high levels of radioactivity and high specific activity, as well
as in the production of radiopharmaceuticals labeled with other positron emitters.

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QUALITY CONTROL OF $[^{18}\text{F}]$FDG INJECTION: BACTERIAL ENDOTOXIN TEST, ALUMINUM IONS TEST AND HPLC ANALYSIS FOR FDG AND CIDG

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1. Introduction
Quality control of 2-deoxy-2-$[^{18}\text{F}]$fluoro-D-glucose ($[^{18}\text{F}]$FDG) preparations for injection, the most commonly used radiopharmaceutical for positron emission tomography (PET), has recently received much attention due to its increasingly widespread use in clinical studies. In the USP and EP tests for specific radioactivity, bacterial endotoxin and chemical impurities such as 2-deoxy-2-chloro-D-glucose (CIDG) have been listed, and maximum permissible levels have been proposed [1,2]. In Japan, in addition to these tests, the aluminum ions test is also mandatory.

A number of methods have been developed for manufacturing $[^{18}\text{F}]$FDG and many automated devices for its manufacture are available commercially. The composition of the manufactured $[^{18}\text{F}]$FDG varies depending on the method and the device used for the manufacture. However, the constituents often influence the results of the endotoxin test and aluminum ions test. In this context, high-performance anion exchange chromatography coupled with pulsed amperometric detector (HPAEC/PAD) has been described in the USP and EP as the method to be used for the determination of FDG and CIDG. However, we have often observed when using HPAEC/PAD to measure reference CIDG samples, that the sensitivity varies from measurement to measurement and differs markedly depending on the ambient temperature in the laboratory.

In the present study, we examined the effects of the constituents of $[^{18}\text{F}]$FDG preparations for injection manufactured using various commercially available equipments on the results of the endotoxin test and aluminum ions test, as well as the effects of the HAPEC/PAD column temperature on the determination of FDG and CIDG.

2. Experimental
2.1. Bacterial endotoxin test and aluminum ions test
The bacterial endotoxin test was performed by the turbidimetric method, and the aluminum ions test was performed using the test paper method and Alizarin Red S method. \[^{18}F\]FDG solutions prepared using the commercially available equipment TRACERlab MX-FDG [GE], using citrate buffer or phosphate buffer, and the \[^{18}F\]FDG synthesizer marketed by SHI, using sodium chloride, were mixed with the standard endotoxin solution or Al\(^{3+}\) solution. These solutions were tested along with endotoxin-free and Al\(^{3+}\)-free \[^{18}F\]FDG solutions. To evaluate the effects of the constituents of the \[^{18}F\]FDG preparations for injection on the results of these tests, citrate buffer, phosphate buffer and sodium chloride solutions were prepared based on the assumption that all of these salts used for the final purification of \[^{18}F\]FDG in the commercially available equipments (TRAЕERlab MX-FDG, MicroLab\textsuperscript{TM} and \[^{18}F\]FDG synthesizer marketed by SHI) would be contained in the final preparations of \[^{18}F\]FDG. These solutions were mixed with the standard endotoxin solution or Al\(^{3+}\) solution and tested. Furthermore, the effects of the salt concentration and the pH value of these buffer solutions on the results of these tests were also evaluated.

2.2. HPLC analysis of FDG and CIDG

The chromatographic separation was performed at a flow rate of 0.3 mL/min, using a Dionex CarboPac PA-1 (4.0 mm i.d. x 250 mm) and CarboPac PA-1 guard (4.0 mm i.d. x 50 mm), and elution was carried out with 200 mM NaOH. Detection of FDG and CIDG was performed using HP 1059A; the detector settings were \(E_1 = 0.15\) V (\(t_1 = 15\) ms), \(E_2 = 0.65\) V (\(t_2 = 20\) ms) and \(E_3 = -0.95\) V (\(t_3 = 30\) ms), between the gold (working) and Ag/AgCl (reference) electrode. To evaluate the effects of the column temperature on the sensitivity of the FDG and CIDG measurement, a standard mixture of 1 \(\mu\)g/mL FDG and 5 \(\mu\)g/mL CIDG was tested at varying column temperatures (25, 30, 35, 40 and 45°C). To confirm degradation of FDG and CIDG in the presence of the mobile phase, a mixture of 1 \(\mu\)g/mL FDG and 5 \(\mu\)g/mL CIDG solution with 200 mM sodium hydroxide solution was prepared. This solution was incubated at 25 and 40°C, and the concentrations of FDG and CIDG were measured sequentially.

3. Results and discussion

In some of the preparations produced using the commercially available \[^{18}F\]FDG-manufacturing equipments, the percent recovery of the added endotoxin was below 50% (that is, meaning failure the test from criteria of the USP), and detection of Al\(^{3+}\) using the test paper method was a failure. These were attributed to the influence of the salts used in the manufacture of the \[^{18}F\]FDG, i.e., citrates and phosphates. The inhibition of endotoxin detection became stronger as the concentrations of these salts increased, or as the pH of the solutions deviated more from the neutral level. On the contrary, in the case of the sodium chloride solution, detection of endotoxin was only slightly inhibited as compared to that in the
control. Citrates and phosphates also markedly inhibited the detection of Al$^{3+}$ by the test paper method, but not by the Alizarin Red S method.

The column temperature was found to be a major factor markedly influencing the sensitivity of CIDG detection by HPAEC/PAD. The peak area corresponding to FDG increased gradually as the column temperature rose from 25°C to 40°C; on the contrary, the peak area corresponding to CIDG decreased markedly as the column temperature increased from 25°C to 40°C. At temperatures over 40°C, the peak area of CIDG was less than 1/30th of that recorded at 25°C. When FDG and CIDG were incubated with 200 mM sodium hydroxide solution, the concentration of FDG remained constant for 60 min, even at 40°C; on the other hand, the concentration of CIDG decreased with time (the decrease being particularly marked at 40°C). Peaks other than those representing FDG and CIDG were noted on the chromatograms and the areas of these peaks increased reciprocally as the peak area of CIDG decreased. These results suggest that the reduced sensitivity of CIDG detection is an outcome of degradation of this substance under the influence of the mobile phase in the column used for HPLC, and that the rate of such degradation is greatly influenced by the column temperature.

Thus, it is important to take these factors into consideration while performing quality control tests on [$^{18}$F]FDG preparations for injection.

References


SYNTHESIS OF 2'-DEOXY-2'-[\(^{18}\text{F}\)]-FLUORO-5-ETHYL-1-\(\beta\)-D ARABINOFURANOSYLURACIL ([\(^{18}\text{F}\)]-FEAU) AND MICRO-PET IMAGING OF HSV-\(\text{tk}\) GENE EXPRESSION IN TUMOR-BEARING NUDE MICE


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Introduction: Herpes simplex virus type-1 thymidine kinase (HSV1-tk) is being used as a suicide gene for gene therapy of cancer [1,2]. An in vivo method to assess the HSV1-tk enzyme activity after gene transfer is desirable to monitor gene expression as an indicator of gene delivery. Imaging of the HSV1-tk reporter gene along with various reporter probes is of current interest [3-6]. We originally developed \([^{18}\text{F}\)]-FHGP and \([^{18}\text{F}\)]-FHBG for PET imaging of HSV1-tk gene expression [5-7] and demonstrated that \([^{18}\text{F}\)]-FHGP is more useful than \([^{18}\text{F}\)]-FHGP for this purpose [7]. \([^{125}\text{I}\)]-FIAU has shown to be a potential PET imaging agent for HSV1-tk gene expression [8], and is superior to \([^{18}\text{F}\)]-FHGP and \([^{18}\text{F}\)]-FHBG. We also demonstrated that radionabeled FMAU can be used as a marker for HSV-tk gene expression, and is superior to \([^{18}\text{F}\)]-FHGP and \([^{18}\text{F}\)]-FHBG [9]. Earlier we reported a synthesis for 2'-deoxy-2'-\([^{18}\text{F}\)]fluoro-5-methyl-1-\(\beta\)-D-arabinofuranosyluracil (\([^{18}\text{F}\)]-FMAU) and some other 5-substituted nucleosides [10,11]. We have synthesized now \([^{18}\text{F}\)]-FEAU, used the tracer for micro-PET imaging of suicide gene expression in tumor-bearing nude mice, and compared the results with earlier studies using \([^{13}\text{C}\)]-FMAU.

Methods: Synthesis of \([^{18}\text{F}\)]-FEAU was performed following our earlier general method [10,11]. Briefly, 2-deoxy-2-trifluoromethanesulfonyl-1,3,5-tri-O-benzoyl-\(\beta\)-D-ribofuranose was reacted with tetrabutyliammonium\([^{18}\text{F}\)]fluoride to produce 2-\([^{18}\text{F}\)]fluoro-1,3,5-tri-O-benzoyl-\(\beta\)-D-arabinofuranose, which was converted to its 1-bromo-derivative by treatment with hydrogen bromide in acetic acid (HBr/AcOH). The \([^{18}\text{F}\)]-labeled bromosuguril was coupled with the protected 5-ethyluracil, and the coupled product was hydrolyzed in base. The crude product was purified by HPLC to obtain the desired product \([^{18}\text{F}\)]-FEAU. In vitro studies were performed in HT-29 cells (human colon cancer) by incubation of \([^{3}\text{H}\)]-FEAU at 30 min, 1h and 2h. Uptake in cells was normalized to dpm/million cells. In vivo studies were performed on tumor-bearing nude mice. Tumors were grown using HT-29 cells, wild type on the left flank and transduced with HSV1-tk on the right flank. When tumor size was approximately 1 cm in diameter animals were used for PET imaging studies. \([^{18}\text{F}\)]-FEAU (0.2 mL, 0.2 mCi) was injected (iv) through the tail and micro-PET imaging studies were performed at 30 min, 1h and 2h post-injection. Biodistribution was performed at 2h post-injection using \([^{3}\text{H}\)]-FEAU on a different group of animals. The biodistribution result was compared with that of \([^{13}\text{C}\)]-FMAU.

Results: The radiochemical yield of \([^{18}\text{F}\)]-FEAU was 17-35% % decay corrected (d. c.) with an average of 24% in 3 runs, and specific activity > 2 GBq/µmol at the end of synthesis. In vitro
uptake of $[^{1}H]$-FEAU was 15-fold to 20-fold higher in transduced cells compared to that in wild type cells (Fig. 1). *In vivo* uptake of $[^{1}H]$-FEAU in transduced cells was 4-fold higher than in non-transduced cells (Fig 2). There was a slight higher uptake of activity in kidney due to renal clearance.

![Fig. 1: FEAU uptake in cells](image1)

![Fig. 2: Biodistribution of FEAU](image2)

Micro-PET images also demonstrated selective uptake of $[^{18}F]$-FEAU in HSV1-tk expressing tumor without any significant uptake in control tumor and organs, consistent with the biodistribution results (Fig. 3).

![30 min coronal](image3)

![2h coronal](image4)

![2h projection](image5)

**Fig. 3: Micro-PET images**

Total uptake in transduced tumors was slightly less than FMAU, however uptake ratio (tk/w) was comparable due to relatively high non-specific trapping of FMAU by the host kinase (Fig. 4).
**Conclusion:** Synthesis of $[^{18}F]$-FEAU has been accomplished. *In vivo* results including micro-PET images demonstrate that $[^{18}F]$-FEAU can be used to visualize suicide gene expression in human colon cancer with PET. Absence of significant trapping in wild type tumor suggests that $[^{18}F]$-FEAU may be superior to $[^{18}F]$-FMAU.

**References**

Tricarbonyl complexes of technetium(I) and rhenium(I) were introduced to radiopharmaceutical chemistry by Alberto et al. [1] who elaborated an easy method for no-carrier-added level (n.c.a.) synthesis of their precursors, $\text{f}_{\text{ac}}$-$\text{[Tc(CO)$_3$(H$_2$O)$_2$]}$ (I) and its rhenium analog. Numerous advantages of tricarbonyltechnetium(I) and analogous tricarbonylrhenium(I) cores in radiopharmaceuticals, in particular kinetic inertness of the central metal ions with $d^6$ electronic configuration, well justify a great research interest in these complexes, especially in those obtained by substitution of a bi- or tridentate chelating ligand for two or three labile water molecules in I. This interest was manifested e.g. by a significant number of 27 relevant presentations at the recent conference on metal complexes in nuclear medicine [2].

Due to the softness (HSAB concept) of Tc(I) and Re(I) centres, chelators with soft donor atoms are preferred as their ligands. Widely studied in this respect were bi- and tridentate derivatives of pyridine and/or imidazole (aromatic N-donors) with other donor atoms, in particular nitrogen and/or sulphur [2]. The aim of our studies is to find novel ligands that form very stable tricarbonyl complexes of Tc(I) and Re(I), which after further functionalization of the ligand can work as precursors of novel radiopharmaceuticals of the 2nd generation.

Advanced (DFT based) quantum-mechanical calculations on the chosen group of amide derivatives of thiopicolinic acid [3] allowed us to select N-methylamide of thiopicolinic acid (N2-methyl-2-pyridinecarboxamide; 2) as an efficient bidentate neutral ligand L in the [Tc(CO)$_3$LCl] complex. This ligand was then synthesized from a mixture of $\alpha$-picoline, N-methylformamide and sulphur, according to the general procedure described in [4]. The crude product was dissolved in chloroform and purified chromatographically on silica gel, then recrystallized twice from ethyl acetate (m.p. 75-79 $^\circ$C, yield 40 %). The composition of the final product was confirmed by elemental analysis, $^1$H-NMR and $^{13}$C-NMR. Lipophilicity of 2 was determined by solvent extraction from aqueous solution (pH = 6.5) to isooctanol. HPLC determination of the concentrations of 2 in the aqueous phase, initial and at equilibrium, gave log$P_L$ = 1.54 (partition constant $P_L$ is the ratio of the concentrations of the same chemical species in the organic and aqueous phases at equilibrium).

For the sake of comparison we also synthesized the oxygen analogue of the 2, N-methylamide of picolinic acid (N2-methyl-2-pyridinecarboxamide; 3). It was obtained by reacting picolinic acid chloride with an excess of methylamine in methanol. The crude product was purified on a silica-gel column. Elution with 2% methanol in CHCl$_3$ followed by evaporation, gave the final oil product (yield 44 %), characterized by elemental analysis, $^1$H-NMR and $^{13}$C-NMR.

99mTc(I) tricarbonyl complexes [Tc(CO)$_3$LY] 4 and 5 (Scheme 1), where Y is an anion (see below) and L denotes 2 or 3, respectively, were obtained according to Alberto’s procedure [1]. An aqueous solution of I (n.c.a.), 2 or 3 (10$^{-3}$ M), 0.4 % NaCl, and of pH 9 was kept at 30 $^\circ$C for 1.5 h. The yields were determined by HPLC (Fig. 1) as the percent of radioactivity of
\[^{99m}\text{Tc}\] in the given peak in respect to the total radioactivity eluted from the column. Formation of the cationic complex, \([(^{99m}\text{Tc})\text{(CO)}_3\text{L}(\text{H}_2\text{O})])^+\], is less probable in view of the results of solvent extraction experiments described below. Complex 4 was formed with a higher yield than 5, and the yield decreased with decreasing ligand concentration, \(C_L\) (Table 1). It is noteworthy, however, that the values shown in Table 1 should be corrected by the amount of \[^{99m}\text{Tc}\] not eluted from the column, e.g. colloidal \[^{99m}\text{TcO}_2\] (see below).

![Graph](image)

**Fig. 1.** HPLC of 4. Gradient H\(_2\)O - methanol, \(C_L=10^{-3}\) M.

**Scheme 1.** Stick formula of 4 (X=S) and 5 (X=O). Y - monovalent anion

The correctness of the formula in Scheme 1 has been confirmed both by the theoretical calculations of the structures 4 and 5 [3], and by X-ray studies on the molecular structure of \([\text{Re(CO)}_3\text{LCl}]\) - the rhenium analog of 4 [5].

**Table 1.** The yields of \([^{99m}\text{Tc(CO)}_3\text{LY}]\): 4 and 5 (1.5 h, 30° C) at various concentrations of 2 and 3

<table>
<thead>
<tr>
<th>(C_L), mol dm(^{-3})</th>
<th>2.5 \times 10^{-4}</th>
<th>5 \times 10^{-4}</th>
<th>1 \times 10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of 4, %</td>
<td>68</td>
<td>92</td>
<td>94</td>
</tr>
<tr>
<td>Yield of 5, %</td>
<td>45*</td>
<td>50</td>
<td>77</td>
</tr>
</tbody>
</table>

*At 50° C the yield was 74% (0.5 h) and 70% (1 h).

The HPLC peaks corresponding to 4 and 5 are not symmetrical (Fig.1), therefore at least two species of similar properties seem to be present in the samples. Assuming that for a given L the ratio of formation constants of neutral \([\text{Tc(CO)}_3\text{LY}]\) complexes (where \(Y=\text{Cl}^-\) or \(\text{OH}^-\)) is equal to that of the respective \([\text{Tc(CO)}_3(\text{H}_2\text{O})_2\text{Y}]\) species, reported in [6], we can expect that – at the actual concentrations of \(\text{Cl}^-\) and \(\text{OH}^-\) ions – the neutral \([\text{Tc(CO)}_3\text{LCl}]\) and \([\text{Tc(CO)}_3\text{LCH}]\) complexes appear in the sample in comparable concentrations. Both complexes are lipophilic and are extracted to organic solvents to a slightly different extent.

Solvent extraction experiments with the \([\text{Tc(CO)}_3\text{LY}]\) complexes (4 and 5) were carried out in the system 1,2-dichloroethane/water. 4 and 5 were previously extracted from the stock aqueous phase, in which they had been formed (pH 9), to equal volumes of the solvent (r.t., 20 min.), giving ca. 65% and 30% \[^{99m}\text{Tc}\] in the organic phase, respectively. The separated organic phase loaded with 4 or 5 was shaken (r.t., 2 h) with the equal volume of water (pH
7.2±8.0) and the aliquots of both phases were collected in known time intervals for the measurements of specific radioactivities, and the determination of distribution ratios (D_M – the ratio of total concentrations of all the forms of M in both phases). The D_Tc values for the systems studied (4 and 5) decreased with time to reach equilibrium within ca. 20 and 40 min, respectively. These long times are not typical for partition equilibria to be established [7], therefore one may interpret them in terms of ligand (Y–) exchange. Assuming that Y– = OH– in the final forms of 4 and 5, the partition constants of the [Tc(CO)5LOH] complexes are equal to 5±2 and 8±2, respectively (preliminary data). The comparison of these P values with the D_Tc values observed in the preparative extractions shows that significant amounts of non-extractable 99mTc, e.g. colloidal 99mTcO2, were formed together with the complexes.

The proximity of the P_4 and P_5 values well corresponds to the similar positions of 4 and 5 peaks on the chromatograms (HPLC). However, this proximity was rather unexpected from the viewpoint of hydration of the complexes in the aqueous phase. It has been demonstrated previously that hydrogen bonding of water to oxygen donor atoms in co-ordinately saturated metal chelates (outer-sphere hydration) makes the oxygen-donor chelates much more hydrophilic than their structural analogs with sulfur donor atoms [7]. This inconsistency requires further studies. On the other hand, extraction of the supposed cationic complex, [99mTc(CO)5L(H2O)]3+, to an organic solvent of low dielectric constant is less probable under the conditions of the experiment. That is because the charged species are extracted as ion pairs together with accompanying counter-ions whose concentration in the aqueous phase should be sufficiently high [8], which is not the case in our study.

The work is in progress. Successful experiments with the bidentate ligand 2, which we consider a model for a histidine-like tridentate anionic ligand with at least two N,S donor atoms, allow us to extend the studies on such a ligand. A candidate has already been advantageously examined by theoretical calculations [3].

Acknowledgements

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References

SYNTHESIS AND RADIOIODINATION OF DI-IODO-EVAN'S BLUE VIA ISOTOPIC EXCHANGE REACTION IN THE MOLTEN STATE AND EVALUATION OF THE KINETICS

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Introduction

Many aryl halides were synthesized from aryl amines such as iodo-trypsin [1], iodo-methylene blue and iodo-toluidine [2]. Methylene blue and toluidine blue are phenothiazinium dyes and were used to localize parathyroid glands visually during surgery [2]. Radioidination of these compounds by using iodine-123 analogues for scintigraphic localization of parathyroids was reported [2]. Radiolabelled dyes administered may also localize in tumor tissues. Evan's blue dye was used to study altered sarcolemmal permeability in dystrophic muscle fibers [3], and in animals to study muscular dystrophy.

In this work Diiodo-Evan's blue was synthesized via Sandmeyer reaction and characterized by mass spectrum analysis. A procedure for labelling DIEB with Na\(^{131}\)I via isotopic exchange in molten medium was developed. The labelling conditions studied for the isotopic exchange of \(^{131}\)I-for-I in DIEB included the effect of temperature and solvents (melt of acetamide, benzoic and pivalic acid). Kinetic studies were performed to obtain \([^{131}\text{I}]\) DIEB with more reliable reaction conditions. Quality control for the final product \((^{131}\text{I})\) DIEB was performed by HPLC.

The structure of the Di-iodo-Evan's blue (DIEB) is given below.

![Structure of Diiodo-Evan's Blue (DIEB)](image)

Experimental

Synthesis of diiodo-Evan's blue (DIEB)

Diiodo-Evan's blue (DIEB) was synthesized by diazotization reaction of Evan's blue dye followed by addition of sodium iodide at 50°C for 6h, finally at 100°C for 1h. The resultant DIEB was purified and precipitated by adding 50mL of ethanol and 100mL of diethyl ether and subsequent centrifugation. The precipitated product (DIEB) was dried by passing a stream of argon gas. The structure of DIEB was established on the basis of mass spectrum.

Labelling technique

The isotopic exchange reaction between DIEB (0.5 - 3 mg) and Na\(^{131}\)I was carried out in its own melt or in that of acetamide, benzoic acid or pivalic acid. The effects of different
parameters affecting the radiochemical yield of $[^{131}]$DIEB were studied under several experimental conditions of reaction time (0 – 70 min), temperature (70 – 100 °C) and different amounts of each solvent (1-3 mg). The radiochemical purity and radiochemical yield of $[^{131}]$DIEB were determined by high performance liquid chromatography (HPLC), similar to a previously used system [4].

**Result and Discussion**

The exchange of inactive iodine by radioactive iodine in DIEB is a homogeneous reaction and its kinetics will follow the exponential exchange law [5]. The concentrations of exchanging species are denoted in mol L$^{-1}$. The data of radiochemical yields obtained without and in presence of acetamide, respectively, were recalculated to obtain F (fraction of exchange). The plots of Log (1-F) against time (t) in (minutes) for the different reaction temperatures gave straight lines with negative slope passing through the origin (see Table 1 and 2).

The specific rate constant (k) at each temperature was calculated from the slope of the plot of Log (1-F) against time [6], with $[^{131}]$I + [DIEB] = [DIEB] = 0.42 and 0.47 mol L$^{-1}$ (M) without and in presence of acetamide, respectively. The amount of n.c.a. $[^{131}]$I iodide tracer was negligible considering that the radioactivity used in each run was only 3.7 MBq compared to the quantity of DIEB. The values of the slope, k and t$_{1/2}$ at different temperatures are summarized in Table 1. It is clear that the value of k increases and t$_{1/2}$ decreases with an increase of the temperature. From this, the activation energy was calculated for both conditions, which is given in Table 2.

**Table 1:** Variation of the slope, specific rate constant (k) and half-life of exchange (t$_{1/2}$) with reaction temperature

<table>
<thead>
<tr>
<th>State of reaction</th>
<th>Temperature °C</th>
<th>Slope min$^{-1}$</th>
<th>k M$^{-1}$ min$^{-1}$</th>
<th>t$_{1/2}$ min</th>
</tr>
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<tbody>
<tr>
<td>Without solvent</td>
<td>80</td>
<td>0.023</td>
<td>0.114</td>
<td>13.04</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>0.028</td>
<td>0.138</td>
<td>10.78</td>
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<td></td>
<td>100</td>
<td>0.050</td>
<td>0.247</td>
<td>6.02</td>
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<td>Acetamide</td>
<td>70</td>
<td>0.046</td>
<td>0.251</td>
<td>6.54</td>
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<tr>
<td></td>
<td>80</td>
<td>0.058</td>
<td>0.317</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.071</td>
<td>0.388</td>
<td>4.23</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.080</td>
<td>0.457</td>
<td>3.76</td>
</tr>
</tbody>
</table>

**Table 2:** Kinetic measurements at different temperatures in the reaction between DIEB and Na$^{131}$I

<table>
<thead>
<tr>
<th>State of reaction</th>
<th>Temperature °C</th>
<th>Slope min$^{-1}$</th>
<th>1/T $\times 10^3$</th>
<th>Log k</th>
<th>E Kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without solvent</td>
<td>80</td>
<td>0.023</td>
<td>2.83</td>
<td>-0.94</td>
<td>10.40</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>0.028</td>
<td>2.79</td>
<td>-0.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.050</td>
<td>2.68</td>
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<tr>
<td>Acetamide</td>
<td>70</td>
<td>0.046</td>
<td>2.915</td>
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<td>0.080</td>
<td>2.68</td>
<td>-0.36</td>
<td></td>
</tr>
</tbody>
</table>

To these data the Arrhenius equation (k = A $e^{E/R \cdot T}$) can be applied by plotting Log k against 1/T; where A is the frequency factor for the reaction, R the universal gas constant (1.987 cal/mol), T the absolute temperature and E the critical energy which the reaction complex
must possess in order the reaction to occur. For a given reaction a straight line should be obtained for the dependence of Log k on T, as shown in Fig. 1, with a slope of -E/R (or -E/2.303R, if ordinary logarithms are used). The activation energies calculated show that the exchange reaction needs only about half (5.53 Kcal/mol) in presence of acetamide than that without (10.40 Kcal/mol), reflecting a much slower exchange reaction without acetamide. Since iodide is the identic substituting and leaving group, the catalytic effect of the acetamide melt must be attributed to facilitation of forming the transton state (ipso complex) of the isotopic exchange.

The radiochemical yields of [131]DIEB decrease with extended reaction times and temperatures due to decomposition reactions. Therefore for practical labelling reasons, the conditions with 1 mg DIEB, 2 mg acetamide, 100 °C and 30 min proved optimal to obtain a radiochemical yield of about 90% within 30 min. Acetamide proved superior to benzoic and pivalic acid as solvent.

Fig. 1 Relationship between reaction rate constant (Log k) and temperature (1/T) without and in presence of acetamide

Acknowledgment

The Authors thank Prof. S. M. Qaim and Dr. M. Holschbach for some useful discussions.

References

SYNTHESIS AND EVALUATION OF $^{18}$F-LABELLED AMINO ACIDS PROMISING FOR CLINICAL PET IMAGING

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Preparation of $^{[18]$F$]}$Fluoro amino acids

In comparison to the short lived $^{11}$C-labelled amino acids $^{18}$F-labelled analogous offer considerable practical advantages for routine clinical practice. Based on the phase transfer mediated no-carrier-added nucleophilic $^{16}$F-fluorination several interesting aromatic and aliphatic $^{18}$F-labelled amino acid derivatives can be produced in high radiochemical yields and distributed to clinical centers according to the satellite concept. Promising candidates especially for tumor imaging are O-(2-$^{[18]$F$]}$fluoroethyl)-L-tyrosine (FET) [1,2] and the diastereomeric aliphatic amino acids cis- and trans-4-$^{[18]$F$]}$fluoroprolines [3].

![Chemical Structures]

The reaction sequence of FET synthesis (see scheme below), including a simple on line HPLC purification, is a convenient and reliable method to produce the $^{18}$F-labelled amino acid with high amounts of radioactivity [2]. The cis- and trans-4-$^{[18]$F$]}$fluoroprolines were also prepared by nucleophilic substitution with n.c.a. $^{18}$F$]fluoride as described earlier [3].

![Reaction Scheme]

The transport and imaging characteristics of these amino acid derivatives are currently under evaluation.
Transport studies with FET in vitro

F98 rat glioma cells were cultured and tracer uptake of FET and [methyl-3H]-L-methionine (MET) was measured after 5 minutes incubation time at 37°C. Experiments were repeated after specific inhibition of the L- and A- amino acid transporters and after deprivation of Na⁺.

FET exhibited similar transport characteristics in F98 glioma cells compared to MET, i.e. mainly a sodium dependent transport similar to system B₀⁺ and sodium independent transport via system L [4].

Evaluation of FET by dual tracer autoradiography

F98 cells were stereotactically implanted into the caudate nucleus of 13 male wistar rats. After 8 days of tumor growth, FET and 3H-MET were injected into a tail vein and tumor imaging of FET or FTyr versus MET was compared by ex vivo dual tracer autoradiography of brain slices 60 min after tracer injection. Comparison of FET with MET uptake in F98 rat gliomas by dual tracer autoradiography demonstrated a significant correlation of tumor to brain ratios and a similar intratumoral tracer distribution pattern [4].

Initial clinical studies using FET PET in human brain tumors have shown similar results compared with MET PET [5]. A superior delineation of solid tumor mass of human gliomas by FET PET compared with MRI has been demonstrated using stereotactic biopsies as reference [6, 7].

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Cis/trans 4-[\textsuperscript{18}F]fluoro-L-proline

The whole body distribution of cis-FPro showed a significant retention in the renal cortex and a slight uptake in the liver and the pancreas, while the remainder of the body exhibited low tracer uptake. In contrast, trans-FPro exhibited no retention in the kidneys, liver and pancreas but uptake in soft tissue and in muscles. This indicates considerable differences in the transport characteristics [8].

Transport experiments in F98-glioma cells showed that system A amino acid transport was selectively relevant for cis-FPro which may contribute to the observed differences in whole body distribution.

Cis-4-[\textsuperscript{18}F]fluoro-D-proline

Recent experiments demonstrated that D-FPro is preferably transported across the BBB different to the L-isomer.

The biological background of this observation remains to be elucidated. The use of the D-isomers of radiolabeled amino acids for PET diagnostics may represent an interesting new field for in vivo imaging of various brain diseases.

References

NEW FLUORINATED LIGANDS FOR THE Dopamine TRANSPORTER: SYNTHESIS AND FIRST BIOLOGICAL EVALUATION IN PIG AND RAT BRAIN

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A change in the density of the dopamine transporter (DAT) is a widely accepted indicator for the integrity of the presynaptic nigrostriatal dopaminergic system. In spite of the advantageous properties of fluorine-18 for PET imaging up to now there is no suitable radiofluorinated DAT ligand available although numerous investigations have been performed by different working groups [1]. Presently the SPECT ligand $[^{123}]$FP-CIT known as DaTSCAN [2] is the only commercially available DAT radiotracer for routine clinical use. The present study describes the syntheses of new fluorinated tropones as potential DAT ligands (Figure) and their first in vitro evaluation in pig and rat brain. Several known DAT ligands are also synthesized and evaluated as standards for comparison.

<table>
<thead>
<tr>
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<th>$R^2$</th>
<th>$X$</th>
<th>No.</th>
</tr>
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<td>1</td>
</tr>
<tr>
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<td>NH-C$_7$H$_5$-F</td>
<td>CH$_3$</td>
<td>2</td>
</tr>
<tr>
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<td>O-C$_2$H$_4$-F</td>
<td>CH$_3$</td>
<td>3 [3]</td>
</tr>
<tr>
<td>(E)-1-CH=CH-CH$_2$</td>
<td>NH-C$_7$H$_5$-F</td>
<td>CH$_3$</td>
<td>4</td>
</tr>
<tr>
<td>(E)-1-CH=CH-CH$_2$</td>
<td>O-C$_2$H$_4$-F</td>
<td>CH$_3$</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure:** New synthesized cocaine derivatives as potential DAT-ligands

The known ester derivatives of cocaine like β-CIT [4], FP-CIT [5], PE2I [6] possess a high affinity ($K_i \leq 10$ nm) for the DAT [1]. The corresponding amides 1, 2 and 4 represent a new class of potential DAT ligands with derivative 1 (CIT-amide [7]) having a $K_i$-value in the nanomolar range. Amides are known to be less susceptible to in vivo hydrolysis than the corresponding esters. In vivo instability is the major problem of the known ligands. The first results on the radiofluorination of the new amides 1 and 2 will be presented (Scheme).

![Scheme](attachment:image.png)

**Scheme:** Radiofluorination of amides 1 ($X=1$) and 2 ($X=ClH_3$)

In competition studies the compounds 1 – 5, β-CIT, FP-CIT, PE2I and cocaine were investigated versus the radioligand $[^{131}]$β-CIT using striatal and cortical membranes from pig, as well as horizontal slices from rat brain for autoradiography. $[^{131}]$β-CIT was prepared in house according to previously reported methods [8, 9].

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Among the new compounds, CIT-amide 1 shows the highest affinity in pig striatum and cortex and also in autoradiographic studies with rat brain slices. The radioligand \(^{131}\text{I}]\beta\text{-CIT}\) has a high affinity for both DAT and serotonin transporter (SERT) binding sites [9]. It is suggested that \(^{131}\text{I}]\beta\text{-CIT}\) binds predominantly to the DAT in striatum and in the cerebral cortex to the SERT [10].

| Table: \(K_s\)-values [nM] were determined using \(^{131}\text{I}]\beta\text{-CIT}\) |
|-----------------|-----------------|-----------------|
| Homogenate      |                  | Autoradiography |
|                  | Pig striatum    | Pig cortex      | Rat brain* |
| 1                | 13.7 ± 5.5      | 20 ± 8          | 52 ± 12    |
| 2                | 306 ± 5.0       | 378 ± 96        | 1193 ± 94  |
| 3                | 125 ± 51        | 156 ± 37        | 118 ± 15   |
| 4                | 258 ± 74        | 272 ± 89        | 4715 ± 1126|
| 5                | 927 ± 377       | 450 ± 156       | 3040 ± 341 |
| \(\beta\text{-CIT}\) | 0.1 ± 0.04      | 0.03 ± 0.01     | 0.5 ± 0.2  |
| FP-CIT           | 2.0 ± 0.2       | 2.4 ± 0.6       | 10 ± 2     |
| PE2I             | 4.6 ± 0.2       | 3.9 ± 1.4       | 22 ± 2     |
| Cocaine          | 360 ± 22        | 192 ± 33        | 387 ± 99   |

* whole brain, except cerebellum

Autoradiography revealed that \(^{131}\text{I}]\beta\text{-CIT}\) binding in rat cortex was about 70% of the binding in rat striatum. All investigated compounds displaced the \(^{131}\text{I}]\beta\text{-CIT}\) binding 70% to 80% at concentrations of 20 μM, with the remaining 20% to 30% corresponding to the nonspecific binding. As result of the present study compound 1 is the most promising candidate with high affinity to rat and pig brain. Since the radiotracer \(^{131}\text{I}]\beta\text{-CIT}\) is a nonselective monoamine transporter radioligand, no direct conclusion about selectivity is possible. Further investigations with fluorine-18 labelled compound 1 will give exact information about binding behaviour and selectivity in vitro and in vivo.

AROMATIC HALOGEN EXCHANGE REACTIONS

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Radioisotopes of halogens are, due to their physical and chemical properties, very useful in numerous medical applications (imaging, therapy, in vitro tracers). In many cases (e.g. m-iodobenzylguanidine, bioconjugates, etc.) the binding site of the radiohalogen atom is on the substituted aromatic benzene ring, besides heteroaromates or another unsaturated bond systems [1]. One way to prepare such labelled arylhalides is the halogen exchange method. Transhalogenation reactions, including isotope exchange, are quite well known and commonly used in radiochemical practice, particularly for iodine and bromine [2-6]. However, in some cases, yields are low and also the systematic mechanistic study, which compares the halogen exchange of fluorine, chlorine, bromine, iodine and astatine is unknown. We have therefore focused on the study of the halogen exchange reactions in variously substituted aryl halides from the mechanistic scope of view.

The effects of added catalysts, type and position of substituents on the substrate, halogens to be exchanged and solvents have been especially examined. We have tried to find out probable reaction mechanisms and optimize reaction conditions. Radiochemical yields were assigned by thin layer chromatography using both UV and radio-detection.

\[
\begin{align*}
\begin{array}{c}
\begin{array}{c}
\text{R}_3 \\
\text{R}_2 \\
\text{R}_1 \\
\text{X}
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\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\begin{array}{c}
\text{R}_3 \\
\text{R}_2 \\
\text{R}_1 \\
\text{Y}
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\begin{array}{c}
\text{X}:	ext{ -F, -Cl, -Br, -I}
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\begin{array}{c}
\text{Y}:	ext{ -F, -Cl, -Br, -I, -At}
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\begin{array}{c}
\text{R}_{1,2,3}:	ext{ -H, -NO}_2, \text{-COOR, -NHAc, -NMe}_2\text{, etc.}
\end{array}
\end{array}
\end{align*}
\]

Fig. 1: Studied aryl halides

Several new catalysts based on transition metal compounds have been tested. Enormous solvent effects of triethylamine and dioxane have been observed, when copper catalysts were used. Already small amount of added solvent to the reaction mixture increased the radiochemical yield significantly, probably due to the formation of complex with catalyst species and substrate. Some neighbouring functional groups on the aromatic ring also influenced the reactions by strong chelating effect. The halogen exchange reactions probably

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occur by organometallic mechanism (oxidative addition – reductive elimination). Although radiochemical yields varied in dependence of used halogen, type of substitution on the aromatic ring and reaction conditions, in some cases they exceeded 90% (non decay corrected) in a relatively short reaction period at mild reaction conditions. Based on the results of the mechanistic study we have tried to develop novel method for preparation of radiohalogenated aromatic conjugates for biomolecules labeling.

![Chemical structure](image)

**Fig. 2:** Potential conjugate for biomolecules labelling

**Acknowledgement**

Authors gratefully thank the Grant Agency of the Czech Academy of Sciences for financial support (grants No.: B 4048302, B 4050408 and S 1048005).

**References**


USE OF METAL-\(^{211}\)At COMPLEXES AS A NEW METHOD FOR PREPARATION OF ASTATINE RADIOPHARMACEUTICALS

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In the field of radioimmunotherapy, the choice of radioisotope is related to the type of disease to be treated. The types of particles emitted are directly related to the tissue penetration and cell killing ability of the isotope. Many radiometals are under investigation for therapeutic applications, most notably the Auger-electron emitter \(^{67}\)Ga (\(t_{1/2}=3.3\) d), \(\alpha\) particle emitters \(^{211}\)At (\(t_{1/2}=7.2\) h), \(^{203}\)Bi (\(t_{1/2}=1\) h), \(^{213}\)Bi (\(t_{1/2}=45.6\) min), and \(\beta\) particle emitters \(^{90}\)Y (\(t_{1/2}=64\) h), \(^{186}\)Re (\(t_{1/2}=17\) h), \(^{153}\)Sm (\(t_{1/2}=46.3\) h), \(^{177}\)Lu (\(t_{1/2}=6.7\) d), \(^{67}\)Cu (\(t_{1/2}=2.6\) d), \(^{109}\)Rh (\(t_{1/2}=35.3\) h), \(^{47}\)Sc (\(t_{1/2}=3.3\) d) and \(^{109}\)Pd (\(t_{1/2}=13.7\) h) [1]. Solid tumors have been successfully treated with \(\beta\) emitters including \(^{90}\)Y, \(^{177}\)Lu and \(^{131}\)I, where the \(\beta\) particle from these isotopes has a tissue range of several millimeters. The tissue range of \(\beta\) particles is not optimum for treatment of small clusters of cells or single cells, micrometastatic disease, leukemia and lymphoma. Treatment of these diseases may be more efficient with \(\alpha\)-emitters, which combine high cytotoxicity and a short tissue range. Considerable effort has been placed in the development of the \(\alpha\)-emitters \(^{212}\)Bi, \(^{213}\)Bi and \(^{212}\)Ac and \(^{211}\)At. Unfortunately, the half-life of both \(^{212}\)Bi and \(^{213}\)Bi is short, potentially limiting applications. \(^{212}\)Ac has also limited applicability, due to decay to intermediate product \(^{222}\)Fr which can easily diffuse from the biomolecule. Actually the most promising is \(^{211}\)At.

\(^{211}\)At decays via two branches to the stable \(^{207}\)Pb. High energy \(\alpha\) particles with mean energy of 6.4 MeV are emitted in the decay, corresponding to a mean range in human tissue of 65 \(\mu\)m. Therefore, this nuclide may be optimum for the treatment of micrometastases. Additionally EC decay gives rise to high intensity Po X-rays making \(^{211}\)At easy to follow with a \(\gamma\) camera [2].

Astatine-211 labelled immunonconjugates have been synthesized and evaluated for their therapeutic potential. Proteins labelled with \(^{211}\)At by direct electrophilic astatination were unstable by virtue of rapid loss of \(^{211}\)At following in vivo administration. Better stabilization, but not fully satisfactory exhibit biomolecules labelled by electrophilic astatode-destannylation of N-succinimidyl-3-(trimethyl stanny) benzoate [3].

In this short note we present preliminary results of our studies on complexing of \(^{211}\)Hg by \(^{211}\)At. The aim of this studies is utilization of metal cation bridge for astatination of biomolecules. As potential metal cations which should form strong complexes with At ligand, Pd\(^{2+}\), Bi\(^{3+}\), Cu\(^{2+}\) and Hg\(^{2+}\) were selected. In the first step the stability constant of Hg-At\(^{+}\) was determined.

The \(^{211}\)At was obtained at AIC-144 cyclotron in Institute of Nuclear Physics in Cracow. The targets were prepared from pure metallic bismuth. Each portion of about 100 mg Bi was molten on a 0.1 mm thick copper foil, by heating over a gas burner during 10 s up to about 1000°C. The
desired thickness of the bismuth layer (ca 50 mg cm⁻²) was obtained by filling off the excessive material. The targets were protected with 2 mg cm⁻² thick aluminium foil and fixed in the aluminium frame on the water-cooled copper tube of the (temporary) internal target assembly in the AIC-144 cyclotron. The targets were activated during 1 hour with the internal beam of 30 MeV alpha particles. Due to limited efficiency of the target cooling in this assembly, the beam current usually did not exceed 1 µA.

The apparatus for separation of ²¹¹At from the metallic target is a home-made one and generally follows the construction described in Ref. [4]. The separation of ²¹¹At is carried out under argon, at the gas flow of 120 cm³ min⁻¹. After flushing the apparatus with argon for 15 minutes, the activated target is placed in the quartz tube inside the resistance furnace, and the heating is switched on. The desired temperature of 650°C is achieved during 30 min., and kept constant during further 15 min. The evolved ²¹¹At is collected in a cold trap consisting of a 1 mm I.D. polyethylene tube, immersed in ethanol cooled with liquid nitrogen down to the temperature between -55°C and -50°C. The obtained ²¹¹At was dissolved in 100 µl solution of Na₂SO₄/ NaNO₂.

The ion exchange method based on the different partitioning of the HgAt⁺ and At⁻ on anion exchange resin was used for complexing studies. The distribution coefficient values were determined using a batch technique in 0.1 M NaNO₃ solutions with 0.001 M Na₂SO₃ as a reducing agent. From plotted relationship between values of the K_d and log[Hg²⁺] (Fig.1), the first stability constants have been determined for HgAt⁺ and also for HgI⁺ for comparison.

![Figure 1](image)

**Fig.1.** Dependence of distribution coefficient of ¹³¹I (a) and ²¹¹At (b) on anion exchanger Dowex 1 from concentration of Hg²⁺ in solution.

The inflection points on the curves indicate that the logKₐ is 5.4 and 4.1 for HgAt⁺ and HgI⁺, respectively. Formation of strong bonding between At⁻ and Hg²⁺ indicates that method of
labelling biomolecules by utilization of metal cation bridge between $^{211}$At and biomolecule is the potentially useful for preparation of astatine radiopharmaceuticals.

References
SYNTHESIS OF THE POSSIBLE RECEPTOR LIGAND
$[^{131}I]$-3-IODO-CYTISINE FOR IN VIVO IMAGING OF THE
nACHRECEPTOR


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Introduction
In-vivo labeling of the nicotinic acetylcholine receptors (nACHRs) could be a useful tool for early diagnosis and evaluating therapies of neurodegenerative disorders. Although central nACHRs contribute to a variety of brain functions, relatively few data are available on their physiological functions and their potential role in neurological diseases [1]. No data have yet been available on the regulation of nACHRs in the disease process of Alzheimer’s disease or other neurodegenerative disorders in living patients. 2-[^{18}F]-A85380 is the first radiotracer to visualize the distribution of nACHR in human brain in vivo [2]. This PET ligand has a high affinity and subtype selectivity for α4β2 nACHR. A reduction of different nACHR subtypes has been reported in post-mortem brains of patients with Alzheimer's disease (AD), Parkinson's disease (PD) and dementia with Lewy bodies (DBL) [3]. 3-Iodo-cytisine displays a high affinity for neuronal nACHRs and subtype selectivity for α4β2 [4] and thus for the radiolabeled analog a high potential can be expected for its clinical use in the diagnostic of neurodegenerative disorders.

Here, we report on an optimized labeling of cytisine with iodine-131 by electrophilic substitution.

Materials and Methods
The n.c.a. iodination of cytisine was carried out by three standard methods for electrophilic substitution (chloramine-T, iodogen and nitric acid). The oxidation agent was added to a solution (500 µl) of n.c.a. iodine-131 (100 µl in phosphate buffer pH 7.4) and cytisine (8.5 µmol). Trifluoroacetic acid (TFA) (chloramine-T, iodogen homogenous reaction), acetic acid (chloramine-T) and several buffers pH 1-9 (iodogen heterogeneous reaction, nitric acid) were used as solvents. The syntheses were optimized with respect to time, temperature and
the amount of cytisine. The reactions were stopped by addition of sodium bisulfite (0.066 M in 2N NaOH-solution) and an aliquot was analyzed by HPLC (UV-detector, RP-18-column, 1 ml/min flow, solvent: 0.1 % TFA).

Results
All investigated oxidation agents enables the $^{131}$I-iodination of cytisine (Table 1). The regiospecific labeling of position 3 of cytisine and the inferior reaction to $[^{131}]$I-ido-cytisine showed the preferred activation of this position for electrophilic substitution. Using iodogen under heterogeneous reaction conditions provided the highest radiochemical yield; minor amounts of $[^{131}]$I-5-ido-cytisine could be observed as labeling side product. The specific activities were calculated as $>$300 GBq/μmol from the invisible corresponding UV-limit of the HPLC-chromatogram. The product was separated by HPLC-purification from hydrophilic compounds and $[^{131}]$I-5-ido-cytisine. For the labeling via the chloramine-T-method a SEP-PAK-purification method is still under investigation. This procedure may fasten the labeling and avoid side products from decomposition as well.

Conclusions
For the first time, iodine-131 labeling of cytisine was succeeded selectively at the position 3. The synthesis could be simply applied to produce $[^{123}]$I3-iodo-cytisine. Sufficient yields and the radiochemical purity after HPLC-purification make this nAChR-ligand available for further evaluation. Our synthesis of $[^{123}]$I3-iodo-cytisine allows 1) the potential labeling of the majority of nAChRs in the human brain, 2) a comparison with 2-$[^{18}]$F-A85380-data and 3) the evaluation of nAChR ligands as a potential diagnostic tool in Alzheimer’s disease and other neurodegenerative disorders.

References
Table 1: Optimized reaction conditions and radiochemical yields (rcy) of 
\([^{131}I]3\)-iodo-cytisine, \([^{131}I]5\)-iodo-cytisine and \([^{131}I]3,5\)-diiodo-cytisine

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<th>Oxidation agent</th>
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<th>% rcy ([^{131}I]5)-iodo-cytisine</th>
<th>% rcy ([^{131}I]3,5)-diiodo-cytisine</th>
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<tr>
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<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1.0 µmol</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iodogen (homogeneous)</td>
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<td>11</td>
<td>&lt;1</td>
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<tr>
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<td>5</td>
<td>&lt;1</td>
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<tr>
<td>1.0 µmol</td>
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<tr>
<td>nitric acid</td>
<td>HOAc, 105°C, 45 min</td>
<td>49</td>
<td>&lt;1</td>
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<td>200µl 2N</td>
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PREPARATION OF $^{188}$RE-HEDP AND ITS PRE-CLINICAL STUDY

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Introduction

It was estimated that about four million deaths occur due to cancer in the world each year. Nearly 50% of patients dying of cancers have skeletal metastases at the time of death. Although external radiation therapy provides significant palliation in approximately 80% of patients with painful bone metastases, its application is inconvenient in patients with multifocal sites of pain. The challenge to develop less toxic but equally effective palliative agents for debilitating skeletal pain due to osseous metastases has been of interest to nuclear medicine physicians for the last 40 years. The initial goal was to develop a therapeutic agent that would localize in metastases and emit both a beta particle suitable for therapy and a gamma ray suitable for imaging and calculating dosimetry. 1-hydroxyethylidene dipiphosphonate (HEDP) is known to concentrate markedly in bone. Rhenium-188 is an attractive radionuclide for therapy. Its maximum beta-energy is 2.1MeV with a 15% abundance of gamma ray emission (155KeV). It has a shorter half-life (16.9hrs) than both $^{153}$Sm and $^{186}$Re. The short physical half-life reduces the problems of radioactive waste handling and storage. In particular, $^{188}$Re is available from an in-house generator system, $^{188}$Re can be obtained from a $^{188}$W/$^{188}$Re generator, which makes it very convenient for clinical use.

In this study, we synthesized (1-hydroxyethylidene) dipiphosphonic acid and prepared $^{188}$Re-HEDP with generator-produced $^{188}$Re. The optimum labelling conditions were systematically investigated. $^{188}$Re-HEDP kit were prepared. The pharmacokinetics of $^{188}$Re-HEDP in mice and the toxicity as well as the stability of $^{188}$Re-HEDP was studied.

Experiments and results

Preparation of $^{188}$Re-HEDP kit: $^{188}$Re-HEDP has the advantage of ready, convenient and on-demand availability from the $^{188}$W-$^{188}$Re generator and a HEDP kit. The influence of some factors on the labeling efficiency of $^{188}$Re-HEDP had been systematically investigated. According to the optimal labeling conditions, the kit formulation was developed. The kit consists of ligand (HEDP), reducing(SnCl2), antioxidant(Vc), excipient and so on. For preparation of the lyophilized kits, under sterile and filled with nitrogen conditions, all starting materials were weighed as the formula ratio, dissolved in water or HCl solution separately, and mixed. The mixture was filtered via a sterile filter and then dispensed into sterile vials of 1 ml each and lyophilized in the Virtus freezer, in which the freeze dried vials can be capped automatically. After the HEDP kit had been reconstituted with the $^{188}$Re-solution, the radiochemical purity of the $^{188}$Re-HEDP injection was over 95 %.

Stabilities of the HEDP kit and $^{188}$Re-HEDP injection. The stabilities of the HEDP kit and
In this study, the biodistribution of the 188Re-HEDP injection was investigated under different storage conditions. The items for the HEDP kit included the labeling efficiency, contents of HEDP and SnCl2, sterility and bacterial endotoxin tests. The examined items for 188Re-HEDP injection included the pH, radiochemical purity, sterility and bacterial endotoxin tests. The influence of light, temperature and humidity on stability was studied. The results indicated that the kits were stable when they had been stored at room temperature for 3 months. When the kits were exposed to strong light, high humidity or at 40°C, they were stable for ten days but not stable at 60°C. It can be stable for 6 months at 2-8°C. 188Re-HEDP injection was stable at room temperature, strong light or high humidity. However, it was unstable at 40°C and 60°C.

**Study of the biodistribution of 188Re-HEDP injection in animal.** Kunming mice weighing 20±2g each were used to determine the tissue biodistribution of 188Re-HEDP. The mice were sacrificed at 1h, 3h, 24h, 48h and 72h (five mice at each time) after injection of approx. 214 MBq/kg 188Re-HEDP in a volume of 0.2 mL via the tail vein. The results indicated the high uptake in the skeletal tissue and the quick clearance in the blood.

**Table 1** The biodistribution of 188Re-HEDP in mice (ID%/g. X±SD. n=5)

<table>
<thead>
<tr>
<th>Tissue</th>
<th>1h</th>
<th>3h</th>
<th>24h</th>
<th>48h</th>
<th>72h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blood</td>
<td>0.91±0.51</td>
<td>0.25±0.04</td>
<td>0.17±0.10</td>
<td>0.06±0.04</td>
<td>0.09±0.08</td>
</tr>
<tr>
<td>Heart</td>
<td>0.23±0.09</td>
<td>0.09±0.02</td>
<td>0.05±0.01</td>
<td>0.05±0.04</td>
<td>0.07±0.05</td>
</tr>
<tr>
<td>Lung</td>
<td>0.56±0.18</td>
<td>0.29±0.07</td>
<td>0.16±0.05</td>
<td>0.08±0.04</td>
<td>0.22±0.11</td>
</tr>
<tr>
<td>Liver</td>
<td>0.34±0.11</td>
<td>0.23±0.06</td>
<td>0.17±0.02</td>
<td>0.19±0.09</td>
<td>0.10±0.09</td>
</tr>
<tr>
<td>Spleen</td>
<td>0.18±0.06</td>
<td>0.09±0.02</td>
<td>0.11±0.07</td>
<td>0.10±0.09</td>
<td>0.09±0.07</td>
</tr>
<tr>
<td>Kidney</td>
<td>2.41±0.90</td>
<td>1.64±0.49</td>
<td>0.98±0.11</td>
<td>0.81±0.16</td>
<td>0.47±0.12</td>
</tr>
<tr>
<td>Intestine</td>
<td>0.32±0.15</td>
<td>0.17±0.04</td>
<td>0.09±0.04</td>
<td>0.08±0.07</td>
<td>0.17±0.15</td>
</tr>
<tr>
<td>Bile</td>
<td>2.05±1.08</td>
<td>2.79±1.15</td>
<td>1.28±0.52</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Muscle</td>
<td>0.22±0.18</td>
<td>0.23±0.19</td>
<td>0.03±0.01</td>
<td>0.03±0.01</td>
<td>0</td>
</tr>
<tr>
<td>Femur</td>
<td>29.39±5.72</td>
<td>31.22±7.53</td>
<td>32.40±6.36</td>
<td>28.56±4.96</td>
<td>26.05±4.02</td>
</tr>
<tr>
<td>Pancreas</td>
<td>0.20±0.08</td>
<td>0.09±0.02</td>
<td>0.04±0.02</td>
<td>0.05±0.04</td>
<td>0.03±0.03</td>
</tr>
<tr>
<td>Marrow</td>
<td>1.06±0.52</td>
<td>3.48±0.71</td>
<td>0.38±0.06</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Spermmary or ovary</td>
<td>0.29±0.21</td>
<td>0.13±0.04</td>
<td>0.06±0.02</td>
<td>0.08±0.06</td>
<td>0.07±0.05</td>
</tr>
<tr>
<td>Bladder</td>
<td>0.90±0.67</td>
<td>1.59±1.47</td>
<td>0.20±0.02</td>
<td>0.16±0.10</td>
<td>0.34±0.33</td>
</tr>
</tbody>
</table>

**Study of the pharmacokinetics of 188Re-HEDP injection.** The mice were injected separately with 395.217.44MBq/kg 188Re-HEDP. The radioactivities of the blood samples collected at 0.5min, 5min, 10min, 0.25h, 0.5h, 1h, 2h, 3h, etc were measured. The results showed that the blood clearance curve corresponded to a two-phase distribution (Fig. 1).
Long-term toxicity examination of $^{188}$Re-HEDP injection. Three dose of 74, 222 and 444 MBq/kg were injected through i.p. to SD rats and other three doses of 37, 74, 148 MBq/kg through i.v. to Beagle dogs once two weeks for a treatment course and it lasted for 4 courses. After the administration, these animals were observed for 27 days (convalescence). At 7th and 27th day after the last injection, respectively, half of the animals in each group were killed and the hematological, biochemical and histological examinations were performed. The results show that the weight and WBC of the higher dose group rats fell obviously after 4 courses. Compared with the control group, there were obvious differences ($p<0.05$, $p<0.01$). After 27 days convalescence, the WBC was still lower than the control ($p<0.05$). During the treatment, compared with the control, the WBC of the middle dose group and the lower dose group rats fell obviously ($p<0.05$) but after 27 days convalescence it was resumed ($p>0.05$). The safe dose was lower than 333MBq/kg once. After 4 courses, the weight and WBC of the dogs in both the higher dose group and middle group and the thrombocyte of the all three groups fell obviously. Compared with the control, there were obvious differences ($p<0.05$). After the convalescence, the thrombocyte of the higher dose group was still lower than that of the control ($p<0.05$). During the treatment, compared with the control group, there was no obvious difference ($p>0.05$), for lower dose group, except thrombocyte fell obviously. All indexes resumed to the normal level in the convalescence period. The safe dose for one application is 74 MBq/kg.

Conclusion
The above results suggest that $^{188}$Re-HEDP is a very good candidate for the treatment of bone pain due to the high uptake in the skeletal tissue and the quick clearance from the blood.
LABELING OF CREATININE WITH TECHNETIUM-99m

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The creatinine (2-amino-1,5-dihydro-1-methyl-4H-imidazol-4-one), nitrogenous final product of creatine metabolism in mammals, is formed by the nonenzymatic cyclization of creatine in muscle tissue. Its level in biological fluids is generally accepted as an indication of the presence or absence of renal failure, muscular and thyroid functions [1-3]. Creatinine is a clinically important index of renal glomerular filtration rate. Urine creatinine levels can be used as a screening test to evaluate kidney function or can be part of the creatinine clearance test. In case of kidney dysfunction or muscle disorders the creatinine concentration in serum/plasma may rise to a higher value than in healthy body [4-6].

Technetium-99m has been used in nuclear medicine and in biomedical research to label molecular and cellular structures employed as radiotracers. \(^{99m}\)Tc is utilized to label molecules and cells, used as radiopharmaceuticals, and also to label biological species. It presents many desirable characteristics. SnCl₂ method is frequently used as a reducing agent in the \(^{99m}\)Tc-labeling process [7]. Creatinine metabolism might be investigated by using labeled \(^{99m}\)Tc-creatinine in healthy or uremic rats.

Creatinine was labeled with Tc-99m by using the tin(II)chloride method. One mg of creatinine was dissolved in 1 mL distilled water and 0.1 mg SnCl₂.2H₂O
solution was added. After 3 mCi (111MBq) Na\textsuperscript{99m}TcO\textsubscript{4} was added into the mixture, it was left to incubate for 15-20 minutes. Labeling procedure was carried out at different pH values by adjusting the medium pH with 0.1 N ammonium hydroxide. One mg ascorbic acid was added into reaction mixture. Quality controls were done by RTLC (Radio Thin Layer Chromatography), RHPLC (Radio High Performance Liquid Chromatography) and paper electrophoresis. The activity was counted using a Cd(Te) detector equipped with a RAD 501 single channel analyzer. Then labeling yield was determined from these chromatograms. To obtain the optimum labeling yield of \textsuperscript{99m}Tc-creatinine, effects of pH of reaction and concentration of stannous chloride were investigated.

**Effect of pH**

The influence of pH on the radiolabeling yield was examined at pH 2, 5, 7 and 9. The effect is shown in Fig.1. The highest yield is obtained at pH between 5 and 7.

![Figure 1](image.png)

**Fig.1.** Effect of pH on radiolabeling yield of \textsuperscript{99m}Tc-creatinine

**Effect of stannous chloride concentration**

The effect of stannous chloride on radiolabeling was studied between 100 and 200 \( \mu \)g stannous chloride concentrations. As seen in Fig. 2, the radiolabeling yield reaches a maximum value when 100 \( \mu \)g stannous chloride is used. As a result, labeling yield was found to be over 85\% when pH of the reaction was 7 and amount of stannous chloride used was 100 \( \mu \)g.
Fig. 2: Effect of stannous chloride concentration on radiolabeling yield of $^{99m}$Tc-creatinine

REFERENCES


Phenolphthalein (dihydroxyphthalophenone) is well known as one of the most widely used of the cathartic drugs, being the basis of many proprietary laxatives. Its precise mechanism of action is unknown. It tends to act longer than other laxatives because it enters the enterohepatic circulation and is re-excreted in bile into the intestine. It acts within 4 to 8 h after ingestion. Starting from this pharmaceutical property of phenolphthalein, in this study we examined the radiopharmaceutical potential of radioiodinated phenolphthalein. Phenolphthalein was radioiodinated with iodine-131 using the iodogen method which was earlier applied to our laboratory for radiiodination of different kinds of chemical compounds having at least one phenyl ring in their structures[1].

The phenolphthalein molecule has two phenyl rings which are activated for electrophilic substitution reactions by –OH groups. Consequently, phenolphthalein was successfully radioiodinated with iodine-131 with a radioiodination yield of about 100%. The radioiodinated phenolphthalein with $^{131\text{I}}$ was intravenously injected to an adult male rabbit via the ear vein after anesthetizing by a mixture of Alfaxyne and Alfamine (Serva) to determine the dynamic and static situations of radiiodinated phenolphthalein in the metabolism. Dynamic and static scintigrams were obtained using a gamma camera of routine nuclear medical imaging studies. For these studies a gamma-camera adjusted to detect γ-radiations of $^{131\text{I}}$ was used. Dynamic scintigrams were obtained over the first half hour with frames of 5 min following the administration of the labeled compound. Static scintigrams were obtained in different time intervals up to about 7 days following the administration of the compound. In addition, an aqueous solution of Na$^{131\text{I}}$ was administrated to another rabbit as a control. As a result, it was observed that radiiodinated phenolphthalein was rapidly accumulated in the bile in about 2 h, and then in the large intestines over about 10 h. The radioactivity in the large intestines only decreased to a smaller value during 1 to 4 days after the administration. On the 7th day the radioactivity was not completely cleared from the large intestines as is seen in the Figure-1. These results have indicated that radiiodinated phenolphthalein may be used as a scintigraphic agent for examining large intestinal diseases.

Figure 1: Static scintigrams of radiiodinated phenolphthalein with iodine-131 which was administered to a rabbit via the ear vein.
MEASUREMENT OF DYNAMIC TRANSPORT PROCESSES IN PLANTS USING SHORT-LIVED ISOTOPES

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Introduction
The carbon isotope $^{11}$C was first used in plant research in 1939 [1], but due to the short half-life (20.4 min) it was not very useful for investigation of the detailed biochemistry of primary interest at that time. Once available, $^{11}$C replaced $^{13}$C and soon led to the discovery of the Calvin Cycle. Today, we see a renewal in the use of the short-lived isotopes with their unique advantages for non-invasive and repeatable measurement on the same plant [2]. Modern radiation detection and data processing techniques are opening a new window for observing the plant’s internal processes with 2- and 3D-imaging.

There are also several other similar positron emitting short-lived isotopes highly applicable in plant research, either to study root mineral uptake (e.g. of N, K, Mg) or to investigate transport of specifically labelled compounds being translocated in plants (e.g. sugars, phytohormones, peptides). A big advantage of $^{11}$C is that it is readily produced as $^{11}$CO$_2$ so it is a near-perfect tracer of atmospheric carbon dioxide, the major substrate of plant growth. Because of this dominant role of carbon dioxide $^{11}$C has been important in studies of plant physiology (e.g. shoot-root interactions, control of carbon partitioning between competing sinks, plant signalling networks, growth regulator, xylem flow), plant pathology (e.g. plant defence systems, host-parasite interactions, xenobiotics), and environmental research (e.g. gaseous and water borne pollution, increasing atmospheric CO$_2$).

In this poster we give examples of $^{11}$C use in qualitative detection of dynamic changes in long-distance transport caused by local changes in oxygen level, and also to obtain quantitative data on partitioning between competing sinks in plants.

Atmospheric oxygen concentration affects import into wheat ears
Carbohydrate source-sink interactions play an important role in determining both crop yield and the distribution of individual fruit sizes. $^{11}$CO$_2$ was applied to leaves to follow in vivo the distribution of photoassimilates in wheat plants where, after heading, the ear with its developing kernels is the major sink for carbon compounds. During the filling period, a large portion of recently fixed carbon is directed towards the ear. Continuous labelling experiments were performed to test the effect of oxygen concentration on carbon import of the ear (Fig. 1). Lowering oxygen at the ear from 21 to 8 % (v/v) resulted in a marked reduction in carbon supply to the kernels. More carbon was then directed to the basal plant parts, an effect which became evident about 1 h after treatment. When the oxygen concentration was returned to 21 % (v/v), allocation of $^{11}$C-labelled photoassimilates into the ear was restored [3].
Measurement of carbohydrate partitioning between developing apple fruit with a time resolution of 1 minute over a long period of time.

While the above approach gives a qualitative description of source-sink interactions, there is little to no mechanistic understanding of the processes involved in the control of the carbon distribution. Short-term changes in partitioning of recently fixed photosynthetic between alternative apple fruits were followed using *in vivo* measurement of photosynthetic movement over a period of 5 days, with a time resolution of 1 minute.

Figure 2. Photograph of experimental set up used to monitor partitioning of recently fixed photosynthetic between apple fruit. 14CO₂ was applied to a bourse leaf contained with a perspex chamber and tracer levels within each fruit were monitored. The U shaped plastic around the upper fruit in the picture was used to direct cooled air around this fruit and not the other.

The data indicates that apple fruit import photosynthesize at a rate that matches their growth/storage capacity, so that increased availability of photosynthetic causes only a small immediate increase in import. Over several hours further and a much larger increase occurs (Fig. 3). This was interpreted as a consequence of increased enzymatic activity within the fruit induced by the increased availability of photosynthese. This interpretation was supported by the subsequent observation that a return to the initial supply of photosynthesize resulted in the fruit continuing to import more photosynthesize than prior to initiation of the change in supply. Such a detailed measurement of the time sequence of changes in supply to a fruit is only possible with non-destructive *in vivo* techniques.
Figure 3. Changes in carbon partitioning between apple fruit induced by altering the temperature of individual fruit (modified from [4]).

Conclusion
Short-lived isotopes have a growing role in the non-invasive measurement of dynamic processes with plants. Recent advances in 2D- and 3D-imaging offers new opportunities in plant science, and will be a central part of the new NIM (non-invasive measurement) Centre at the Forschungszentrum Jülich.

Acknowledgement
We thank the Institute of Nuclear Chemistry, Forschungszentrum Jülich GmbH, for a continuous online supply of $^{13}$CO$_2$ at the Baby Cyclotron (BC 1710).

References
PRODUCTION OF $^{62}$Zn, $^{65}$Zn AND $^{208}$Pb RADIOISOTOPES FOR
STUDYING THE TRANSPORT OF ZINC AND LEAD IN PLANTS

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In the Carpathian Basin, significant percentage of watershed area and floodplains of
rivers are utilised agriculturally. Several potential sources of poisonous metal
pollution have been identified in these areas. Because of spills from some of them a
few severe accidents have happened especially in the watershed area of Tisza River
during the last decades. The motivation of our present work was to produce $^{62,65}$Zn
and $^{208}$Pb radioisotopes because they can be used especially as tracers for studying the
kinetics of uptake, transport and accumulation of zinc and lead by plants under
different circumstances.

The $^{62}$Zn, $^{65}$Zn and $^{208}$Pb radioisotopes were produced via the nuclear reactions listed
in Table 1. The Q-values of the nuclear reactions and the decay properties of $^{62}$Zn,
$^{65}$Zn and $^{208}$Pb are also collected in Table 1.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life (h)</th>
<th>$E_γ$ (keV)</th>
<th>$I_γ$ (%)</th>
<th>Contributing reaction</th>
<th>Q-value (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{62}$Zn</td>
<td>9.26</td>
<td>548.38</td>
<td>15.2</td>
<td>$^{63}$Cu(p,n)$^{62}$Zn</td>
<td>-13.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>596.70</td>
<td>25.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>5862.24</td>
<td>1115.55</td>
<td>50.6</td>
<td>$^{65}$Cu(p,n)$^{65}$Zn</td>
<td>-2.1</td>
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</tr>
<tr>
<td>$^{208}$Pb</td>
<td>51.87</td>
<td>279.197</td>
<td>81</td>
<td>$^{205}$Tl(p,n)$^{205}$Pb</td>
<td>-1.8</td>
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<tr>
<td></td>
<td></td>
<td>401.32</td>
<td>3.35</td>
<td>$^{205}$Tl(p,3n)$^{203}$pb</td>
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<tr>
<td></td>
<td></td>
<td>680.516</td>
<td>0.75</td>
<td></td>
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</tr>
</tbody>
</table>

Table 1. Decay data and Q-values of the contributing reactions.

Target preparation and irradiation

Irradiations were done at the vertical radioisotope production facility at the MGC-20E
cyclotron of ATOMKI (Debrecen, Hungary). For fabricating the targets the central parts of 3 mm thick and dia 53 mm copper discs were partly removed by a miller. A
dia 12 mm and 2.8 mm deep bore-hole was formed in each target in this way. In the
case of $^{62}$Zn and $^{65}$Zn production, the copper bottom of the bore-hole was irradiated with 17 MeV protons. In the case of production of $^{205}$Pb, 404 mg melted Thallium of
natural isotopic composition was pressed into the bore-hole and the obtained 0.4 mm
thick thallium layer was irradiated with 17 MeV protons. The diameter of the beam
spot on the target was around 1 cm in both cases. During irradiation the backside of
the target structures was cooled with de-ionised water while a He-gas stream was used
to cool the bombarded surface. After irradiation the activated dia 12 mm bottoms of
the bore-holes were removed by pressing them out from the copper disc using a
special tool.

\[ ^{62,65}\text{Zn production} \]

\(^{62}\text{Zn} \) is formed via the \(^{63}\text{Cu(p,2n)}^{62}\text{Zn} \) nuclear reaction below 17 MeV using natural
copper target. The result of estimation of the thick target yield of \(^{62}\text{Zn} \) was 0.40
mCi/µAh (14.8 MBq/µAh) using evaluated cross-section data taken from literature
[1]. According to the long half-life of \(^{62}\text{Zn} \), the calculated theoretical yield of the
accompanying \(^{62}\text{Zn} \) radioisotope is only 0.24 µCi/µAh (9.2 kBq/µAh) [2] up to 17
MeV, although the \(^{68}\text{Cu(p,n)}^{65}\text{Zn} \) nuclear reaction has a relative high cross-section
maximum at 10.5 MeV (around 220 mb) [1]. At the end (EOB) of a four hours long
irradiation with 5 µA proton beam the resulting \(^{62}\text{Zn} \) activity was 8 mCi while the
\(^{62}\text{Zn} \) activity reached 5 µCi. These values were in good agreement with the calculated
values.

The separation of the zinc radioisotopes was done using a radiochemical method we
described earlier [3]. The activated copper was dissolved in 1 ml concentrated nitric
acid. 70 mg natural Zn was also added to the solution as carrier. The dissolved target
with the carrier Zn was evaporated to dryness. The solid salt was dissolved in 2 mol/l
HCl acid. An anion-exchanging column prepared freshly (DOWEX1-8 resin, size
100-200 mesh, length 12 cm, and internal dia 10 mm, treated 1 day earlier) was used
for the separation in 2 mol/l HCl media. After the separation the \(^{62}\text{Zn} \) and \(^{65}\text{Zn} \)
isotopes were eluted by distilled water. The chemical yield was around 79%. The
radioactivity of the final solution was 178 MBq (4.8 mCi) for the \(^{62}\text{Zn} \) and 137 kBq
(3.7 µCi) for the \(^{65}\text{Zn} \). This solution was used for tracer studies.

\[ ^{203}\text{Pb production} \]

The \(^{203}\text{Tl(p,n)}^{203}\text{Pb} \) reaction was employed [4, 5]. The target was activated with beams
of 4 µA in two irradiations. The first irradiation lasted for 4 hours. It was followed by
a 20 hours long break due to other scheduled duties of the cyclotron. The second
course of activation was 6 hours long. According to our measurement, the EOB
activity was around 40 µCi. It is worth to mention that we could loose some activity
during the irradiation because of the low melting point (303 °C) of the thallium target
material. The radiochemical separation of \(^{203}\text{Pb} \) from the target material was based on
the different solubility of thallium and lead ions in alkali media. First the thallium was
removed from the Cu backing. (Only 3% of the activity were lost due to the
implantation of \(^{203}\text{Pb} \) into the target holder.) The thallium (together with 70 mg lead
carrier) was dissolved in 2 ml concentrated (65 w%) nitric acid and then the thallium
was precipitated by 50 w% sodium hydroxide. The lead remained in the solution in
anion form of plumbate. The precipitate was filtered and washed by 0.5 ml NaOH.
The original and the washing solution was summed and neutralised by nitric acid.
This liquid was diluted by distilled water and from it four samples of 10 ml were
prepared for monitoring study. The chemical yield was 74% and activity of each final
sample was 9.25 MBq (0.25 mCi) approximately.
Transport studies

Demonstration purpose laboratory experiments have been performed to follow the accumulation of the produced radioisotopes in maize (Zea mays), sunflower (Helianthus annuus) and Areca lutescens plants. The maize and sunflower plants were grown in containers containing commercial gardening soil. The Areca lutescens palm was grown in a hydroponics culture. The radioactive solutions were introduced to the bottom part of the containers via glass tubes. The transportation of $^{65}$Zn and $^{203}$Pb was followed via detecting the emitted gamma quanta with two 1x1” and two 2x2” NaI(Eu) scintillation detectors embedded in lead shielding. Each detector was connected to an ATOMKI QNMS-87 type 4 x 1-channel analyser system. The detector signals could be also connected to a CANBERRA S80 multi-channel analyser to measure separately the spectra of the radioisotopes. The long-term accumulation of $^{65}$Zn was followed by counting leaf samples with a calibrated HpGe detector connected to a PC based multichannel analyser.

In the Areca lutescens palm some Zn appeared in the foliage within 1–2 hours after introducing the $^{65}$Zn tracer. Probably it was transported by the transpiration induced water flow. On a few-hours-scale the $^{65}$Zn uptake was less than 1% of the introduced activity. On a few-week-scale the $^{65}$Zn level increased gradually in the foliage. On a few-month-scale a complex, unexplained kinetics of Zn uptake was observed. On a few-days-scale $^{203}$Pb accumulated in the aboveground parts of the maize and sunflower plants with a superimposed diurnal periodicity (especially in the case of maize) which suggests a transport with water flow. Ten days after tracer introduction the plant averaged $^{203}$Pb activity of unit mass for sunflower was about ten times as much it was for maize. In maize the amount of foliar Pb was about ten times more than in the stem. Absolute activity measurements revealed that up to 62% of the introduced Pb was accumulated in sunflower and about 40% in maize.

The results show that the $^{65}$Zn and $^{203}$Pb radioisotopes can be used for studying the uptake and transport kinetics of Zn and Pb in plants. Further research is needed to clarify the methodology and feasibility of tracer studies in field experiments.

References

7. Radioactive Indicators in Research and Industry
RESEARCH, DEVELOPMENT AND APPLICATIONS OF PROCESS ORIENTED RADIOTRACER METHODS IN THE OIL & GAS AND PETROCHEMICAL INDUSTRY

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Quite often it is suggested that ‘radiochemistry’ has matured and does not need any further development. Next to this, it is stated that ‘radiochemical’ methods have been outrun by new, non-nuclear methods and actually have lost their ‘raison d’être’. Even with a view on process-oriented research, these statements may only partly be true as far as fundamental research is concerned as during the last decades some interesting nuclear-based techniques have been developed and applied to various processes.

Some recent research and development studies may contradict the pessimistic view ventilated in the first paragraph. For a proper assessment of the amount of displaceable oil in underground oil reservoirs, recently a radiotracer method has been developed, in which the radiotracer compound partitions over the oil/water phase present [1]. Even the most sensitive non-nuclear based analytical techniques could not establish e.g. the leach-ability of polymer packing material into the contained food, or the rate of metal volatilisation loss from catalysts radiotracer methods with ultra-low detection techniques in an analytical hostile environment. Consequently ‘radiochemical’ methods have been developed.

Though attempted with for instance magnetic resonance imaging, this non-nuclear method could not provide the information provided by nuclear-based techniques, i.e. fairly detailed visualisation of ‘process flow’ [2-7] and even flow of ‘reacting radiotracers’ [8-10] inside model reactors. In these developments single particles, either loaded with a single γ-photon [4,5] or a β⁺-emitter [6,7], have been exploited. ¹¹C, ¹⁵N and ¹⁵O being β⁺-emitters, offer unique opportunities to monitor ‘reactive flow’ inside operating catalysts amply applied in petrochemical based industries [8-10] or to study atmospheric reactions [11]. As a spin-off of the latter studies, new catalytic synthesis routes for dedicated ¹³C-labelled compounds [12] have been developed.

In view of the strong incentive to improve the return on average capital employed, within the process-oriented industry there is still a strong need for analytical monitoring techniques capable of providing information under actual process conditions (in situ) without any disturbance of process flow changing product quality or operational production capacity. Of course, this is the strongest point for the application of a γ-radiotracer technique, which has been recently applied for better understanding of the actual process (production yield improvement [13]) or during malfunctioning of distinct process equipment (operational integrity [14]). Here, it should especially be noted that never one sole technique will be ‘soul-saving’ and that the main progress should be sought into close deliberations with issue-owners of critical businesses (e.g. catalyst research & development, reaction & reactor engineering) and into co-operation with other disciplines like additional analytical techniques, computational (reaction) modelling. In addition
to this radiotracer studies on operational process equipment may be an excellent tool for validating Computational Fluid Dynamics (CFD) simulations of that process [15].

This (limited) review will present some of these recent applications, and will substantiate these with associated relevant radiochemical issues and some results obtained.

References
POSITRONIUM FORMATION IN SUPERCRITICAL FLUID N₂O

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Introduction
A number of positron annihilation lifetime (PAL) measurements have been carried out for liquid and solid phases in terms of materials science [1,2], but studies of positron annihilation in supercritical fluids are limited. To produce insights into positronium (Ps) formation processes, or the other hand, PAL spectra have been measured in low density gas targets by means of low-energy positron beams, since the measured annihilation rate reflects a single positron-molecule collision and the results can be directly compared with theoretical calculations [3]. Although PAL spectra have been measured in a variety of gaseous species [4,5], only a few measurements have been conducted in dense gases near supercritical fluid (SCF) phases [6].

The PAL measurement has an advantage in investigating the many-body effects and microscopic structures of SCFs, because the positron annihilation rate is very sensitive to electron densities that can be varied widely in SCFs. In the present work, we measured PAL spectra in N₂O as a function of the density that was continuously controlled from the gas to liquid phases via the SCF phase to acquire a knowledge on the Ps formation process in denser media.

Experimental
PAL spectra were obtained by a conventional fast-fast coincidence system with BaF₂ scintillators (ϕ 30 mm x 10

Figure 1. Phase diagram (thick line) of N₂O (Tc = 309.6 K, Pc = 7.24 MPa). The closed circles show measured points. The open circle shows the critical point. The thin lines show isochore.
mm) having a time resolution of 0.24 ns at FWHM. A positron source ($^{22}$Na, 4.0 MBq) was sandwiched between two sheets of kapton film (7.5 μm thick) where 20% of positron was annihilated with one lifetime component (0.37 ns). The positron source was put into the cell (15 ml) which was kept at constant temperatures $dT \leq 0.1$ K and pressures $dP/P \leq 2\%$. The N$_2$O sample was prepared with a purity of 99.9999%. Figure 1 shows a phase diagram of N$_2$O in the vicinity of the critical point together with the measured points.

**Results and Discussion**

The accumulated PAL data were analyzed using the PATFIT code [7] with four components of the lifetime. Figure 2 shows both the lifetimes ($\tau_i$) and intensities ($I_i$) as a function of the number density of N$_2$O. The first component ($\tau_1=0.12$ ns) is ascribed to the p-Ps free decay. The second component ($\tau_2$) is ascribed to the free positron annihilation with an electron. The lifetimes $\tau_1$ and $\tau_4$ are much longer than those calculated with the Dirac’s free positron annihilation cross section, and these two components are ascribed to the pick-off annihilation of o-Ps. In addition, the ortho-para ratio of the intensities, $(I_3+I_4)/I_1$, fulfilled the spin statistics, the correction based on the three $\gamma$ decay of o-Ps being taken into account for the lifetime.

The lifetime $\tau_2$ gradually decreased with an increase of the density $n$, and the effective number of electrons for the free positron annihilation, $Z_{eff} = 1/(\tau_2 \pi \hbar^2 n)$, decreased from 100 to 20. The $Z_{eff}$ extrapolated to a single positron–molecule collision limit is larger than the literature value $Z_{eff} = 78$ [4]. This is explained by considering an increase of the local density...
around the positron arising from the positron–molecule attraction. Since the mean intermolecular distance (0.8–0.4 nm) is much shorter than the de Broglie wavelength of thermalized positron (λ=3 nm), the positron having a rather high kinetic energy due to a quantum effect should be confined in an intermolecular space. The decrease of Z_{eff} from 100 to 20 would reflect energetic positron–molecule collisions.

When the density was larger than 4.5 nm⁻³, the third lifetime component appeared, while the fourth component (the longest) was observed in a wide range continuously from the gas phase (3 nm⁻³) to the liquid phase (13 nm⁻³). With a combined Ore-plus-spur model, the density and temperature dependence of the Ps formation in molecular gases has been semi-quantitatively explained such that a fraction of o-Ps produced by the Ore process is rather independent while the other fraction of o-Ps formed by the spur processes depends on the density and temperature [5]. From the density dependence of the o-Ps intensity observed in the present experiment, the fourth component (τ₄) is ascribed to o-Ps produced by the Ore process (Ore-o-Ps) and the third component (τ₃) is due to o-Ps produced by the spur processes (spur o-Ps).

The significant difference between these two o-Ps lifetimes suggests that the o-Ps pick-off annihilation takes place in different environments. The spur o-Ps should be formed near a terminal spur and its lifetime might be shortened by chemical reactions with species created in the spur. The Ore o-Ps is, on the other hand, free from such chemical reactions, because the mean free path of energetic Ps is much longer than that of the other species produced in the terminal spur.

The Ore o-Ps lifetime (τ₄) showed a rapid drop in the high density region beyond 8 nm⁻³. Similar behavior observed in ethane gas was explained by taking account of Ps self-trapping [6]. Supercritical fluids are very inhomogeneous media in terms of molecular distribution. And the density fluctuation is large near the critical point. The interaction between a Ps and the medium is repulsive, and a decrease in the local density around the Ps would reduce the pick-off annihilation rate of o-Ps.

References
ISOTOPIX TRACER STUDIES OF CHEMICAL BEHAVIOR OF RARE EARTH ELEMENTS IN ENVIRONMENTAL AND BIOLOGICAL SCIENCES

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Rare earth elements (REE), a group of elements with atomic numbers from 57 to 71, have been widely applied in recent years not only in industry but also in agriculture, forestry, animal husbandry and medicine. Numerous anthropogenic activities make REE to easily enter the environment and finally the human body via the food chain. Therefore, detailed studies on chemical behavior of these metals in environmental and biological systems are imperative. Isotopic tracer method is especially suited to such studies and has played an important role in assessing the environmental effects of REE. In this report, some recent progress in the study of chemical behavior of REE in environmental and biological sciences made by the isotopic tracer method is outlined.

Chemical behavior of REE in the aquatic and soil-plant systems

Application of REE in industry and agriculture leads to discharge large amount of dissolved REE to the environment, particularly to the aquatic and soil environment. Several radioactive trivalent REE tracers, such as $^{149}$La, $^{147}$Ce, $^{147}$Nd, and $^{137}$Pm in nitrate form, have been used for studying the distribution, accumulation, and speciation of REE in simulated aquatic ecosystems, which generally consist of water, sediment, and aquatic organisms. After adding the radioactive REE to the water, the concentrations of the spiked REE$^{3+}$ decreased rapidly within the first few hours accompanied by their strong accumulation in sediment during the same period [e.g. 1-3]. The sediment thus served as a major reservoir for REE in the aquatic environment [1, 2]. REE levels in the aquatic organisms increased to their maximum values in one to several days, then decreased slowly, and the magnitude of the REE concentration factor was: water plant >> shell fish > fish [1, 2]. Water plants have the highest capacity of concentrating REE. Thus, they can be used as the biomonitor and scavenging agents for contamination of REE in water. The uptake of REE in fish was mainly in the viscera, whereas the REE concentrations in edible parts, e.g. muscle, were very low [1].

The adsorption rates of REE$^{3+}$ ions in soil were extremely rapid and nearly full adsorption took only 30 s, while the desorption rates of REE, on the contrary, were much slower [4, 5]. The concentration of exchangeable REE in soil was correlated significantly with the content of REE in wheat seedling. Phosphate can dramatically precipitate REE$^{3+}$ and the REE phosphate precipitates may set limits on the concentration of exchangeable REE observed in soil [6]. When $^{141}$Ce(NO$_3$)$_3$ was added to the culture media of several plants, such as cole, Panax, or wheat, a significant concentration-dependent accumulation of $^{141}$Ce was found in these plants. The accumulation in the plant roots was much higher than that in the upper parts [7, 8] and REE concentrations in the seeds were very low.

Absorption, distribution and chemical species of REE in animals

Metabolism of REE has been investigated by oral, intravenous (i. v.), and intraperitoneal (i. p.) administration of REE radiotracers in rats, mice, rabbit, pigs, and chicken [9-11]. In general,
systemic absorption of REE after administration of simple, soluble salts increases in the order oral << i. p. << i. v. Intravenously injected REE were almost completely absorbed and the clearance of REE from blood is rapid. When injected intraperitoneally, REE tend to remain within the abdominal cavity and the fraction of REE transported to other tissues is small. The absorption of REE from the gastrointestinal tract (G. I.) was extremely poor (less than 0.1 %). However, despite the huge range in efficiency of absorption, the organ distribution of the physiologically available material remains qualitatively constant. The liver and the skeleton are the main sites of REE accumulation. When REE are introduced into the body as chelates, they become absorbed more completely. Further, the rates of excretion increase and the distribution pattern may alter. The more stable a REE complex is, the lower its fractions combined with bone plus liver and the higher its urinary excretion will be.

Although the mechanism is still unclear, increasing evidence suggests that REE can be transported across the blood brain barrier (BBB) and can accumulate in brain following G. I., i. v. or i. p. introduction into animals. We recently examined the accumulation and regional distribution of $^{169}$Yb in rat brain following i. v. injection of $^{169}$YbCl$_3$. It was found that the concentration of $^{169}$Yb in the brain was much higher than that in blood at ≥7 days post injection. The result suggests that REE may bind specifically to endothelial sites in the brain. The regional concentrations of $^{169}$Yb were in the following order: thalamus>hippocampus>cerebellum>the other regions at 7 days post injection. Epidemiological survey of local populations residing in the REE-high background regions showed that the intelligence quotient of children there was obviously lower than that from the normal regions [12]. All these facts clearly indicate that the impact of REE on brain function is not negligible, especially for the people living in REE-high background regions.

A knowledge of the chemical species of REE formed in vivo is necessary to understand their behavior and effects in organisms. The first REE-binding protein found in organisms was isolated from Tetrahymena pyriformis cells that were cultured in a proper medium in which radioactive REE ($^{144}$CeCl$_3$ or $^{169}$YbCl$_3$) was spiked [13]. By means of size-exclusion chromatography (SEC), two soluble REE-binding proteins with MWs of about 68 and more than 40 kD were found in rat livers after the rats were intravenously injected with enriched stable isotope tracer of $^{153}$Sm and $^{168}$Yb.

Sotogaku et al. [14] examined the binding affinity of REE to blood components using the radioactive multitracer technique. The blood drawn from rats was separated into plasma, corpuscles, and erythrocyte ghosts. Similar binding percentages of Ce, Eu, Gd, Tm, Yb, and Lu were found for each of the blood components, with the highest percentage being observed for plasma proteins.

Across membrane transport of REE

The question whether the cell membranes have significant permeability to REE$^{3+}$ ions is critical in assessing the biological effect of REE. Most studies suggest that REE$^{3+}$ ions are highly bound to membrane components but poorly internalized [15]. However, it is difficult to make a quantitative assessment of intracellular REE$^{3+}$ ions because the concentration of the extracellular bound REE generally exceeds that of intracellular REE$^{3+}$ ions by several orders of magnitudes. This problem can be overcome by using a unique experimental system (giant intermodal cells of the algea Chora corallina) in which cytosol can be surgically isolated with minimum risk of cross
contamination. This approach combined with radiotracer method has provided the first direct measurement of Al transport across a plasma membrane and tonoplast in single cells [16]. This technique is being applied in our laboratory to study the transport of REE across membrane by using $^{149}$La as a tracer. Batches of cells were incubated in a radioactive solution, then rinsed and separated into cell wall and intracellular fractions. Less than 0.01% of cell-associated $^{149}$La was found inside the cell even after 48 h incubation. Further studies on the mechanisms of REE transport across membrane are in progress.

**Conclusion**

Isotopic tracer method has been proven to be an effective technique for studying the chemical behavior of REE in environmental and biological sciences. In the aquatic system or soil-plant system, extraneous REE were absorbed rapidly in sediment or soil, and no enlargement of REE along the food chain was found. Plants can absorb REE to some extent and in most cases the REE content in the plant roots was much higher than in upper parts. Although the absorption of REE from the gastrointestinal tract was extremely poor, the toxicity of REE is not negligible, especially with regard to brain function. Since the biological effects and mechanisms of REE are not thoroughly known, more extensive studies, including chemical species of REE in organisms, are required.

**Acknowledgement**

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**References**

THE BEHAVIOR OF CESIUM IODIDE RADIOAEROSOLS DURING Csl SUBLIMATION FROM METAL SURFACE

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One of the biologically most dangerous volatile fission products getting into the environment during hypothetical severe accidents at NPPs are Csl radioaerosols. This is the reason why great attention is now being devoted to a study of the behavior of Csl radioaerosols in the steam-gas phase.

We studied the behavior of Csl aerosols using a setup made of a steam generator, a reaction chamber with a Pt heater, a condenser, bubblers with a Na2S2O3 solution, and a Petryanov filter. The method of radionuclide diagnostic was used for study of the Csl behavior during sublimation from the metal surface. The theoretical mass ratio between cesium and iodine in the Csl molecule is equal to 1.04. So an upward deviation from this theoretical value will show an increase in the amount of cesium, and, respectively, a downward deviation will indicate an increase in the amount of iodine. Thus, change in the Cs/I ratio was a parameter with the help of which we considered estimating the extent of the oxidation hydrolysis of Csl aerosols.

Table 1. Dependence of 137Cs and 131I distribution on the gas phase composition during the sublimation of 1 mg of Csl from the Pt heater (initial chamber temperature 403-423 K)

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Fraction</th>
<th>Content of, %</th>
<th>Cs/I mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>133Cs</td>
<td>131I</td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>30.71</td>
<td>30.15</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>69.29</td>
<td>69.85</td>
</tr>
<tr>
<td></td>
<td>Air (3-4 vol.% of steam)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>32.76</td>
<td>29.65</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>67.24</td>
<td>70.35</td>
</tr>
<tr>
<td></td>
<td>Steam - air mixture (93 vol.% of steam)</td>
<td>50.56</td>
<td>38.97</td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>49.44</td>
<td>61.03</td>
</tr>
</tbody>
</table>

To reveal the influence of H2O and O2 on the conversion of Csl, the behavior of Csl radioaerosols in the atmosphere of Ar, air, a steam-air mixture in which the steam concentration was up to 93 vol.% was studied. Table 1 shows that during the sublimation of 1 mg of Csl in Ar flow the Cs/I mass ratio in the chamber is close to the theoretical value. In air, the Cs/I ratio is different from the theoretical value for Csl, which shows some increase in the amount of 137Cs in the chamber and consequently, a larger conversion of Csl in air as compared with that in Ar. This increase is explained by a partial oxidation of Csl and the
formation of CsOH aerosols. In a steam-air mixture (steam content ~93 vol.%), the Cs/I mass ratio is equal to 1.30. An increase of about 25% in the Cs/I ratio as compared with the theoretical value is explained by an increase in the extent of CsI oxidation hydrolysis in the presence of a large amount of steam leading to the formation CsOH aerosols.

Table 2 shows the influence of the temperature in the reaction chamber on the behavior of CsI aerosols formed during sublimation. At a reaction chamber temperature of about 293 K, the Cs/I mass ratio in the chamber increases by 20% as compared that of 430-423 K. This confirms the formation of CsOH aerosols during CsI sublimation from the metal surface in air flow. Low temperature of the reaction chamber provokes a faster agglomeration of aerosols, including CsOH particles, and their precipitation in the reaction chamber.

Table 2. Dependence of $^{137}$Cs and $^{131}$I distribution on the initial reaction chamber temperature during the sublimation of 1 mg of CsI from the Pt heater

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Fraction</th>
<th>Cs/I mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial chamber temperature 293 K</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>1.31</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>initial chamber temperature 403-423 K</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 3 presents the results of experiments allowing a comparison of the influence of the initial ratios between the amounts of CsI and O$_2$ in the air flow on the behavior of the oxidation hydrolysis products. During the sublimation of 1 mg of CsI (molar ratio CsI : O$_2$ = 1 : 1100), the Cs/I ratio in the chamber is significantly different from the theoretical value. On the other hand, during the sublimation of 100 mg of CsI (molar ratio CsI : O$_2$ = 1 : 11), the ratio in this fraction is close to the theoretical value. These results allow us to conclude that the extent of the CsI oxidation hydrolysis depends on the CsI concentration in the gas phase.

Table 3. Dependence of $^{137}$Cs and $^{131}$I distribution on the initial molar ratio between CsI and O$_2$ during the sublimation of CsI from the Pt heater (initial chamber temperature 293 K)

<table>
<thead>
<tr>
<th>Fraction number</th>
<th>Fraction</th>
<th>Cs/I mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CsI : O$_2$ = 1 : 1100 (1 mg of CsI)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>1.31</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>CsI : O$_2$ = 1 : 11 (100 mg of CsI)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>In the reaction chamber</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>After the reaction chamber</td>
<td>0.99</td>
</tr>
</tbody>
</table>

It should be noted that the data obtained during sublimation of 1 and 100 mg of CsI in air and Ar at different steam concentrations in the gas phase also are different among themselves. As
follows from the Table 4, during sublimation of 100 mg of CsI oxidation hydrolysis of CsI aerosols in Ar is insignificant even when the steam concentration in it is 52 vol.%. This follows from the virtually constant Cs/I ratio in the chamber in the argon atmosphere containing 52 vol.% of a steam and in air containing 3-4 vol.% of steam. An increase in the steam concentration to 33-50 vol.% in the air the Cs/I ratio practically did not change. This factor allows us to conclude that the extent of CsI oxidation hydrolysis during sublimation of 100 mg of CsI from Pt heater into air under experimental conditions is very small.

Table 4. Dependence of $^{137}$Cs and $^{131}$I distribution on the steam concentration during the sublimation of 100 mg of CsI from the Pt heater (initial chamber temperature 293 K)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Steam concentration in the steam-gas flow, vol.%</th>
<th>Fraction number</th>
<th>Fraction</th>
<th>Content of, %</th>
<th>Cs/I mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^{137}$Cs</td>
<td>$^{131}$I</td>
</tr>
<tr>
<td>Air</td>
<td>3-4</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>47.89</td>
<td>44.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>52.11</td>
<td>55.38</td>
</tr>
<tr>
<td>Air</td>
<td>32.7</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>50.58</td>
<td>47.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>49.42</td>
<td>52.73</td>
</tr>
<tr>
<td>Air</td>
<td>50.5</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>44.81</td>
<td>42.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>55.19</td>
<td>57.32</td>
</tr>
<tr>
<td>Ar</td>
<td>52.3</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>35.44</td>
<td>32.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>64.56</td>
<td>67.45</td>
</tr>
</tbody>
</table>

At the same time as follows from the Table 5, during sublimation of 1 mg of CsI oxidation hydrolysis of CsI aerosols in air is significant even when the steam concentration in it is 3-4 vol.%. It is interesting that an increase in the steam concentration to 89 vol.% in the air the Cs/I ratio practically did not change. These results allow us to conclude that the oxidation hydrolysis of CsI during its sublimation from a metal surface into the atmosphere of a steam-air mixture depends on not only the amount of steam and oxygen in the gas phase, but also the initial molar ratio between CsI and O$_2$ in the reaction chamber.

Table 5. Dependence of $^{137}$Cs and $^{131}$I distribution on the steam concentration during the sublimation of 1 mg of CsI from the Pt heater (initial chamber temperature 293 K)

<table>
<thead>
<tr>
<th>Steam concentration in the steam-gas flow, vol.%</th>
<th>Fraction number</th>
<th>Fraction</th>
<th>Content of, %</th>
<th>Cs/I mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^{137}$Cs</td>
<td>$^{131}$I</td>
</tr>
<tr>
<td>3-4</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>82.14</td>
<td>67.05</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>17.86</td>
<td>32.95</td>
</tr>
<tr>
<td>89.1</td>
<td>1</td>
<td>In the reaction chamber</td>
<td>64.67</td>
<td>55.89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>After the reaction chamber</td>
<td>35.33</td>
<td>44.11</td>
</tr>
</tbody>
</table>

The work was done thanks to financial support by the Russian Fund for Fundamental Research (grant 03-03-32145).

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KINETICS OF HYDROLYSIS AND PARTITION CONSTANTS
OF NEUTRAL METAL CHELATES AS RADIOTRACERS.
SOLVENT EXTRACTION OF
TRIS(THENOYLTRIFLUOROACETONATE)THALLIUM(III)

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Hydrolytic properties of certain metal ions make many of their complexes in aqueous solution unstable against substitution of water and/or hydroxide ion for the original ligands. However, if such complexes (labelled with radionuclides) are inert, they remain in solution intact for a time long enough to use them as radioactive indicators. When hydrolysis proceeds in the time-scale of minutes to hours, exact measurements require correction for ligand replacement. On the other hand, inertness is an important feature of metal complexes, in particular metal-essential radiopharmaceuticals. That is because no excess of the ligand is available in vivo to stabilize the original complex against ligand exchange, the more that other potential ligands (e.g. amino acids) compete for the central metal ion in the molecule.

Kinetics of ligand exchange in metal complexes was widely studied using either spectroscopic methods or radioactive indicators [1]. The latter method requires chemical separation of different species labelled with the radiotracer. The present work describes the application of radioactive indicators with continuous solvent extraction separation of the original complex from the products of its hydrolysis - a new method developed for the determination of both the rate of hydrolysis of neutral metal chelates in aqueous solution and their partition constants in two-phase (organic solvent/water) systems [2]. Partition constant, $P$, defined as the ratio of the concentrations of a given complex in the organic and aqueous phase at equilibrium, is the measure of lipophilicity of metal complexes, which is an important characteristic of certain radioactive indicators, in particular radiopharmaceuticals [3].

The aim of the present work was to study this new method in more detail, including the effect of pH on the rate of hydrolysis. Tris(thenoyltrifluoroacetone)thallium(III), $\text{TI(tta)}_3$, the neutral chelate of suitable lipophilic-hydrophilic properties, was selected for detailed studies.

Due to strong hydrolysis of thallium(III) ions [4], direct determination of $P$ of its neutral complexes is not possible, because the equilibrium concentration of such complexes in the aqueous phase can hardly be reached. In fact, thallium(III) can be extracted by numerous chelating extractants, but the reliable $P$ values of the chelates are scarce [5]. However, the slowed down kinetics of hydrolysis of thallium(III) in its chelates makes it possible to extrapolate the kinetic data to the zero time. The appropriate kinetic equation was therefore derived and compared with experimental data.

The distribution of thallium(III) between an organic and an aqueous phase was studied in back-extraction experiments with the organic phase previously loaded with $\text{TI(tta)}_3$ (further denoted as $\text{ML}_{\text{org}}$), labelled with $^{203}\text{Tl}$. This organic phase, of the chelate concentration $[\text{ML}_{\text{org}}]_{\text{org}} = 1.5 \times 10^{-5}$ mol dm$^{-3}$, was obtained by extraction of the metal ion from a slightly acidic ($\text{H}_3\text{SO}_4$) aqueous phase to 0.1 mol dm$^{-3}$ Hta in toluene. It was found that $\text{TI(tta)}_3$ in the
toluene solution was kinetically inert, nevertheless the solution was always prepared fresh, immediately before further back extraction to a fresh aqueous phase, thallium-free and containing an excess of strongly oxidizing ammonium persulfate to stabilize incoming thallium(III) chelate. Equal volumes of the phases were shaken, and the aliquots of both were collected for activity measurements in several minutes intervals. The experimental details are given in [2].

The ratio of specific activities of both phases, equal to distribution ratio, $D = \frac{[\text{ML}_n]_{\text{aq}}}{[\text{ML}_n]_{\text{org}}}$, where $[\text{ML}_n]_{\text{aq}}$ is the sum of concentrations of all chemical forms of the metal in the aqueous phase, decreased with time. After fast decrease within the first $3 \text{ - } 5 \text{ min.}$, a further continuous drop in $D$ was observed, with moderate, pH-dependent rates. It was assumed that the fast process observed at $t < 10 \text{ min.}$ was due to the transfer of the neutral chelate from the organic to the aqueous phase, while the slow decrease – to the slowest step in back extraction, which is either hydration ($S_n2$) or dissociation ($S_n1$) of the neutral chelate in the aqueous phase. The neutral chelates in the aqueous phase do not hydrolyze until hydrated (or dissociated), while the transient species formed undergo fast base hydrolysis, hydrophilic products of which remain in the aqueous phase. The rate of the hydrolysis is thus equal to the rate of hydration (or dissociation); it is therefore proportional to the concentration of $\text{ML}_n$ in the aqueous phase (the first-order reaction). However, because the partition equilibrium has already been established, the decrease in $[\text{ML}_n]_{\text{aq}}$ is being instantly and continuously compensated (in part) by transfer of $\text{ML}_n$ from the organic phase. Therefore, both $[\text{ML}_n]_{\text{org}}$ and $[\text{ML}_n]_{\text{aq}}$ are the momentary values depending on time, $t$. The total change in $[\text{ML}_n]_{\text{aq}}$ is equal to:

$$\frac{d[\text{ML}_n]_{\text{aq}}}{dt} = \frac{d[\text{ML}_n]_{\text{org}}}{dt} = \frac{d[\text{ML}_n]_{\text{org}}}{dt}$$

which, taking into account the definition of $P$, can be transformed to:

$$\ln[\text{ML}_n]_s = \ln[\text{ML}_n]_s - \frac{k}{P + 1} \cdot t$$

where index $s$ denotes either the aqueous (2a) or organic (2b) phase, provided the volumes ($V$) of both phases are equal; $[\text{ML}_n]_s$ are virtual (extrapolated to $t=0$) initial concentrations of $\text{ML}_n$ in the phase $s$; and $k$ is the rate constant of hydrolysis of $\text{ML}_n$. The $[\text{ML}_n]_{\text{org}}$ values are proportional to the experimental specific activities, therefore eq. (2b), which is linear in the part corresponding to the slow decrease in $D$, can easily be plotted. Extrapolation gives $[\text{ML}_n]_{\text{org}}$ from the intercept. Because $P = \frac{[\text{ML}_n]_{\text{org}}}{[\text{ML}_n]_{\text{org}} - [\text{ML}_n]_{\text{aq}}} = \frac{1}{[\text{ML}_n]_{\text{org}}}$, we can obtain $k$ from the slope.

Specific activity of the aqueous phase is proportional not to $[\text{ML}_n]_{\text{aq}}$ but to $[\text{ML}]_{\text{aq}}$. As long as the hydrolysis products (including e.g. colloidal hydroxides) remain in the aqueous phase evenly distributed within, we have (at $V_{\text{org}} = V_{\text{aq}}$) $d[\text{ML}]_{\text{aq}} = -d[\text{ML}]_{\text{org}}$, and eq. (2) can be transformed to the following form, more convenient in practice:

$$\ln \left( \frac{D}{D+1} \right) = \ln \left( \frac{P}{P+1} \right) - \frac{k}{P+1} \cdot t$$

By plotting the set of experimental $\ln \{D/(D+1)\}$ values vs time (Fig.1) we calculated $P$ and $k$ directly from the intercept and slope.
The experimental data, collected at 5 min. intervals (from 10 to 65 min. since the start of back extraction) in the pH range of 2.18 to 4.55, determine a bunch of straight lines of different slopes but of almost the same intercept from which we obtain the average partition constant of Tl(tta)$_2$, $P = 5.78 \pm 0.30$. The increase in $k$ with decreasing pH, starting from the minimum at $4.0 < pH < 4.5$ (Fig. 2), similar to the picture observed for other metal chelates [6], may be interpreted in terms of acid-catalysed hydrolysis of the chelate. In more acidic solutions ($pH < 4$) the dependences are not linear and do not converge to the same intercept. We conclude that a very fast protonation [6] of the chelate molecule occurs at high acidities. This results in the presence of ML(H$^+$) in the aqueous phase from the very beginning at appreciable concentration, and also in a change in the mechanism of hydrolysis. Therefore, under these conditions, i.e. with the more acidic solutions, the assumptions leading to equations (1-3) are no more valid.

References
A RADIOKINETIC STUDY OF THE $^{60}$Co$_2$O$_4$, $^{60}$Co$_2$ AND $^{60}$Co(SCN)$_2$ CRYSTALS GROWTH IN HYDROGELS

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The first systematic study on the crystal formation and growth in hydrogels was done by Lisegang [1]. His name is related especially to the regulated “rings” that appear on the glass plates coated with a thin layer of gelatine or agar, when in a central point of it some droplets of a concentrate solution of Ag$_2$CrO$_4$ or Ca$_2$(PO$_4$)$_2$ were poured. Later, the nucleation process for other crystals like AgI, BaWO$_4$, CaC$_2$O$_4$ was studied and then, the exponential increase of the interest in this field led to the true monographic works writing [2,3].

This paper is a continuation of some earlier studies concerning the use of radioisotopes in the kinetic study of the crystal formation and growth in gels, when radioactive cations such as: $^{60}$Co$^{2+}$, $^{137}$Cs$^+$, $^{204}$Tl$^+$, $^{55}$Fe$^{3+}$, $^{51}$Cr$^{3+}$ were used in the presence of different anions.

“U” shaped tubes made of PVC, with the inner diameter of 1.5 cm, the length of the horizontal branch of 8 cm and the length of the vertical branches of 7 cm, were used for the radiokinetic study of the crystals growing in polyvinyl alcohol (PVA) 11% and 13% hydrogels. The tubes filled with hydrogels were kept at a constant temperature of 4°C. Then, in each tube were introduced the solutions that contained the reagents. In one of the vertical branches of the tube were introduced 8 ml of the radioactive solution of $^{10}M$ $^{60}$Co, with a specific activity of 3.7·10$^4$ Bq/ml, and in the other vertical branch, were introduced 8 ml from aqueous solutions of K$_2$C$_2$O$_4$, KI or KSCN respectively, all having a concentration of 10$^{-3}$M.

The migration of the $^{60}$Co$^{2+}$ radioactive cation was studied by measuring from time to time, the radioactivity, in the horizontal branch of the tube, at the following distances from an initially established start line: 0.5 cm, 3 cm and 7 cm using a special device [4]. The PVC tubes were placed in the neighbourhood of a runner which makes possible the changing of place of the Geiger- Müller CMC detector that was connected to a Vakumtronika VA-M-14 decimal scaler. A lead sheet was used as radiation shield for the CMC detector, keeping only a slot with a diameter of 2 mm, oriented to the horizontal branch of the tube.

The $^{60}$Co$^{2+}$ radioactive ions diffusion from the aqueous solution (d=0.5 cm) and through the PVA hydrogel (d = 3 cm and 7 cm) is a process that could be considered a first order reaction and could be described by the following integral equation:

$$\ln\left[\frac{[M]}{[x]}\right] = k_{\text{diff}} \cdot t$$

On the other hand, the nucleation process could be described by the general chemical equation [where the reaction product could be the crystal of $^{60}$Co$_2$O$_4$, $^{60}$Co$_2$, or $^{60}$Co(SCN)$_2$]

$$\text{M} + \text{A} \xrightarrow{k} \text{MA}$$

The rate of this second order reaction could be written as follows:

$$\frac{dx}{dt} = k\left[\frac{[M]}{[x]}\right] \cdot [A] \cdot -k'x$$

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In this equation, “x” is the amount of the reacting ions which left the initial solutions and that led to the crystal formation. Because the reversible reaction of the obtained crystal dissolution could take place with a small probability, the second term of (3) could be neglected. As a consequence, by integration of the equation (3), it will be obtained:

\[
\ln \left( \frac{[M]}{[A][A-x]} \right) = k \cdot t
\]

(4)

Because the amount of radioactive ions is proportional to the measured total radioactivity “R”, the equations (1) and (4) could be written as follows:

\[
\ln R = f(\text{M-x}) = f(t)
\]

(5)

Fig. 1. Kinetic diagrams for the diffusion of \(^{60}\text{Co}^{2+}\) ions through PVA.
By plotting \( \ln R = \text{f}(t) \), for the R values measured at different times (Figure 1), in the established positions: 0.5 cm, 3 cm and 7 cm, linear dependencies were obtained and from their slopes both the values of the diffusion rate constants for the radioactive ions could be calculated: from the aqueous solution in the PVA hydrogel (at 0.5 cm): \( k_{\text{diff}} \); in the hydrogel (at 3 cm): \( k'_{\text{diff}} \) and the values of the rate constants of the interactions between the reacting ions that led to the crystals formation in the PVA hydrogels (at 3 cm): \( k \).

The straight lines 1 and 2 represent the \(^{60}\text{Co}^{2+}\) ions diffusion from the solution in the PVA hydrogel, vs. the time, when the radioactivity determinations took place at 0.5 cm. At the beginning, an increase of the measured radioactivity can be seen. Then, after reaching the maximum value, a decrease of the radioactivity could be noticed. It can be concluded that, in time, the majority of the radioactive ions migrated into the hydrogel. If the values of the measured radioactivity at 3 cm from the start line, where the nucleation begins, were plotted against the time, two different slopes were obtained (straight lines 3 and 4). The straight line 3 describes the diffusion of \(^{60}\text{Co}^{2+}\) ions through the hydrogel.

The straight line 4 is related to the nucleation process, because in this zone the different shapes of crystals begin to grow: \(^{60}\text{CoC}_2\text{O}_4\): red crystals with an unidentified geometrical shape; \(^{60}\text{Co}_{12}: \) “plates” red-brown crystals with an unidentified geometrical shape; \(^{60}\text{Co(SCN)}_2: \) red-violet needle-shaped crystals. The line 5 has no meaning, because it represents a nonotone increase of the measured activity in the position “7 cm”.

From the slopes of the lines 1, 3 and 4, the values of the above mentioned rate constants were calculated and are shown in Table 1.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>PVA concentration, %</th>
<th>( k_{\text{diff}} ), ( \text{h}^{-1} )</th>
<th>( k'_{\text{diff}} ), ( \text{h}^{-1} )</th>
<th>( k ), ( \text{l mole}^{-1} \cdot \text{h}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{60}\text{CoC}_2\text{O}_4)</td>
<td>11</td>
<td>( 2.48 \times 10^3 )</td>
<td>( 1.39 \times 10^3 )</td>
<td>( 5.46 \times 10^3 )</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>( 1.52 \times 10^3 )</td>
<td>( 1.29 \times 10^3 )</td>
<td>( 5.25 \times 10^3 )</td>
</tr>
<tr>
<td>(^{60}\text{Co}_{12})</td>
<td>11</td>
<td>-</td>
<td>( 2.40 \times 10^3 )</td>
<td>( 1.08 \times 10^3 )</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>-</td>
<td>( 2.31 \times 10^3 )</td>
<td>( 1.04 \times 10^3 )</td>
</tr>
<tr>
<td>(^{60}\text{Co(SCN)}_2)</td>
<td>11</td>
<td>-</td>
<td>( 2.22 \times 10^3 )</td>
<td>( 9.42 \times 10^3 )</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>-</td>
<td>( 2.01 \times 10^3 )</td>
<td>( 9.40 \times 10^3 )</td>
</tr>
</tbody>
</table>

The \( k_{\text{diff}} \) and \( k'_{\text{diff}} \) values are close one another because they are related with the diffusion of the same cationic specie \((^{60}\text{Co}^{2+})\) from the aqueous solution in the hydrogel (the straight line 1) or through the PVA hydrogel (straight line 3). The small differences between the constant values could be attributed to the different anion types, which penetrate the hydrogel with different rates.

The values of the interaction rate constants \( k \), which practically characterize the nucleation process, are different in function of the nature of the anion that participated in the \(^{60}\text{Co}_{12}\), \(^{60}\text{Co(SCN)}_2\) and \(^{60}\text{CoC}_2\text{O}_4\) crystals formation. The smaller concentration of the polymer in the hydrogel determines higher values of the diffusion and nucleation rate constants in comparison with the hydrogels with a higher polymer concentration.

APPLICATION OF TRITIUM LABEL IN INVESTIGATION OF ANION EXCHANGE IN LAYERED DOUBLE HYDROXIDES

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Development of drug delivery systems is very timely problem [1]. One of the solutions of this problem is the use of layered double hydroxides (LDH) intercalated with biologically active compounds [2]. It is based on a unique property of these materials to exchange anions in aqueous solution.

LDHs have a general formula $\text{M}^{2+1-x}\text{M}^{3+ x}(\text{OH})_2[(\text{anion}^n)_{2x}\cdot\text{H}_2\text{O}]$, where $\text{M}^{2+}$ and $\text{M}^{3+}$ are metals in the oxidation state +2 and +3, respectively, and anion$^n$ is virtually any inorganic or organic anion, which does not form a stable complex with $\text{M}^{2+}$ or $\text{M}^{3+}$. The structure of an LDH consists of positively charged hydroxide layers $[\text{M}^{2+1-x}\text{M}^{3+ x}(\text{OH})_2]^{1+}$ bound with negatively charged anions, which occupy the interlayer space [3].

We investigated the exchange process between ethylenediaminetetraacetate (EDTA) anions ($\text{H}_2\text{edta}^{2-}$) in Mg-Al LDHs and some organic and inorganic anions in aqueous solution. An interest to EDTA anions is connected with the wide use of EDTA due to its ability to form complex compounds with different cations as a drug for intoxications of various kinds.

Investigation of anion exchange in LDHs is a non-trivial experimental task and requires an application of special approach. We suggested using radioactive tritium label to monitor this process due to high sensitivity of radioactivity detection, taking into account the fact that tritium-labelled compounds chemically are absolute analogues of non-labelled ones.
Fig. 1. The setup for tritium labeling: 1 – reaction vessel, 2 – tungsten wire, 3 – target (sample for labeling), 4 – vessel with tritium gas, 5 – palladium tube, 6 and 7 – vacuum detectors, 8 – vessels with liquid nitrogen, 9 – catcher, 10 – vacuum pumps.

Labelled EDTA anions were obtained by means of bombardment of lyophilized frozen solution of Na₂(H₂edta) with the stream of atomic tritium in a special vacuum setup (Fig. 1). The method is based on the high reactivity of tritium atoms produced via thermal dissociation of tritium molecules on a tungsten filament heated to 2000 K [4].

Tritium labelled H₂edta²⁻-anions were intercalated into LDH interlayer space by reconstruction of Mg-Al layered double oxides [5]. The materials obtained were treated with aqueous solutions containing different anions. Masses of samples of labelled LDH and volumes of anion solutions were permanent and excess of anions in solution was used. Dependencies of the suspension radioactivity versus time of anion exchange were obtained using liquid scintillation spectrometry (Mark III, Tracer Analytic, USA) (Fig. 2).

It was shown that anion exchange in LDHs depends on chemical properties of exchangeable anions. The size of replacing anions did not affect exchange rate directly. The presence of protons in the solution accelerated the exchange process. It was found that the anion exchange period could be rather long, and LDHs intercalated with biologically active compounds can be used as depot drugs.
Fig. 2. Kinetic curves of radioactivity increase in the course of anion exchange.

References
DIFFUSION OF RADIOACTIVE TRACERS (\(^{204}\text{Tl}, {^{110m}\text{Ag}}\))
AND IONIC CONDUCTIVITY IN MEMBRANE MATERIALS
FOR THE CHEMICAL SENSORS

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Introduction
The studies of diffusion process, ionic conductivity and calculation of the correlation factor are essential for the investigation of membrane transport mechanism of the chemical sensors based on superionic conductors. But the lack of data on diffusion for most of the solid electrolytes is a considerable experimental drawback in this area of research. In the present study the diffusion of thallium and silver in the superionic conductors Tl\(_2\)HgI\(_6\), Ag\(_2\)HgS\(_2\)I\(_6\) and others has been investigated for the first time.

Experimental
Solid electrolytes were obtained by means of two stage solid-state reactions. The starting materials (TlI, HgI\(_2\), AgI, Ag\(_2\)S and others) in necessary proportions with the particle size of 20-50 micrometers were thoroughly mixed, ground and pressed into pellets (1.5-2.0 cm thick and 1.0 cm in diameter) by 2 t/cm\(^2\) pressure. The pellets were then heated at 300 - 400°C for three hours in a dry inert atmosphere. After grinding the samples were subjected to the second stage of the solid-phase reaction.
Samples for diffusion and conductivity measurements were pressed by 4 t/cm\(^2\) pressure to form cylinders 1.0 cm diameter and about 0.5 cm thick. The diffusion coefficients of thallium and silver in the samples of solid electrolytes were determined with radioactive tracers \(^{110m}\text{Ag}\) and \(^{204}\text{Tl}\) by means of diffusion from a thin layer with further sectioning of the sample and determination of the radioactivity of the obtained sections. Labeled thallium and silver were deposited on the surface of the samples from Ag\(_n\)NO\(_3\) and Tl\(_{2}\)NO\(_3\) solutions, in which the face of a sample was dipped for a few seconds. After the solution was removed away the radioactivity of the surface was measured. Diffusion cell was thermostated from 100 to 160°C for 100 - 500 s. After diffusion annealing the samples were sectioned on a microtome by layers of 0.05-0.1 mm thick. The activity of specimens was measured using scintillation counter. Conductivity measurements (ac) were carried out from 0.5 to 20 kHz. An extrapolator to the infinite frequency was applied since the frequency dispersion of silver- or carbon-contacted samples in the above frequency range could not be neglected.

Results and discussion
The temperature dependence of ionic conductivity, for example, for Ag\(_2\)HgS\(_2\)I\(_6\) can be described by the equation:

\[ \delta T = (8.3 \pm 1.1) \times 10^3 \exp(-0.134 \pm 0.004 \text{ eV/kT}) \quad (20-140^\circ\text{C}) \] (1)
It is to be pointed out that in diffusion experiments with solid electrolytes the errors of time and temperature determination require special attention as the errors increase considerably at comparatively low temperatures and at a short time of diffusion. The temperature of the sample during the annealing was controlled by thermocouples connected to the sample. The special corrections were used in the cases, when it was impossible to get ideal heating-cooling steps because of the changes of sample shape, heater parameters or insulating material properties.

The calculation of diffusion coefficients was performed using a formula for the distribution of radioactive ions in the case of diffusion from a thin layer:

\[
\ln A = \text{const} \left( -x^2/4D' t \right) \tag{2}
\]

where \( A \) is the activity of a section (counts/min); \( x \) is a distance from the surface containing radioactive ions (cm); \( t \) is the annealing time (s); \( D' \) is the diffusion coefficient (cm\(^2\)s\(^{-1}\)).

The diffusion coefficients \( D' \) were calculated for selected plots from the relation:

\[
tg \alpha = -\frac{1}{4} D' t \tag{3}
\]

Some of the dependencies are shown in Fig.1, for example, for \( \text{Ag}_{90}\text{HgS}_2 \)l.0.

---

Fig.1. Activity-penetration curves for diffusion of radiotracer silver into \( \text{Ag}_{90}\text{HgS}_2 \)l.0.
There one cannot see any appreciable peaks at $x \neq 0$. This confirms that the diffusion from an infinitely thin layer and bulk processes does occur in the samples under investigation. Fig.2 shows the temperature dependence of the diffusion coefficients $D^*$ measured by the radioactive tracer method (eq.3) and $(D_0)$ calculated from the ionic conductivity data using the Nernst-Einstein equation.

![Graph showing temperature dependence of diffusion coefficients](image)

**Fig.2.** Temperature dependencies of the diffusion coefficients measured by the radioactive tracer method ($D^*$) and calculated from ionic conductivity data $(D_0)$ for Ag$_2$HgS$_2$I$_6$.

From the ionic conductivity and diffusion data obtained the correlation factors $H_R$ (the Haven ratio) can be calculated, for example, for Ag$_2$HgS$_2$I$_6$ $H_R = 0.9$. Experimental data including Haven ratio values obtained from the investigation of temperature dependence of thallium and silver diffusion and ionic conductivity in membrane materials of the chemical sensors based on superionic conductors confirm the existence of essential differences in transfer properties for wide range of solid electrolytes.
THE STUDY OF CsClO₄ SOLUBILITY IN MIXED SOLVENTS BY RADIOACTIVE INDICATORS METHOD

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Before the burial of liquid radioactive wastes of nuclear power plants there is a necessary step of separation and concentration of radioactive substances, which often contain compounds of Cs. The purification of liquid radioactive wastes from Cs can be proceeded via different methods, also by means of extraction from water phase with extractive solvents, e. g. polyethylene glycols, as well as method of coprecipitation of Cs in the water with low solubility perchlorate. In both the processes the solubility plays the main role and is the query number one in the technology of decontamination of fluid radioactive waste.

The precipitation of Cs depends directly on solubility of precipitated compounds, and in case of extraction – the data about solubility of the precipitated compound give the possibility to estimate the difference of energy in solvation and hydration, which define the stage of converting of compounds from water phase into no water phase.

CsClO₄ solubility in 1,2-propylene glycol over the temperatures studied is higher than in ethanol, which may be due to the influence of dielectric permeability upon CsClO₄ solubility (εₑ₂₅ (1,2-propylene glycol) = 29.0, εₑ₂₅ (ethanol) = 24.3). CsClO₄ solubility logarithm deviations from additive values have been calculated and discussed.

Standard thermodynamic characteristics of CsClO₄ solubility process in 1,2-propylene glycol mixtures have been calculated and discussed on the basis of caesium perchlorate solubility data.

8. Radionuclides in Geo- and Cosmochemistry
COSMOGENIC RADIONUCLIDES IN ICE CORES

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Production of cosmogenic radionuclides

Cosmogenic radionuclides are produced continuously by cosmic rays penetrating from the space into the atmosphere. When cosmic ray particles impinge on the atmosphere they induce nuclear reactions producing secondary particles and a variety of new nuclides most of which are radioactive [1]. Depending on the energy of the primary particle a cascade develops through the atmosphere until all the secondary particles are used up in nuclear reactions or stopped by collisions and ionization processes. Since the main target elements of the atmosphere are nitrogen, oxygen, and argon most of the radionuclides produced have masses smaller than 40. In Table 1 some basic properties of the main cosmogenic radionuclides produced in the atmosphere are listed. The production rates are given as estimated mean global values. Some of the radionuclides, marked with an asterisk, are also produced artificially in considerable amounts by nuclear bomb tests, nuclear reactors, and accelerator facilities.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Target</th>
<th>Half-Life</th>
<th>Prod. Rate (atoms cm⁻² s⁻¹)</th>
<th>Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>3H*</td>
<td>N, O</td>
<td>12.3 y</td>
<td>0.2</td>
<td>3 kg</td>
</tr>
<tr>
<td>7Be</td>
<td>N, O</td>
<td>53.4 d</td>
<td>0.04</td>
<td>20 g</td>
</tr>
<tr>
<td>10Be</td>
<td>N, O</td>
<td>1.5 10⁶ y</td>
<td>0.02</td>
<td>100 tons</td>
</tr>
<tr>
<td>14C*</td>
<td>N</td>
<td>5730 y</td>
<td>2</td>
<td>60 tons</td>
</tr>
<tr>
<td>26Al</td>
<td>Ar</td>
<td>7.3 10⁵ y</td>
<td>0.0002</td>
<td>1 ton</td>
</tr>
<tr>
<td>32Si</td>
<td>Ar</td>
<td>150 y</td>
<td>0.0004</td>
<td>1 kg</td>
</tr>
<tr>
<td>36Cl*</td>
<td>Ar</td>
<td>3 10⁵ y</td>
<td>0.001</td>
<td>4 tons</td>
</tr>
<tr>
<td>129I*</td>
<td>Xe</td>
<td>1.6 10⁷ y</td>
<td>0.00003</td>
<td>20 tons</td>
</tr>
</tbody>
</table>

Table 1: Cosmogenic radionuclides which are produced in the atmosphere [1]. Asterisks indicate radionuclides which are also produced artificially. In addition 129I is a natural product of the spontaneous fission of uranium. The global inventory is based on the present production rate.

Transport and deposition of cosmogenic radionuclides

As a consequence of the nuclear interaction of the galactic cosmic rays with the atmosphere and the shielding effect of the geomagnetic field the production rate of the cosmogenic radionuclides depends mainly on altitude and latitude (Fig. 1). After production the radionuclides are subject to different processes according to their geochemical properties. For example 14C is oxidized to 14CO₂ and 10Be becomes attached to aerosols. Since the
stratosphere is thermally stratified and separated from the troposphere by the tropopause, the mean residence time for aerosols in the stratosphere is about 1-2 years. In the troposphere precipitation removes most atmospheric constituents within a few weeks.

![Graph showing the dependence of the $^{10}$Be production rate on atmospheric depth (0: top of atmosphere; 1033: sea level) and latitude for the present geomagnetic field intensity and the solar modulation [1].](image)

**Fig. 1** Dependence of the $^{10}$Be production rate on atmospheric depth (0: top of atmosphere; 1033: sea level) and latitude for the present geomagnetic field intensity and the solar modulation [1].

**Detection of cosmogenic radionuclides**

As shown in Table 1 cosmogenic radionuclides are very rare resulting in very low isotopic ratios ($10^{-10}$ - $10^{-14}$). Such low ratios cannot be determined by conventional mass spectrometry due to background problems. In most samples isobars and molecules with the same mass are present in much higher concentrations which leads to serious interferences with the radioisotope to be analyzed.

One way to detect cosmogenic radionuclides is to make use of their radioactive decay. This technique is straightforward and works well as long as the half-life is short (<1000 y). However, for longer half-lives decay counting becomes inefficient. Conventional mass spectrometry is not sensitive enough to measure such extremely small isotopic ratios. Going to much higher energies by using accelerator mass spectrometry (AMS) provides the key. This technique is able to detect as few as a million atoms [2].

**Archive ice**

Some of the cosmogenic radionuclides are deposited in natural archives were they are stored for thousands of years preserving information about their production and transport history. Beside sediments and tree rings ($^{14}$C) ice cores proved to be excellent archives because they directly sample all the fallout from the atmosphere. Polar ice sheets are formed from snow. The snowflakes grow together to grains which slowly increase in size. Due to the pressure of
the overlying new snow layers, the grains become more and more compacted and finally turn into ice.

A special property of ice is that it slowly flows towards the margin of the ice sheet, where it partly melts and partly breaks up as icebergs. As a consequence of the horizontal movement of the ice, the annual layers become thinner with increasing depth leading to a non-linear relationship between depth and age. This has the advantage that the recent past can be studied in detail whereas the far past is still covered, though with low resolution. The disadvantage however, is that dating of ice cores is difficult.

**Cosmogenic radionuclides and solar variability**

The production and transport of cosmogenic radionuclides in the atmosphere are shown schematically in Fig. 2. These processes are influenced by several factors.

![Diagram of production, transport, and storage of cosmogenic radionuclides in an ice sheet. These processes are influenced by several factors such as solar activity, geomagnetic field intensity, atmospheric mixing, precipitation rate and various processes within the ice sheet.](image)

*Fig. 2: Schematic diagram of production, transport, and storage of cosmogenic radionuclides in an ice sheet. These processes are influenced by several factors such as solar activity, geomagnetic field intensity, atmospheric mixing, precipitation rate and various processes within the ice sheet.*

Within the solar system there are two effects caused by the Sun and the Earth giving rise to fluctuations in the cosmic ray flux. Both are due to magnetic shielding effects on the charged cosmic ray particles.

The first is related to the solar activity. The sun emits solar wind from coronal holes that carries "frozen-in" magnetic fields. The emission of solar wind leads to significant fluctuations of the cosmic ray flux. The most prominent feature is the 11-year Schwabe cycle. But there are also longer periodicities (e.g. 88 year Gleissberg cycle, 205 year Suess cycle)
and decadal periods of low solar activity such as the Maunder minimum (1645-1715 AD). The heliomagnetic shielding affects primarily the particles with low energies. Reconstruction of solar activity became an especially important issue because direct measurements of solar irradiance (solar constant) with satellite-based radiometers revealed variations in phase with the 11-year Schwabe cycle over the last two decades [3]. The yearly averaged amplitude of this cycle is too small (0.1%) and the changes are too fast to induce relevant climatic changes. However, this does not mean that over longer time scales, the solar irradiance did not undergo much larger changes, which may have significantly affected the climate [4]. In fact, there are clear indications that solar forcing has controlled the drift of sea ice in the North Atlantic during the Holocene [5].

The second modulation effect is related to the geomagnetic dipole moment. From the analysis of the magnetic remanence measured in sediments and volcanic rocks it is known that the Earth’s dipole field changes continuously and sometimes even reverses its polarity. The geomagnetic dipole field has a shielding effect on the intensity of low-energetic particles penetrating into the atmosphere. This effect is largest at low latitudes and disappears at the poles leading to a latitude-dependent production rate (Fig. 1). The production rate of cosmogenic radionuclides is especially sensitive to periods of low geomagnetic field intensities such as the Laschamp and the Mono Lake event 40’000 and 30’000 years before present [6].

The transport and the deposition are affected by atmospheric mixing processes such as the exchange between stratosphere and troposphere and the precipitation rate. Hence, at a specific site, the fallout of a cosmogenic isotope bound to aerosols depends very much on the local precipitation rate. The more it rains the more radionuclides are removed and the concentration is rather constant. If however, as during glacial periods, the mean global temperature drops and the water cycle is reduced on a large scale, then less water removes the same amount of cosmogenic radionuclides leading to higher concentrations [7]. In regions with low precipitation rates (deserts, Antarctica) dry deposition has also to be taken into account.

Finally even after deposition on an ice sheet some processes can occur. As an example, measurements of $^{36}$Cl show that depending on the accumulation rate and the acidity of the snow, some of the $^{36}$Cl may form H$^{36}$Cl and escape from the ice back into the atmosphere [8].

In conclusion, measuring cosmogenic radionuclides in ice cores provides a wealth of information on cosmic rays, solar activity, geomagnetism, and atmospheric transport and deposition processes. Separation of the different components can be achieved by combining different radionuclides from different sites.

References
THE EFFECT OF PARAMETER UNCERTAINTY ON BLIND PREDICTION OF NP(V) SORPTION ONTO HAEMATITE USING SURFACE COMPLEXATION MODELLING

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Introduction
Still, the $K_D$ concept of empirical distribution coefficients is the most often utilized approach for description of sorption phenomena. However, as an empirical concept it can not correct portray the complex processes on the surfaces. A better approach is the use of Surface Complexation Models (SCM) capable of describing the sorption processes at the mineral-fluid interface on a scientific, quasi-thermodynamic basis. SCM are available in various versions, in which the Diffuse Double Layer Model (DDL), Constant Capacitance Model (CC) and Triple Layer Model (TL) are the most important and applied submodels.

Certainly, during the next decade SCM will replace $K_D$ only in some simple systems or systems dominated by one mineral. However, SCM can help to verify measured $K_D$'s, to identify the most sensitive experimental parameters, to assign uncertainty limits, to fill gaps difficult to access in sorption experiments, and to help to gain a better process understanding.

RES$^3$T [1] – the Rossendorf Expert System for Surface and Sorption Thermodynamics – is a digitized version of a thermodynamic sorption database as required for the parametrisation of SCM, namely in risk assessment studies. As an example to illustrate the effect of parameter uncertainty in blind predictions the Np(V) sorption onto haematite was selected.

Protolysis model set-up
The data collection is fully based on RES$^3$T. The values of $pK_1$ and $pK_2$ refer to the protolysis steps for the reactions from $=\text{FeOH}_2$ to $=\text{FeOH}$, and from $=\text{FeOH}$ to $=\text{FeO}$, respectively.

Querying RES$^3$T resulted in 6/4/12 independent CC/DDL/TL data records for the haematite surface protolysis. Because the reported data are related to different site densities, a normalization procedure according to Kulik [2] (reference surface site density 12.05 sites/nm$^2$) was followed. This value was also used for subsequent predictive modelling. The data are extrapolated to infinite dilution by the Davies equation if necessary. As some protolysis constants were not provided with the respective ionic strength, weighting factors of 1 (ionic strength not specified or with only range), 2 (various defined ionic strengths) or 3 (calculation for one ionic strength) were adopted. This led to the following weighted average of $pK \pm 2\sigma$ for the SCM submodels CC, DDL, and TL:

<table>
<thead>
<tr>
<th>Model</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>5.95 ± 1.00</td>
<td>9.74 ± 0.86</td>
</tr>
<tr>
<td>DDL</td>
<td>6.63 ± 1.05</td>
<td>10.25 ± 0.90</td>
</tr>
<tr>
<td>TL</td>
<td>6.04 ± 0.65</td>
<td>10.82 ± 0.51</td>
</tr>
</tbody>
</table>
Neptunium sorption model set-up
The Diffuse Double Layer model was chosen as SCM submodel to keep the number of parameters at a minimum. To account also for experiments under gas atmospheres containing CO₂, carbonate surface species had to be considered too. From the surface species reported so far, the following species were selected after a critical data review: \( =FeO-HCO_3 \), \( =FeO-CO_3^2- \), \( =FeO-NpO_2 \), and \( =FeO-NpO_2(HCO_3)^2- \). Below the selected species are given, with their normalised DDL reaction constants \( \log K_m \) taken from the REST database. The reaction constants refer to equations based on \( H_2CO_3(aq) \) as master species for carbonate.

\[
\begin{align*}
=FeO-HCO_3 & \quad \log K_1 = 3.10 \pm 0.29 \quad \Rightarrow =FeO-NpO_2 & \quad \log K_3 = -3.31 \\
=FeO-CO_3^2- & \quad \log K_2 = -4.75 \pm 0.41 \quad \Rightarrow =FeO-NpO_2(HCO_3)^2- & \quad \log K_4 = 11.25
\end{align*}
\]

The aqueous speciation of Np(V), as well as auxiliary data for the carbonate equilibria, were based on the thermodynamic data recommended by the NEA [3].

Blind predictive modelling
The modelling was performed with the FITEQL code, version 3.2 [4]. The experimental data sets by Kohler et al. [5] which were used for evaluating the predictions are comprised of 52 data points for the Np(V) sorption at varied pH, ionic strength, solid/liquid ratio, Np content, and carbonate partial pressure in the atmosphere in contact with the solution. The experimental value for the specific surface area of hematite, also used for the modeling, was 14.4 m²/g.

Figure 1 shows the difference between predicted and experimental distribution coefficients \( \log K_{dp} \). The simulation congruence for all data subsets is within one order of magnitude when focusing on the conventional distribution coefficient \( K_{12} \). Such a spreading is considered to be reasonable for performance assessment software.

![Graph showing differences in \( \log K_{dp} \) between predicted and measured Np(V) sorption onto hematite](image)

**Fig. 1.** Differences in \( \log K_{dp} \) between predicted and measured Np(V) sorption onto hematite

Uncertainty analysis
Because the protolysis constants can not be varied independently, the point of zero charge (PZC) and \( \Delta \text{pK} \) was calculated based on experimental pK₁ and pK₂. Consequentual we generated 20 pK data sets with the aid of 40 gauze distributed random numbers. The following figure shows the varied pK values and the resulting difference between predicted (result of FITEQL modelling) and experimental distribution coefficients \( \Sigma \text{abs(\Delta log } K_{dp})/n \).
Fig. 2. Randomly distributed pK of haematite (○: varied pK, Δ: experimental mean pK) plotted in a surface of the resulting $\Sigma$abs$(\Delta$og $K_D)/n$ (see numbers on the contour-lines)

**Conclusions**

It can be concluded that the application of SCM can indeed be very valuable for estimating $K_D$ values for contaminants in well defined mineral systems. The SCM database so far assembled within the RES$^2$T project is able to provide the respective parameter sets following the stepwise strategy of species selection, data collection, normalisation and averaging. None of the randomly generated pK parameter sets did deliver unacceptable blind predictions for the distribution coefficients. The vast majority of measured $K_D$ values were predicted within one order of magnitude.

Thus the formally large spreading of the pK values as extracted from literature (even after normalization and extrapolation to infinite dilution) is actually not critical. For well-defined mineral systems, provided a suitable database is accessible, the SCM approach seems to be very promising. This will be confirmed by further studies extending the range of minerals and contaminants.

**Acknowledgement**

The development of the mineral-specific sorption database RES$^2$T is funded by the German Federal Ministry of Economics and Labour (BMWA) under contract No. PtWt+E 02E9471, which is gracefully acknowledged.

**References**


RADIONLABELLING OF HUMIC SUBSTANCES WITH $^{131}$I AND $^{14}$C
AND THEIR USE FOR ADSORPTION STUDIES ON GEOMATRICES
UNDER CONDITIONS NEAR TO NATURE

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The reactive carbon compounds (humic substances, HS) of the dissolved organic matter (DOC) dominate the spreading of inorganic and organic pollutants in the biogeo sphere [1-3]. The classical analytical methods such as TOC-detection and UV-spectroscopy are of limited use in the lower concentration range (< 1 mg/l), usually found in environmental samples. By using radiolabelled HS, scenarios near to nature in the µg/l-HS-concentration range can be studied [4-8]. Based on our promising results of the HS radiolabelling with $^{19}$F diazonium ions, we applied this procedure first time to $^{14}$C diazonium ions as radiolabelling precursor. Besides, HS were radiolabelled via the IODOGEN-method with $^{131}$I [6]. [U-$^{14}$C]aniline hydrochloride (Amersham) was transferred with nitrite to the diazonium ion in hydrochloride solution. The diazonium ion reacts with the activated aromatic residues of HS under mild reaction conditions (Figure 1). The purification was performed by repeated precipitation or ultrafiltration. After every synthesis and purification step, aliquots were taken for liquid scintillation counting.

Figure 1. Reaction scheme for the labelling of humic substances with $^{14}$C.

The natural HS (humic acid HA, fulvic acid FA) were purified by the IHSS-procedure [9], Aldrich-HA (AHA), Gorleben-HA (GoHy-532), an aquatic HA (HS3), a terrestrial HA (HS4), a lignite HA (HAL) and a aquatic FA (FS3) were used for our investigations. A synthetic HA (M42) was provided by the Forschungszentrum Rossendorf [10]. The HS-concentration in mg/l was determined by extinction measurement at 254 nm. The
chemical (HS) and radiochemical ($^{14}$C) yields and the specific activities are given in Table 1.

Table 1. Chemical (HA) and radiochemical ($^{14}$C) yields and specific activities for the diazotisation of various HS with $[^{14}$C]aniline; pH 9.5; 0 °C; 45 min; Purification by triple precipitation (FA ultrafiltration)

<table>
<thead>
<tr>
<th>HS</th>
<th>Origin</th>
<th>Chemical yield %</th>
<th>Radiochemical yield %</th>
<th>Specific activity MBq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHA</td>
<td>commercial</td>
<td>67.8</td>
<td>5.6</td>
<td>12.7</td>
</tr>
<tr>
<td>GoHy-532</td>
<td>Gorleben</td>
<td>90.6</td>
<td>2.6</td>
<td>7.6</td>
</tr>
<tr>
<td>HS3</td>
<td>aquatic, bog</td>
<td>46.9</td>
<td>4.9</td>
<td>5.4</td>
</tr>
<tr>
<td>HAL</td>
<td>lignite</td>
<td>81.3</td>
<td>2.8</td>
<td>4.4</td>
</tr>
<tr>
<td>M42</td>
<td>Synthetic</td>
<td>65.4</td>
<td>2.1</td>
<td>4.0</td>
</tr>
<tr>
<td>HS4</td>
<td>terrestrial, bog</td>
<td>72.5</td>
<td>2.1</td>
<td>3.7</td>
</tr>
<tr>
<td>FS3</td>
<td>aquatic, bog</td>
<td>48.6</td>
<td>2.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The radiolabelled HS were contacted in aqueous solution with a sandy soil, granite, diabase and kaolinite in batch experiments under conditions near to nature. In Figure 2 the adsorption isotherms of various radiolabelled humic acids and a sandy soil are shown. The behaviour of the radiolabelled HS was not influenced by the labelling procedure as demonstrated in Figure 2. With the use of radiolabelled humic substances a concentration range below mg/l can be studied.

![Figure 2. Adsorption isotherms of various radiolabelled humic acids on a sandy soil; pH 5; 0.1 M NaClO$_4$; 4 ml HS-solution / g sandy soil; Batch experiment.](image)

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This work has been supported by funding from the German Federal Ministry for Education and Research (BMBF) under the contract No. 02 C 0932.

EFFECT OF HUMIC COLLOIDS ON THE pH-DEPENDENT ADSORPTION OF TERBIUM(III) ONTO GEOGENIC SOLIDS – CHANGEOVER FROM MOBILIZATION TO DEMOBILIZATION

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Introduction

In case of a release from subterranean radwaste repositories, migration of actinides can be facilitated considerably by interaction with aquatic colloids. In particular, the complexing ability of humic and fulvic acids (HA, FA), main constituents of the dissolved organic carbon (DOC), can dominate the speciation of multivalent metals [1]. The impact of colloid-borne migration is, however, not sufficiently described by complex stability since the mobilizing effect is also determined by the solid-liquid partitioning of the carrier colloids. The underlying processes are dependent on the geochemical circumstances, which cannot be regarded as invariant in pertinent scenarios. For the development of site-specific transport models, it is therefore necessary to identify the respective conditions leading to an enhancement or confinement of migration.

In the present study, the pH dependence of the influence of humic acid on metal adsorption onto different geogenic solids (kaolinite, phyllite, diabase, granite, sand) was investigated with Tb(III) as an analogue of trivalent actinides (Am, Cm) using $^{150}$Tb as a radiotracer. Humic substances (HS) were radiolabelled with $^{131}$I to enable comparative studies at a low DOC level as encountered in natural systems. A multi-partitioning approach was employed to reproduce the findings quantitatively on the basis of the constituent processes. For this purpose, humate complexation of Tb(III) and adsorption of humic acid were likewise investigated in pH-dependent experiments.

Materials and methods

Granite, phyllite and diabase were collected in the “Mansfelder Land” (Saxony-Anhalt, Germany), sea sand was purchased from Merck (Darmstadt, Germany). A 2-3 mm grain size fraction was used in the experiments. Kaolinite KGa-1b standard material was obtained from the Clay Minerals Society of America (Boulder, USA). Natural aquatic and soil HS were sampled from the raised bog “Kleiner Kranchsee” (Saxony, Germany), a further HA was obtained as sodium salt from Sigma-Aldrich (Taufkirchen, Germany). Isolation / purification of HA and FA was accomplished by standard methods. Synthetic humic acid M42 [2] was supplied by the Forschungszentrum Rossendorf. Radiolabelling with $^{131}$I was performed by the iodogen method [3, 4]. $^{150}$Tb ($T_{1/2} = 72.3$ d) was produced by neutron activation of $^{150}$Tb at the TRIGA Mark II reactor of the University of Mainz.

Experiments on adsorption and complexation were conducted batchwise in PE vials. Systems were equilibrated at 20 °C for 48 hours. The anion exchange method [5] was applied for metal speciation, using Sephadex DEAE A-25 (Sigma-Aldrich) to separate the organically bound
fraction. Depletion was determined radioanalytically with a gamma counter 1480 Wizard (Wallac, Finland).

Results and discussion

The effect of HA on metal adsorption proved to be strongly dependent on the pH value. For all geogenic solids under study, there is a crossing of the pH-dependent adsorption functions in the absence and in the presence of HA. At pH values above the crossing point, the humic acid effects a mobilization, yet below, a demobilization of the metal compared to the corresponding solid-liquid distribution in the absence of DOC (see Figure 2). For kaolinite, diabase, granite and sand, the reversal already occurs at slightly acidic pH values (pH 5 – 6.5) and is thus relevant in view of geochemical systems. Only for phyllite, the pH required for demobilization is so low that the presence of humic colloids would be unfavourable in general.

The changeover from mobilization to demobilization is mainly explained by the fact that adsorption of HA becomes important on a minor decrease in pH, which was shown by pH-dependent measurements for the 5 solids. In contrast, Tb-humate complexation was found to decrease considerably on lowering the pH because the ligands are blocked by protonation. With increasing pH, dissociation of acidic groups leads to a corresponding gain in binding sites at the colloids and also to a hindrance of colloid-solid interaction due to the build-up of an electrostatic barrier. Accordingly, a competitive situation arises between metal adsorption and humate complexation, and migration would be facilitated. On acidification, the HA adopts a mediating function in that additional Tb is co-adsorbed as a humate complex. Consequently, the presence of DOC turns from a source to a sink in terms of actinide migration, thereby relativizing the problematic role of humic colloids.

The situation may be described by a multi-partitioning model (Figure 1) in which the single processes are considered as a system of interdependent equilibria, represented by distribution coefficients $K_d$ where the superscripts M, HA, M-HA and S stand for “metal”, “humic acid”, “metal-humate complex” and “solid”, respectively.

$$K_d^{M+M-HA/S} = \frac{K_d^{M-HA} - K_d^{M-HA/S} c_{HA}}{1 + K_d^{M-HA} c_{HA}}$$  \hspace{1cm} (1)
In this way, the pH-dependent influence of HA on metal adsorption can be reproduced by means of the experimentally determined $K_d$ values of the constituent processes. Figure 2 shows the results of such a calculation for granite as an example.

![Graph showing adsorption of $[^{60}$Tb$]$Tb(III) (10$^{-7}$ M) onto granite in 0.1 M NaClO$_4$ depending on the pH value in the absence and in the presence of Aldrich HA (5 mg L$^{-1}$).

Although there is a significant discrepancy between experimental and calculated values, the transition from mobilization to demobilization is reproduced properly. The deviations indicate that humate complexation is overrated in the calculation, which is mainly due to the fact that competitive effects in consequence of mineral leaching were not taken into account.

In order to enable more general conclusions in view of the diversity of natural organic colloids, adsorption isotherms of various humic and fulvic acids were compared. In all cases, adsorption was found to be significant already at pH 6. Thus, it can be inferred that the capability to demobilize metal ions on acidification is not confined to the Aldrich material.

Acknowledgements

This work was supported by funding from the German Federal Ministry of Economics and Labour (Bundesministerium für Wirtschaft und Arbeit, BMWA), project ref. No. 02 E 9329. Technical support by the University of Mainz, Institute of Nuclear Chemistry, is gratefully acknowledged.

References

COSMOGENIC NUCLIDES IN THE MARTIAN METEORITES
ALHA 77005, LAFAYETTE AND ZAGAMI

Th. Bastian¹, U. Herpers¹, P.W. Kubík², K. Knie³, U. Ott⁴, R. Michel⁵


The availability of effective physical models for the calculation of production rates of cosmogenic nuclides in meteorites [1, 2] allows an exact analysis of the irradiation history of meteorites. The relative errors of calculated production rates lay below 10%. At present, concentration ratios of cosmogenic nuclides can be calculated even with errors of less than 3% [1].

The model used in this work calculates the part of the nuclide production which comes from the interaction of the galactic cosmic radiation with the meteoroid matter. For this reason any other additional production is easily identifiable. Such overproductions are basically caused by two phenomena: complex irradiation histories and the solar cosmic radiation (SCR-effect). In this work the SCR-effect for the cosmogenic radionuclides $^{10}$Be, $^{26}$Al and $^{53}$Mn is demonstrated.

For this purpose the irradiation history of 10 Martian meteorites was investigated in detail. Initially the concentrations of the radionuclides $^{10}$Be, $^{26}$Al and $^{53}$Mn in 10 Martian meteorites were measured via AMS (Accelerator Mass Spectrometry) at the accelerator facilities of the ETH Zürich and the TU-München. Additionally the cosmogenic fractions of $^3$He, $^{21}$Ne, $^{22}$Ne, $^{36}$Ar, $^{83}$Ar, $^{86}$Kr und $^{85}$Kr were measured and calculated at the MPI Mainz. All measurements were performed with the same sample material, which led to the special quality of the data obtained in this work, because only same sample data of cosmogenic nuclides can be consistently discussed. A data set of this extension has been measured here for the first time.

Overall production rates depended on sample depth and meteoroid radius was then calculated using the elemental production rates of Leya et al. [1, 2]. Input parameter was the chemical bulk composition data of Lodders [3]. These production rates were plotted against each other in an adequate way and compared with the measured nuclide concentrations (cf. e.g. Figs. 1 and 2).

A complete set of same sample data of cosmogenic nuclide was measured in bulk samples of the meteorites (Tables 1 and 2). The analysis of the radionuclide concentrations showed overproductions of $^{22}$Ne and of $^{53}$Mn in ALHA 77005, Lafayette and Zagami. The noble gas exposure ages calculated with the physical model of Leya et al. [1, 2] were higher than exposure ages previously reported by Eugster et al. [4, 5] due to a $^3$He and $^{22}$Ne overproduction.
Table 1: Measured concentrations of cosmogenic radionuclides.

<table>
<thead>
<tr>
<th></th>
<th>$^{10}$Be [dpm/kg]</th>
<th>$^{26}$Al [dpm/kg]</th>
<th>$^{53}$Mn [dpm/kg Fe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALHA 77005</td>
<td>-</td>
<td>-</td>
<td>127 ± 15</td>
</tr>
<tr>
<td>Lafayette</td>
<td>21.0 ± 1.7</td>
<td>80.7 ± 6.6</td>
<td>318 ± 36</td>
</tr>
<tr>
<td>Zagami</td>
<td>-</td>
<td>-</td>
<td>317 ± 34</td>
</tr>
</tbody>
</table>

Table 2: Measured concentrations of cosmogenic noble gases. Values are the cosmogenic fraction, measured and corrected by S. Schwenzer, MPI Mainz [6].

All concentrations are given in $10^{-8}$ cm$^{-3}$ g$^{-1}$ STP (except for $^{83}$Kr: $10^{-13}$ cm$^{-3}$ g$^{-1}$ STP)

(STP: standard temperature and pressure)

<table>
<thead>
<tr>
<th></th>
<th>$^{3}$He</th>
<th>$^{21}$Ne</th>
<th>$^{22}$Ne</th>
<th>$^{26}$Ar</th>
<th>$^{38}$Ar</th>
<th>$^{83}$Kr</th>
<th>$^{85}$Kr</th>
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</thead>
<tbody>
<tr>
<td>ALHA 77005</td>
<td>7.989</td>
<td>1.023</td>
<td>1.313</td>
<td>0.094</td>
<td>0.141</td>
<td>-</td>
<td>2.3</td>
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<tr>
<td>Lafayette</td>
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<td>2.123</td>
<td>2.569</td>
<td>-</td>
<td>2.204</td>
<td>10.2</td>
<td>94.5</td>
</tr>
<tr>
<td>Zagami</td>
<td>4.74</td>
<td>0.568</td>
<td>0.692</td>
<td>0.251</td>
<td>0.377</td>
<td>2.0</td>
<td>1.70</td>
</tr>
<tr>
<td>± 1.023</td>
<td>± 0.076</td>
<td>± 0.075</td>
<td>± 0.011</td>
<td>± 0.009</td>
<td>± 0.087</td>
<td>± 5.5</td>
<td>± 1.2</td>
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<tr>
<td>± 1.50</td>
<td>± 0.135</td>
<td>± 0.064</td>
<td></td>
<td></td>
<td>± 0.087</td>
<td>± 5.5</td>
<td>± 1.2</td>
</tr>
<tr>
<td>± 0.34</td>
<td>± 0.030</td>
<td>± 0.053</td>
<td></td>
<td>± 0.009</td>
<td>± 0.011</td>
<td>± 1.2</td>
<td>± 0.22</td>
</tr>
</tbody>
</table>

* Neutron induced component

The correction of the measured radionuclide concentrations to saturation activities was performed using the exposure ages of Eugster et al. [4, 5] because with the model used in this work a quantitative correction of SCR-Effects is not possible so far. With these well approved exposure ages all radionuclides showed partly considerable overproductions (Figs. 1 and 2).

Fig. 1: Lafayette: $^{10}$Be production rate vs. $^{22}$Ne/$^{21}$Ne-ratio, calculated for different meteoroid radii. The measured $^{10}$Be saturation activity is about 30% higher than the values calculated by the model (dots without error) considering GCR-production.

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Complex irradiation histories (pre-irradiation on the meteorite parent body) seem to be not very likely because all investigated cosmogenic nuclides were present in excess (cf. Bastian [7]). Another hint for SCR effects is the lack of such nuclide excesses in other samples of these meteorites analysed previously by other authors (cf. e.g. [4]). This is comprehensible if one assumes that these samples were derived from deeper preatmospheric depths. Hints of SCR effects in Martian meteorites were formerly found in ALHA 77005 [8] and Zagami [9] by means of Ne-isotopes. SCR effects in $^{10}$Be, $^{26}$Al and $^{53}$Mn in Lafayette and Zagami are reported here for the first time.

Summary

With three meteorites of ten, a relative large amount of Martian meteorites shows SCR effects. This fits to investigations of Wetherill [10] who had calculated low entrance velocities for Martian meteorites using Monte-Carlo-simulations. Thus the ablation is small and the matter lying right below the preatmospheric surface was preserved.

9. Nuclear Fuel Cycle
NEW NUCLEAR FUEL CYCLE OPTIONS FOR WASTE MINIMISATION AND SUSTAINABLE DEVELOPMENT OF NUCLEAR ENERGY

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1. Introduction

The need for improved and sustainable fuel cycles is at the heart of any future development of nuclear energy. As an outstanding example, the GENERATION-IV international initiative requires not only new and innovative reactors but at the same time the development of appropriate fuel cycle technologies, which include fuel processing and separations, fuel fabrication, waste forms and disposal technologies, in order to reduce spent fuel volume, separate long-lived, highly radiotoxic elements to optimise waste management and to increase its overall proliferation resistance.

2. The Role of Partitioning and Transmutation

In this context, the objective of Partitioning and Transmutation (P/T) is to develop technologies which can help to reduce the burden on a final deep geological storage in terms of masses, heat load and radiotoxicity. These objectives are valid whatever scenario is considered for nuclear energy development. In reference [1], four general schemes have been developed, which cover most of the options envisagable for nuclear energy development. In fact, P/T technology can be of relevance in such extreme cases as the sustainable long term development of nuclear energy with and increased role in energy production, or nuclear energy phase-out. This feature is important, since it opens the way to wide international collaborations, where partners can have different national policies with respect to nuclear energy. The four general schemes (Fig. 1) represent, a) waste management directly associated to the development of a sustainable nuclear energy, based on fast neutron reactors, b) waste management in dedicated system, associated to the use of existing reactors for energy production; c) waste management initially (and partially) performed with existing reactors, in order to represent a kind of “delay line” towards a later introduction of fast reactors and d) waste management partially performed with existing reactors in order to make it easier their successive transmutation in dedicated system, both from the view point of cost and technical feasibility. All the proposed scenarios, imply the use of spent fuel processing techniques and, are beyond the “open cycle” strategy. As far as Pu, the first three scenarios consider it as an asset, and the fourth scenario can be tuned to a drastic Pu stocks reduction. All the scenarios require a deep geological storage, but reduce significantly the burden on it.

3. Transmutation Technology and Issues

To assess quantitatively the potential effect of P/T strategies in different scenarios, it is necessary to develop and to validate processes and technologies both in the domain of the actinide separation chemistry, and in the domain of transmutation in a neutron field. The physics of transmutation is based on a generalisation both of the concepts of “neutron balance” in a fission reactor core, and of the Bateman equations, which allow to calculate the evolution with time of nuclei under neutron irradiation [2].
These generalized tools allow in particular to intercompare different reactor concepts, characterized by their neutron spectrum (e.g. fast neutron vs thermal neutrons) and the level of the neutron flux (e.g. in the range $\sim 10^{14} - 10^{16}$ n/cm$^2$.sec), and their potential to transmute elements such as Pu, Am, Np, Cm, each being characterized by its neutron interaction cross-sections.

For example, the generalized neutron balance equation is written in terms of neutron "excess" $N$:

$$N = -D_{\text{comb}} - L + C$$

where $D_{\text{comb}}$ is the neutron consumption associated to the transmutation of a specific fuel ($D_{\text{comb}} = \sum x_i D_i / \sum x_i$, where $D_i$ is the neutron consumption associated to the isotope $i$ present in the fuel with a fraction $x_i$), $L$ and $C$ are the neutron consumption associated to the neutron leakage out of the core and to parasitic captures (structures, fission products etc.), respectively. The form of equation (1), indicates that the transmutation is only possible, if the $D_i$ are such that $N > 0$. An investigation of the $D_i$ of the important TRU isotopes, indicates [2] that only a fast neutron spectrum can support easily the transmutation of any TRU isotope. On the other hand the use of the generalized Bateman equation in an equilibrium regime (i.e. when production and disappearance of each nuclei are equal), allows to intercompare the transmutation of all TRU in a LWR or in a FR, and the selective recycling of MA in LWRs. For this last case (see Table 1), the potential burden of Cm multi-recycling is indicated by the high Cm inventory. The Cm inventory is in any case higher in LWRs with respect to FR. This feature affects in a relevant manner the fuel cycle, and underlines the advantage of fast neutron spectra. As indicated in table 1, one can limit the recycling to Am and Pu. The Cm initially produced in UOX-PWRs and further produced during the multi-recycling of Pu and Am, has to be managed separately. One possibility, is to store the Cm temporarily, waiting for its decay in order to process it further to separate the Pu produced by decay, which can be successively transferred to future fast reactors or future dedicated systems. As far as Am, several possibilities have been investigated, in order to limit the penalties associated to its recycling in LWRs, essentially at the level of the core performances. Am in a MOX-loaded core results in a hardening of the spectrum due to its captures, and that makes the coolant void reactivity coefficient less negative. Hence the Pu content should be reduced and the U-235 enrichment increased. Both homogeneous and heterogeneous recyclings of Am have been investigated. The heterogeneous mode can in principle limit the penalties at fuel fabrication. However, the effectiveness of transmutation is lower than in the case of homogeneous recycle, and the number of reactors to be equipped with target-bearing assemblies is very high (~50% of the total power park).

Finally, as far as the type of dedicated transmuter, the ADS concept allows to envisage practically any type of fuel loading in the core (i.e. any ratio of MA/Pu, according to the chosen strategy), since the adverse effects of low Doppler effect and delayed neutron fraction, intrinsically associated to any fuel without U and with a high percentage of MA, are managed via the subcriticality of the core and its dynamic behaviour.

4. Consequences of P/T

All scenarios in which Pu and MA are separated, used in reactors and further reprocessed, allow to reach a substantial radiotoxicity reduction, directly related to the separation effectiveness. For example, whatever the scenario and the reactor type, a factor ~100 of reduction is obtained, if the losses during successive reprocessing steps are limited to ~0.1% for both Pu and MA. However, it is probably as important or even more relevant on the short term, to evaluate the impact on the repository in terms of heat load and volume reduction.
These studies applied to the case of Yucca Mountain are presently systematically done at ANL, and first results indicate the potential benefits of separating Pu and Am, but also of Cs and Sr in terms of heat load reduction and repository monitoring. Finally, as far as non-proliferation, if the proliferation risk is considered proportional to the Pu inventory, the once-through fuel cycle presents a risk which is steadily increasing as the spent fuel in the storage is growing with time. The introduction of reprocessing, for a “short” time (few decades) could potentially increase the risk (since some Pu is separated), but the consequent reduction of the Pu stocks and its “contamination” with MA can bring the potential proliferation risk to much lower values than in the case of the open cycle strategy, and this in a time frame of only few decades.

5. Conclusion

The separation of Pu and MA from the spent fuel together with transmutation, offer a wide variety of options for the fuel cycle, which can answer to different objectives, from sustainability, to waste minimisation, to optimized (from the technical point of view) and more acceptable (from the public point of view) repositories, and even to enhance proliferation resistance. The types of technologies to be deployed vary from established (e.g. PUREX and MOX-LWRs), to innovative (e.g. pyrochemistry) or very innovative (e.g. ADS). However, it can be envisaged a gradual introduction in the present fuel cycles, of the more innovative technologies. The recognized role of nuclear energy, requires that a maximum effort is focused on the fuel cycles which can answer in an exhaustive manner to present requirements, as indicated for example in the frame of the GEN-IV initiative.

6. References


<table>
<thead>
<tr>
<th>Table 1 - Pu+MA multirecycling in a MOX-PWR with enriched U-235 support</th>
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<tbody>
<tr>
<td><strong>Pu(U+Pu+MA) in Feed</strong></td>
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<tr>
<td>--------------------------</td>
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<tr>
<td>Total Pu (gPu/TWhc)</td>
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<td>Total Pu (gPu/TWhc)</td>
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<td>Total MA (gMA/TWhc)</td>
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<td>Total Cm (gCm/TWhc)</td>
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<td>Total Cm (gCm/TWhc)</td>
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<td>Total Cm (gCm/TWhc)</td>
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</table>
Figure 1: Four general schemes of P/T
ACTINIDE PARTITIONING: PAST, PRESENT AND FUTURE

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To respond to 21st century demands for preserving the livability of planet earth, no currently available large scale energy production technology has greater potential for benefit and wide scale application than nuclear fission. As global climate change emerges as perhaps the greatest modern threat to civilization, nuclear power becomes more attractive as it produces no greenhouse gases as a byproduct of electricity generation. Unlike the competing/complementary energy production technologies of wind/solar/hydroelectric, nuclear power plants occupy a comparatively small area relative to their power production potential (much like fossil fuel plants), hence its “power density” is also the greatest among possible options. Nuclear power is also the perfect complement to the proposed “hydrogen economy” as the hydrogen transportation fuel can be produced with essentially no waste byproducts other than the spent fuel. Aside from actinide recycle, other valuable byproducts (137Cs for irradiation sources, 90Sr as a remote heat source, precious metals (Pd, Rh, Ru, Ag)) can also be recovered from spent fuel. The unfortunate trade-off of greenhouse gas avoidance by fission-based nuclear power is the creation of intensely radioactive spent fuel that must be sequestered from the biosphere/hydrosphere for 10^4 to 10^5 years. In truth, the need to demonstrate a clear pathway to the sequestration of this waste and prevention of nuclear weapons proliferation are the largest obstacles to its expanded use. Another motivation for closing the loop on nuclear fuels is that a shortage of fissile material would emerge within a few decades if the utilization of nuclear power for energy production were to expand dramatically [1]. Conversion of fertile 238U or 232Th to fissile 239Pu or 233U in a full recycle breeder reactor power cycle, as was explored extensively in the 1970’s and 1980’s, could address this limitation. Success in both enhancing safety margins and assuring the availability of adequate fuel supplies hangs on the expansion and improvement of nuclear fuels recycle technologies. Improving the technology will rely on improving the science that supports the technology.

 Though a once-through fuel cycle (in which spent fuel is sent to a geologic repository as the waste form) is presently employed in the U.S., other industrialized nations have successfully operated closed loop fuel cycles to recover fissile 239Pu and 235U residues from commercial fuels. The so-called minor actinides (Np, Am, Cm) and fission products are at present routed to waste, as they have been from the earliest days of industrial scale nuclear fuel recycle. A closed-loop fuel cycle offers at least three important benefits: increased energy production potential through recycle of U and Pu as fresh fuel; a shortened radioactive lifetime for the remaining wastes, particularly if minor actinides are recovered and transmuted; and extension of the lifetime of geologic repository (by reducing the volume of wastes that must be emplaced and allowing
closer placement of wastes in the repository due to reduced heat loads). At the heart of nuclear fuel recycle is the need for effective and efficient separations of the actinides (and long-lived fission products) from the roughly 1/3 of the Periodic Table that is created as a result of thermal neutron induced fission.

Though initially deployed almost 50 years ago, the PUREX process, which is based on the selective solvent extraction of U and Pu from spent fuel from nitric acid by tributyl phosphate, remains the only industrial-scale actinide recycle process in operation around the world. This process continues to undergo modification and development with research focusing on adapting its unique properties to a more contemporary view of how spent fuel must be processed. However, TBP and PUREX are not without their problems and limitations. Among the limitations of this system in the context of reprocessing in the 21st century are the rejection of minor actinides, the introduction of phosphate into the waste stream (which impacts the volume of byproduct wastes requiring repository emplacement), interference of degradation products (for example, dibutyl phosphate) in separation efficiency, solubility limitations at high loading conditions leading to undesirable creation of extra liquid phases (third phase formation), and the possibility of creating explosive mixtures if care is not taken with solutions kept in storage (organic compounds, nitric acid, and radioactive heavy metals have created mixtures with considerable explosive potential when left unattended). In 50 years of process-scale application experience, most of these problems have been recognized and engineering solutions have been developed.

The problem demanded by a full recycle/transmutation fuel cycle for which there are no acceptable solutions (within PUREX) to the rejection of minor actinides by TBP, hence the recovery of minor actinides demands the development of new separations materials and processes. Much of the research being conducted globally today addresses this particular limitation of PUREX. A number of different separations materials and processes have been investigated in the last two decades, many of which have progressed to the pilot scale testing phase. Among the processes having received the greatest development (and each possessing unique advantages) are the TRUEX process and variations on the basic process (based on multifunctional organophosphorus extractants), the DIAMEX process (developed principally in France and relying on multifunctional diamide extractants which offer the advantage of complete incinerability), the DIDPA process (relying on a different class of organophosphorus reagents), the TRPO process (relying on yet another organophosphorus solvent extraction reagent), and various electrometallurgical processes, the premier example being the Integrated Fast Reactor (IFR) fuel cycle developed at Argonne National Laboratory. Though each of these options has experienced extensive testing, none has as yet been put into production-scale operation.

A subset of this separation challenge is the even more demanding need to separate fission product lanthanides (representing about 40% of the non-uranium mass of spent fuel) from the chemically similar transplutonium actinides. This separation is needed for most scenarios of actinide "incineration" because of the considerable neutron absorbing capabilities of the rare earths. The separations challenge represented in this system lies in the extremely close similarity between the chemistries of trivalent transplutonium actinides and lanthanides. The absence of
any important redox chemistry for these metal ions (except for the M(III)/M(0) transition at the heart of electrometallurgical separations in molten metal/molten salts) essentially eliminates the options that made PUREX work from consideration. The importance of this separation was recognized in the earliest days of actinide chemistry in the work of Diamond et al. [2] who observed that an effective trivalent actinide/lanthanide separation was achieved most readily through the agency of ligand donor atoms softer than oxygen (Cl, N, S). This fundamental observation carries over today in efforts to create viable separations systems based on reagents containing these atoms. Mixed successes in the laboratory have yet to lead to viable production scale systems, but progress has been steady.

Ongoing research and development activities today focus on developing cleaner, safer and more proliferation resistant approaches to spent fuel recycle than was practiced during the first 50 (largely nuclear defense-driven) years of spent fuel reprocessing. A new philosophy of considering the entire fuel cycle is developing in which minimization of the volume and toxicity of wastes generated while maximizing the stability of the products to be sequestered from the bio-hydrosphere has become a central focus. Because of the 50 years of experience in the application of solvent extraction to nuclear fuels processing and because this technique alone (at present) offers the best combination of efficiency and high throughput, a significant fraction of the ongoing research on this topic focuses on hydrometallurgical approaches to reprocessing. The 50 year head start of solvent extraction (and ion exchange as a polishing technique) is the underlying cause of this emphasis. But the application of fresh operational philosophies that respond to contemporary environmental protection demands could lead to further improvements in the performance of aqueous processing options. Alternative (non-aqueous) approaches based on the application of molten metal or molten salts have in recent decades received intensive investigation. These methods have certain clear advantages over hydrometallurgy in terms of process complexity, but suffer serious technological impediments that require intensive work (primarily in materials science) to truly enable them as viable technologies. More exotic approaches involving "unconventional" materials like supercritical fluids (CO2) or room temperature ionic liquids (RTIL's) may also have a useful role to play, though in each case the road from current science to eventual technological application may be long and difficult. Ultimately, success may well require that aqueous and non-aqueous processes be employed in tandem to achieve the goals demanded by 21st century environmental concerns.

In this presentation, results of some of the latest international research on actinide partitioning will be discussed within the context of the historic perspective of 50 years of industrial-scale processing experience that has already been accumulated. The emphasis will be on evaluating the prospects for a successful outcome in the development of a 21st century nuclear fuel cycle.

TRANSMUTATION EXPERIMENTS ON $^{129}$I, $^{139}$La AND $^{237}$Np USING THE NUCLotron ACCELERATOR


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5 Dept. of High Energy Physics, University of Sydney, Sydney, NSW 2006 (Australia)
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Experiments were carried out with the GAMMA-2 target setup [1] at the NUCLotron accelerator using protons in the energy range from 0.53 GeV to 4.15 GeV. Fig.1 gives a schematic view of the GAMMA-2 experimental setup together with its beam monitoring system.

![Schematic diagram of the GAMMA-2 setup.](image)

Figure 1: Schematic view of the GAMMA-2 setup. The target is composed of 20 lead disks with 8 cm diameter and 1 cm thickness, the paraffin moderator shell has 20 cm outer diameter, 6 cm thickness and 31 cm length. The Al-monitor contains a stack of three thin aluminium foils where the center foil is used. Polaroid films were used for beam alignment before each irradiation.

Five scintillation detectors C1 to C5 and a 1 g/cm$^2$ PE target were used to monitor the beam. Aluminium activation foils were used to determine the integral proton fluence on the target. The Al monitor foil stack was placed approx. 60 cm upstream the Pb target in order to avoid activation from backwards emitted particles. In each experiment a stack of three Al foils with a thickness of 31 μm (1.883*10$^{20}$ atoms*cm$^{-2}$) was mounted in an aligned position with the target and perpendicular to the beam axis as shown in Fig. 1, and irradiated during the whole run. The beam intensity was determined via the $^{27}$Al(p,3n)$^{24}$Na reaction in the center foil.

Samples containing 1 gram of lanthanum each were placed on top of the target assembly at distances of 5 cm, 10 cm, 15 cm, 20 cm, and 25 cm from the front side of the paraffin block,
i.e. the first sample sits just above the location where the proton beam hits the Pb. B-values for each of the five samples (corrected for neutron anisotropy) were measured in every experiment. The B-value is an absolute cross section which is specific for each experimental setup and defined for the example nuclide \( ^{140}\text{La} \) as:

\[
\text{B}^{(140}\text{La}) = \text{Atoms of} \ 140\text{La produced in 1 gram of} \ 139\text{La sample by 1 primary proton}
\]

In order to compare neutron densities from various experiments we have calculated the integrated B\(^{(140}\text{La}) \) for \( ^{140}\text{La} \) on the GAMMA-2 setup by fitting the five data points with a modified (skewed) Gaussian function. The function is used because it has a suitable shape and not because of any physical significance.

![B values from La spectra: 0.53 GeV](image)

**Figure 2:** B-values for \( ^{140}\text{La} \) along the top of the paraffin moderator in the irradiation with 0.53 GeV protons on the GAMMA-2 target. The distance \( d=0 \) cm corresponds to the upstream end of the 20 cm long Pb target, i.e. the point of proton impact.

The fitted distributions quantify findings from earlier experiments [2,3] that the shapes of B-value distributions (i.e. the neutron densities over the target) are almost identical over the entire proton energy range studied. The maximum of the B-values is always found at about 10 cm downstream the beginning of the lead target and the widths of the distributions are essentially the same for each energy in the 0.53 GeV \( \leq E_p \leq 4.15 \text{ GeV} \) range.

The integrated B\(^{(140}\text{La}) \) values divided by the proton beam energy \( E_p \) are plotted in Fig. 3 as a function of proton energy \( E_p \). This picture shows the effectiveness of the GAMMA-2 setup for transmutation of \( ^{138}\text{La} \) via neutron capture reactions. Thus, it also displays the effectiveness of the GAMMA-2 setup for the production of low-energy neutrons. It is interesting to note that the effectiveness of GAMMA-2, which has only 20 cm Pb target length, for low-energy neutron production is best at low proton energies.

![Normalized B-values for 140 La on the GAMMA-2 setup](image)

**Figure 3:** Normalized B-values for \( ^{140}\text{La} \) on the GAMMA-2 setup. The dotted line serves to guide the eye.

Three data points at 0.65 GeV, 1 GeV and 1.5 GeV proton energy from earlier measurements show the necessity for the measurement of anisotropy of the neutron distribution in every experiment and concurrent correction of measured B-values.

In Figures 4 and 5 the corresponding functions of B-values/E\(_p\) are shown for the transmutation of \( ^{129}\text{I} \) and \( ^{237}\text{Np} \). In these experiments samples of approx. 1g of radioactive target material, which was welded into Al-containers, were exposed to the secondary neutron fluence on top of the paraffin moderator on the GAMMA-2 target setup.
The lines in Figs. 4 and 5 serve to guide the eye. Considering results from Figures 3 to 5 it is clear that the transmutation effectiveness B/E_p on the GAMMA-2 target is always highest at low proton energy and gradually falls off with rising bombarding energy. This may favour the use of proton beam energies that are lower than it has been assumed in other design studies. Operating at lower energy would of course be commercially attractive. However, the gradual fall may be a consequence of the size of the target where the small diameter and short length do not allow the intra- and inter-nuclear cascades originating from incident protons to be completed. Further experiments shall answer that question very soon.

References


RADIONUCLIDE IMMOBILIZATION IN CEMENT SYSTEMS

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Cementitious materials have been used worldwide as engineered barriers for the safe disposal and long-term storage of nuclear wastes. For example, the use of cementitious materials is foreseen in the planned Swiss repository for long-lived intermediate level radioactive waste in the Opalinus clay host rock of Northern Switzerland. Cement is used to condition the waste materials and to build the engineered barrier system (container, backfill and liner materials). The migration of radionuclides in the near field is retarded due to interaction with the engineered barrier system. In performance assessment (PA) studies retardation of safety relevant radionuclides by the near-field barrier together with solubility considerations is taken into account to deduce the source term for radionuclide migration.

An important feature of cementitious systems is the presence of trace element impurities, which are inherently associated with the cement matrix. Cement is manufactured by blending a calcareous material, typically limestone, with an argillaceous one, typically clay or shale. Both constituents contain impurity elements at trace levels. For example, the stable isotope concentration of selected safety-relevant radionuclides in hardened cement paste, which was prepared from a sulfate-resisting Portland cement (Haute Teneur en Silice (HTS) cement, Lafarge, France), is listed in Table 1. HTS cement has been used to solidify and stabilize low- and intermediate-level waste in Switzerland.

Table 1: Stable isotope concentrations of hydrated HTS cement

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CONCENTRATION [ppm]</th>
<th>UNCERTAINTY [ppm]</th>
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<tbody>
<tr>
<td>Sr</td>
<td>1290</td>
<td>±146</td>
</tr>
<tr>
<td>Pb</td>
<td>38.5</td>
<td>±10.3</td>
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<tr>
<td>Ni</td>
<td>19.9</td>
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</tr>
<tr>
<td>Co</td>
<td>1.0</td>
<td>±0.42</td>
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In the large body of existing sorption studies conducted on cementitious systems, solution compositions are given, if at all, only in terms of the main parameters and components, e.g., pH and the concentrations of cement-derived elements such as Na, K, Ca, Al, Mg, Si and S. Information on the inventories of trace elements in solution is almost always lacking. Nevertheless, it is to be noted that in sorption studies, the concentrations of radioisotopes added to the cement systems may often be orders of magnitude less than the concentrations of the corresponding trace element already dissolved in the pore water. Furthermore, lack of information on trace element inventories gives rise to uncertainties concerning the nature of the uptake processes. In particular, stable isotope concentrations are relevant in connection with solubility limits, which are fixed according to the total concentration of an element (stable and unstable isotopes) rather than the concentration of the radioisotope alone.

The importance of stable isotope inventories for understanding the immobilization processes of Cs, Sr, Ni and Pb in cementitious systems will be discussed in the present study. An experimental approach will be outlined which allows the partitioning of the radionuclides between hardened cement paste (HCP) and cement pore water (CPW) to be assessed and associated distribution ratios \(R_d\) values to be deduced. The approach is based on mass balance considerations for the above-mentioned elements in cement systems. Experimentally, the concentration of the element of interest in CPW is determined as a function of the solid to liquid (S/L) ratio. A schematic presentation of typical features of the expected concentration profiles is shown in Figure 1. \(R_d\) values for the stable isotope fractions can be deduced from the resultant concentration profiles. The \(R_d\) values can then be compared with \(R_d\) values obtained from in-house uptake studies using radiotracers or reported in the open literature, respectively, i.e., \(R_d\) values for \(^{137}\text{Cs}, ^{85}\text{Sr}, ^{63}\text{Ni}\) and \(^{210}\text{Pb}\) (see review in [1]). The results show that the total inventories of Cs, Sr and Pb are accessible to isotopic exchange, which is indicated by the good agreement of the \(R_d\) values obtained from the concentration profiles of stable isotope and radiotracer experiments. In the case of Ni, however, the concentration in CPW was found to be almost constant, ranging from \(\sim 5 \times 10^{-8}\) M to \(\sim 2 \times 10^{-7}\) M, irrespective of the S/L ratio of the cement system. Furthermore, the measured concentration profile could not be interpreted in terms of a reversible adsorption-type process without assuming unrealistically high sorption values for Ni. This finding suggests that a solubility-limiting process controls the partitioning of stable Ni in cement systems rather than a sorption-type process. Solubility limitation can account for the constant aqueous Ni concentrations determined in these experiments. An earlier X-ray absorption spectroscopy (XAS) study on the formation of Ni precipitates in cement systems further substantiates this finding [2]. The study indicates that mixed Ni-Al layered double hydroxides (LDH) may form in cement systems, which can be regarded as the solid phases being potentially present in the waste matrix and governing Ni uptake.
Figure 1: Schematic view showing the dependence of the concentration of an element in CPW on the solid to liquid (S/L) ratio of the cement system for a typical range of distribution ratios ($R_d$ values) [1]. The $R_d$ value describing the partitioning of the element between HCP and CPW determines the shape of the concentration profile. Arbitrary scales are chosen. Absolute values depend on the initial concentrations of an element in HCP and CPW.

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References


FUNCTIONALIZED IONIC LIQUIDS: NEW AGENTS FOR THE
EXTRACTION OF ACTINIDES/LANTHANIDES

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Room-Temperature Ionic liquids (RTILs) are promising solvent alternatives in organic
synthesis, catalysis, electrochemistry and separation processes [1,2]. They appear as
interesting media for the elaboration of separation processes in the nuclear fuel cycle.
However, the partitioning of metallic species in liquid-liquid extraction is largely limited by
the low complexation properties of the hydrophobic ionic liquids: in general,
hydrophobic RTILs are non-coordinating, and the highly hydrated metal ions remain in
the aqueous phase [3].

Several attempts have been made to enhance the affinity of metal ions towards the IL
phase. For example, the addition of organic coordinating compounds increases
significantly the distribution ratios of metal ions between the ionic liquid and the aqueous
phase [4,5].

Partitioning of metal ions can be achieved by grafting complexing moieties on the
organic cation of the IL. This approach may minimize leaching of the extracting
compound to the aqueous phase. Furthermore, various functions can be grafted on the
RTIL, giving rise to task-specific ionic liquids (TSILs) which allow a selective separation
of targeted metal ions.

We focused on the synthesis of functionalized ionic liquids for the partitioning of
actinides and lanthanides. Our contribution describes the synthesis of functional ionic
compounds bearing different types of metal complexing groups (β-diketones, 2-hydroxy-
benzylamines and malonamides) (figure 1) and their utilization in liquid-liquid extraction
processes.

Our results show that grafting metal complexing groups increases the affinity of metals to
the IL phase and gives rise to suitable media for the liquid-liquid extraction of actinides.

First results of extraction of Am3+ with these TSIL will be presented (Figures 2 and 3)
and mechanisms of metal ion partitioning will be discussed.

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Fig 1: Examples of functionalized Ionic Liquids

Fig 2: Distribution ratios for Am$^{3+}$ with increasing concentration of 2-hydroxy-benzylamine in BmimPF$_6$ at aqueous pH 3
Fig 3: Distribution ratios for Am$^{3+}$ with 2-hydroxy-benzylamine as a function of aqueous-phase pH

References

Sustainable development of nuclear power is one of the basic strategies of electricity and heat production in the Czech Republic and in the future it will be advantageous to use advanced nuclear reactor types. One of these systems represented by the Molten Salt Reactor (MSR) is attractive due to its possibility to be used both for the generation of electricity and heat and for transmutation of transuranium elements and long-lived fission products. The Czech national programme in the area of partitioning and transmutation (P&T) is based on the development of fuel cycle technologies of the Molten Salt Transmutation Reactors (MSTR) connected with pyrochemical reprocessing of liquid fuel composed of molten salts. The MSRs with “on-line” pyrochemical reprocessing of the fuel could also work under the thorium – uranium fuel cycle with minimized production of long-lived radioactive wastes. There are two pyrochemical techniques developed in the Czech Republic for partitioning of the spent nuclear fuel. The first technology called Fluoride Volatility Method is intended above all for primary reprocessing of spent fuel from PWR. Main part of uranium should be removed as uranium hexafluoride by the process of flame fluorination and the oxidic form of the PWR spent fuel is simultaneously transformed into the fluoride form. Molten fluorides were selected to be the medium used for study of the following partitioning process – electrochemical separation, which is the other developed technique. This technique is planned to be utilize both as the final process of transuranium molten salt fuel preparation and the “on-line” purification of circulating liquid fuel in the MSR primary fuel circuit (Fig. 1).
This paper describes a study dealing with electrochemical separation of the lanthanides from actinides in molten fluorides. The work was focused on determination of the exploitable potential range of the used fluoride melt and the deposition potentials of the selected actinides and lanthanides by the Linear Sweep Cyclic Voltammetry Method. Electrochemical behaviour of uranium, thorium, neodymium, gadolinium and europium was investigated in molten eutectic mixture of LiF-NaF-KF at 530°C under inert atmosphere of highly pure argon. Measured voltammograms for uranium and for neodymium and gadolinium can be seen in Fig. 2 and Fig. 3, respectively.

![Fig. 2 Voltammogram of system FLINAK – UF₆ (1.0 mol. %) on Mo working electrode, scan rate 50 mV/s](image)

![Fig. 3 Voltammograms of systems FLINAK – NdF₃ (blue line) and FLINAK – GdF₃ (red line) on Mo working electrode, scan rate 50 mV/s](image)
The technical background for measurement is described including complete electrochemical set-up with specially designed nickel electrolyser, reference electrode and conditioning of used chemicals during carrier melt preparation. The reference electrode enabling measurements in molten fluoride media is based on Ni/Ni$^{2+}$ red-ox couple, it was originally designed and constructed and its electrochemical stability was verified during short-term experiments. Based on the reached results (Tab. 1), separation possibilities of studied elements in this medium were assessed and applicability of the electroseparation method within the proposed MSTR technology is described.

Tab. 1 Summary of experimentally determined red-ox potentials vs. used Ni/Ni$^{2+}$ reference electrode in the melt FLINAK at the temperature 530°C

<table>
<thead>
<tr>
<th>Red-ox couple</th>
<th>U$^{3+}$/U$^0$</th>
<th>U$^{4+}$/U$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E [V]</td>
<td>-1.75</td>
<td>-1.20</td>
</tr>
<tr>
<td>Red-ox couple</td>
<td>U$^{3+}$/U$^{2+}$</td>
<td>U$^{4+}$/U$^{3+}$</td>
</tr>
<tr>
<td>E [V]</td>
<td>0.40</td>
<td>1.40</td>
</tr>
<tr>
<td>Red-ox couple</td>
<td>Th$^{3+}$/Th$^{2+}$</td>
<td>Th$^{4+}$/Th$^{3+}$</td>
</tr>
<tr>
<td>E [V]</td>
<td>~ -2.00</td>
<td>-0.65</td>
</tr>
<tr>
<td>Red-ox couple</td>
<td>Nd$^{3+}$/Nd$^{4+}$</td>
<td>Nd$^{4+}$/Nd$^{3+}$</td>
</tr>
<tr>
<td>E [V]</td>
<td>&lt; -2.05</td>
<td>~ -1.00</td>
</tr>
<tr>
<td>Red-ox couple</td>
<td>Gd$^{3+}$/Gd$^{4+}$</td>
<td>Gd$^{4+}$/Gd$^{3+}$</td>
</tr>
<tr>
<td>E [V]</td>
<td>&lt; -2.05</td>
<td>~ -0.90</td>
</tr>
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X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY
INVESTIGATIONS OF THE STRUCTURE OF Cm(III)/Eu(III)
COMPLEXED WITH D(Chlorophenyl)DITHIOPHOSPHINIC
ACID AND DIFFERENT SYNERGISTIC AGENTS

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Introduction

Partitioning is proposed to be used in nuclear waste management to isolate long-lived radionuclides from waste produced by nuclear fuel reprocessing for later transmutation to shorter lived nuclides in specially designed reactors or for their conditioning and immobilisation into special matrices for disposal [1]. Synergistic mixtures of di(chlorophenyl)dithiophosphinic acid ((CIPh)2PSSH) and neutral O-bearing extractants such as tri-n-octylphosphine oxide (TOPO), tributylphosphate (TBP) and tris(2-ethylhexyl)phosphate (T2EHP) are promising candidates for separation of the minor actinides americium and curium. The (CIPh)2PSSH-synergetic systems selectively extract trivalent actinides over trivalent lanthanides from up to 1 M nitric acid [2]. A comparative EXAFS study of the coordination structures of Cm(III) and Eu(III) complexes with (CIPh)2PSSH and different neutral organophosphorus synergetic compounds was performed. The goal of this study was to ascertain if there is a structural origin for the observed high selectivity for trivalent actinides. Specifically, Cm and Eu L3 EXAFS data were analyzed to obtain metric parameters describing the structure of the complexes and the coordination sphere of the Cm(III) and Eu(III) metal cations.

Methods and materials

Curium samples were prepared by extracting an aqueous solution of 5 mmol/L (1.23 mg/mL) Cm-248 in 0.01 M HNO₃ into 0.5 M (CIPh)2PSSH and different synergistic compounds, TOPO, TBP or T2EHP (0.25 M), dissolved in tert-butylbenzene. Europium samples were prepared by extracting an aqueous solution of 20 mmol/L Eu(III) in 0.01 M HNO₃ into 0.5 M (CIPh)2PSSH, containing TOPO or TBP (0.25 M), dissolved in tert-butylbenzene.

EXAFS measurements were performed at the BESSRC beamline 12BM (APS, Argonne National Lab), using Si(111) crystals in the double-crystal monochromator. The samples were measured contained in sealed polyethylene vials, mounted in the Actinide Facility’s sample changer, in fluorescence mode using a Canberra LEGe 13-element solid state detector. The EXAFS was extracted using standard procedures. Theoretical least squares fits to the EXAFS were performed in R-space to obtain the metric parameters for the different coordination shells (i): coordination numbers (Nᵢ), interatomic distances (Rᵢ), mean square radial displacements or EXAFS Debye-Waller factors (σ²ᵢ) and relative shifts in ionization potential (ΔE₀). The amplitude reduction factor S₀² was fixed at 1. Single scattering phase shift and backscattering amplitude functions are calculated with feff8 [3].
Results

The $k^2$-weighted Cm and Eu L3 EXAFS for the (CIPh)$_2$PSSH-synergist extracted complexes and their corresponding Fourier transform (FT) data are compared in Fig. 1. The corresponding results of fits of the Cm data are given in Table 1. Comparison of the spectra with one another shows the Cm spectra are significantly different than their Eu counterparts.

![Graphs showing EXAFS and FT data for Cm and Eu](image_url)

Fig. 1: $k^2$-weighted L3 edge EXAFS (left) of the (CIPh)$_2$PSSH-synergist extracted Cm$^{3+}$ (top) and Eu$^{3+}$ (bottom) complexes and their corresponding Fourier transform (FT) data (right). The different synergist compounds used are indicated.

Table 1. Metric parameters obtained from fits to the Cm L3 edge R-space data in Fig. 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R [Å]</th>
<th>$\sigma^2$ [Å$^2$]</th>
<th>$\Delta E_a$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm$^{3+}$ aquo ion</td>
<td>O</td>
<td>8.7</td>
<td>2.47</td>
<td>0.0103</td>
<td>1.6</td>
</tr>
<tr>
<td>Cm-(CIPh)$_2$PSSH -TOPO</td>
<td>O</td>
<td>2.4</td>
<td>2.32</td>
<td>0.004</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>4.5</td>
<td>2.92</td>
<td>0.011</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>2.6</td>
<td>3.57</td>
<td>0.004</td>
<td>7.3</td>
</tr>
<tr>
<td>Cm-(CIPh)$_2$PSSH -TBP</td>
<td>O</td>
<td>2.9</td>
<td>2.34</td>
<td>0.004</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>3.0</td>
<td>2.96</td>
<td>0.011</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>1.5</td>
<td>3.60</td>
<td>0.002</td>
<td>10.6</td>
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<tr>
<td>Cm-(CIPh)$_2$PSSH -T2EHP</td>
<td>O</td>
<td>1.6</td>
<td>2.34</td>
<td>0.002</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>4.8</td>
<td>2.93</td>
<td>0.010</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>4.7</td>
<td>3.58</td>
<td>0.008</td>
<td>4.1</td>
</tr>
</tbody>
</table>
The amplitude differences cannot solely be explained by differences in their backscattering amplitude functions. This means that the Cm and Eu complexes have different coordination structures. Furthermore, we find that both metal cations have oxygen, sulfur and phosphorous nearest neighbors. However, visual inspection of the spectra show them to differ in the intensities for each of these coordination shells.

Discussion

From the observed short curium-oxygen bond distance in the extracted complexes, we conclude that the cation is directly coordinated by the oxygen of synergist molecules. The Cm-O distance in the Cm complex is approx. 0.15 Å shorter than the Cm-O distance observed in the Cm$^{+}$ aquo ion. This is experimental evidence for theoretical results reported in [4], which propose coordination of both dithiophosphinate and synergist molecules in the inner sphere of the metal cation. Comparison of the Cm-S and Cm-P distances with those reported by Jensen et al. [5] indicates bidentate complexation of Cm by (ClP)$_2$PSSH. General trends in the different FT intensity ratios of the S (near 2.5 Å) and O (near 1.8 Å) peaks in Fig. 1 and N(S)/N(O) from the results in Table 1 is observed. We find upon comparing spectra for Cm and Eu samples extracted with the same synergist that the S/O intensity ratio is always higher for Cm. We also observe the S/O intensity ratio and N(S)/N(O) values decrease in the order T2EHP > TOPO > TBP for spectra of Cm samples with different synergists and TOPO > TBP for Eu sample spectra. We draw two conclusions from these observed trends: 1) The Cm and Eu complexes have different coordination spheres. Curium is more favorably complexed by sulfur and less favorably by oxygen of the synergist. We suggest that this leads to more covalency in the bonds of the curium complex and this is probably the reason for the selectivity. 2) A high separation factor (SF) between An(III) and Ln(III) seems to be generally correlated with a high S/O intensity ratio in the EXAFS spectra. $SF_{Cm/An}$ is in the range of 100 when using T2EHP as synergist, whereas it is near 10 for TOPO and TBP. Coordination numbers listed in Table 1 are 6-7. These are lower than the expected values of approx. 9. We believe that destructive interference due to small distortions in the coordination structure (i.e., a spread of bond lengths) is the reason for the relatively low coordination numbers observed. Further study is needed to check this hypothesis.

Acknowledgments

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References

FIRST DEMONSTRATION OF MA RECOVERY FROM GENUINE HIGH ACTIVE CONCENTRATE

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Waste management and waste minimisation are of primary importance regarding the future use of nuclear energy. As a promising waste management option partitioning and transmutation (P&T) offers the possibility to reduce the long-term radioactivity of nuclear waste. Essential for successful P&T scenarios is the efficient recycling of the radiotoxic higher actinides (Np, Pu, Am, Cm) in dedicated reactors in which they are transmuted to shorter-lived and less radiotoxic isotopes.

Today, U and Pu are industrially reprocessed in the well-established PUREX process, which can be adapted to include also Np recycling. However, the minor actinides (MA), Am and Cm, are not separated and form together with fission products the high level waste fraction of the PUREX process, the so-called High Active Raffinate (HAR). The present HAR waste management is based on vitrification in a borosilicate glass matrix for final storage. In view of P&T, several extraction processes have been developed world wide for the separation and recovery of Am and Cm from HAR. One of the most promising is the French DIAMEX process, currently further developed in European collaborations, which uses diamides in an organic diluent as solvent. Besides the excellent extraction capabilities, the adaptation to the PUREX process is quite easy and the solvent is completely combustible and yields therefore no solid secondary residues. The combined PUREX - DIAMEX process has previously been successfully demonstrated [1, 2, 3] using genuine HAR fuel solutions. In view of a process industrialisation, the next step has been the development of a DIAMEX process for the recovery of minor actinides from concentrated HAR solutions, the so-called high active concentrate (HAC). The main advantage is the volume reduction – up to 10 times is conceivable - which reduces waste volumes, makes an industrial process more compact and thereby more economic.

In order to produce a representative HAC, a concentration-denitrification process was applied to a HAR solution produced by small scale PUREX reprocessing of a MOX fuel solution. The fuel solution originated from the dissolution of about 1.8 Kg of irradiated MOX fuel (33 GWd/HM). In the concentration step the volume was reduced by evaporation followed by a denitrification step, using concentrated formic acid, in order to reduce the acidity to adjust the HAC solution for the following extraction process. As the high metal concentrations increase the risk of MA co-precipitation, the process of concentration and denitrification had thus to be optimised. Several experiments using simulated HAR solutions confirmed that a concentration factor (CF) of 10 could be reached. At this concentration level precipitation of lanthanides, which are expected to behave as minor actinides, was less than 0.1 %. These
positive results led to a successful hot concentration/dentration test, in which 0.4 litres of HAC, having a CF of 10 and an acidity of 4 M, was produced from more than 4 litres of HAR. The precipitate formed was mainly composed of Sr, Zr, Mo, Sn and Ba. Losses of MA due to precipitation was less than 0.001 % of the total amount of MA originally present in the HAR solution.

In parallel, experimental conditions to carry out the hot DIAMEX-HAC test in centrifugal extractors were established based on results coming from batch extraction experiments using simulated and genuine HAC solutions. From these results an optimised flow-sheet could be calculated, which was tried out in a full centrifugal test (16 extractors) using a simulated HAC solution spiked with MA tracers. This test was very successful and indicated decontamination factors well above 10³ and recoveries for MA and Ln in the range of 99.99 %. One important result was that the acidity of the strip solution needed to be increased from originally 0.1 M to 0.3 M HNO₃ in order to avoid entrainment of aqueous phase in the outgoing organic fraction. Based on these experiences the hot DIAMEX experiment could finally be carried out in a 16-stage centrifugal extractor battery, installed in the hot cell facilities at ITU. The flow sheet is shown in Fig. 1. The 16 centrifugal contactors used were divided into 5 stages for extraction, 7 stages for scrubbing and 4 stages for back-extraction. Before the experiment the feed concentrations of oxalic acid and HEDTA were optimised and properly adjusted to avoid precipitation of Zr, Mo and Pd.

![Flow sheet for DIAMEX-HAC experiment](image)

Figure 1. The flowsheet used for the “hot” DIAMEX-HAC experiment.

Fig. 2 shows the aqueous concentration profiles at steady state conditions obtained for the most relevant elements. Up to 5 extraction stages were sufficient to efficiently extract (>99.9%) MA’s and lanthanides (represented by La). The back extraction proved to be very efficient, yielding in 4 stages recoveries for Am and Cm in the Ln/An effluent above 99.7 and 99.9 % respectively. The addition of oxalic acid and HEDTA efficiently prevented co-extraction of Mo, Zr and Pd, which are normally strongly extracted in the DIAMEX system.

Table 1 shows the feed decontamination factors (DF) and the fraction recovered in the raffinate and An/Ln fractions. The DF is defined as the element concentration ratio between the feed and the raffinate and is therefore a measure how well an element has been extracted. Also tabulated is the recovery of some representative elements in the raffinate and in the An/Ln fractions.

DF values were for the most abundant Ln > 5000, for Am > 20000 and for Cm > 10000, which shows the efficiency of DIAMEX process for MA extraction. Most fission products were not extracted, the exception being Tc which has a DF = 217, Y a DF = 85 and Ru a DF = 1.1. In spite of the increased strip solution acidity, the back-extraction proved to be very efficient and yielded high recoveries for all the trivalent actinides, lanthanides and yttrium. Only 0.3 % of the An and less than 0.1 % of the Ln were found in the organic solvent. Even better results can be achieved by process optimisation, e.g. increasing the number of stages in the stripping section.
Figure 2. Aqueous concentration profiles of some relevant elements during the “hot” DIAMEX-HAC process.

In order to reach a significant reduction in the radiotoxicity potential of waste repositories, it is generally defined, that P&T scenarios should reach recoveries of MA around 99.9%. This target was reached in the present very successful experiment. We consider that this work is a major contribution in the field of partitioning and an important step towards the industrial implementation of MA partitioning.

<table>
<thead>
<tr>
<th>Element</th>
<th>DF</th>
<th>Recoveries from the feed (%)</th>
<th>Raffinate fraction</th>
<th>An/Ln fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>85</td>
<td>1.2</td>
<td>98.8</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>&gt; 99.99</td>
<td>&lt; 0.01</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>99.3</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>217</td>
<td>&lt; 0.01</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>1.1</td>
<td>92</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>1</td>
<td>98.8</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Ln</td>
<td>&gt;5000</td>
<td>&lt; 0.1</td>
<td>&gt; 99.9</td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>50</td>
<td>2</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>20000</td>
<td>0.005</td>
<td>99.7</td>
<td></td>
</tr>
<tr>
<td>Cm</td>
<td>10000</td>
<td>0.01</td>
<td>99.9</td>
<td></td>
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SELECTIVE REMOVAL OF URANIUM AND EVALUATION OF N,N,N',N' TETRA OCTYL DIGLYCOLAMIDE (TODGA) FOR ACTINIDE-PARTITIONING FROM HIGH-LEVEL WASTE (HLW)

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Management of radioactive high-level waste (HLW) generated during the reprocessing of spent nuclear fuel is a challenging task in view of its radiotoxicity, acidity and presence of long-lived radionuclides such as unextracted $^{238}$U, $^{237}$Pu, minor actinides (viz. $^{237}$Np, $^{241}$Am and $^{243}$Cm), fission products, structural materials, and activation products. The nature of HLW largely depends on (i) off-reactor cooling of spent nuclear fuel, (ii) type and burn up of fuel, (iii) process efficiency during reprocessing and (iv) concentration factor for conversion of High Active Waste (HAW) to HLW. The development of suitable extractants for actinide-partitioning from HLW is one of the challenging areas of research for separation chemists. Two main processes developed for this purpose viz. TRUEX and DIAMEX are based on the use of CMPO (Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide) and DMDBTDMA (N,N,N',N' dimethyldibutyltetradeyl malonamide respectively [1,2]. The diamides have advantages of complete incinerability and innocuous nature of chemical / radiolytic degradation products. Continuous efforts are being made to modify the diamide structure to improve the extractability in general and trivalent metal ions in particular. A tridentate ligand, tetroctyl diglycolamide (TODGA) has been proposed as a potential extractant of actinides from nitric acid medium (Fig.1) [3,4]. However, it exhibits a third phase formation tendency under high metal loading conditions prevalent in high-level waste. Though the $D_{Am}$ is quite high (~300 at 3M HNO$_3$) for 0.1M TODGA/n-dodecane; the limiting organic concentration (LOC) for Nd is quite low (~0.008M Nd at 3 M HNO$_3$). It is, therefore, desirable to look for suitable phase modifiers.

In the present paper, an attempt has been to optimise the conditions for the selective extraction of U over Pu, Np, Am and fission products from Simulated High-Level Waste (SHLW) employing TBP as extractant. Reductants such as hydroxylamine nitrate (HAN), N,N-diethyl hydroxyamine nitrate (DEHAN) and hydrazine nitrate (HN) were evaluated in the present work as they are incinerable and may help in waste volume reduction. The SHLW solution was prepared by taking only those ions, which were present in significant concentration after the reprocessing of Al-clad natural uranium research reactor spent fuel [5].

A systematic attempt has been made to evaluate various dialkyl amides viz. dibutyl decanamide (DBDA), dif(2-ethylhexyl) acetamide (D2EHAAC), dif(2-ethylhexyl) propionamide (D2EHPRA) and dif(2-ethylhexyl) isobutynamide (D2EHBIA) as phase modifiers during Nd(III) extraction. Extraction behaviour of various metal ions has been investigated at varying acidities under simulated high-level waste (SHLW) condition. Whereas dialkyl amides were synthesised in our
laboratory, TODGA was synthesised in the laboratory of Prof. V. S. Parmar at Chemistry Department, University of Delhi, INDIA under DAE-BRNS Project (2000/37/4/BRNS).

For selective extraction of U(VI) over Pu, their extraction behaviour was studied at 1 and 2M HNO₃ in the presence of a synthetic waste using 30% TBP as extractant. Dₚ and Dₚ₃ values were 19.8, 4.0 (1M HNO₃) and 19.4, 8.0 (2 M HNO₃) respectively. Dₚ₃ during extraction under the simulated HLW conditions at 1M HNO₃ was 0.52. To back extract co-extracted Pu and Np towards the aqueous raffinate, keeping U in the extracted organic phase, scrubbing step was introduced. Table 1 lists the distribution ratio data for Pu during scrubbing step (at 0.5/1M HNO₃) using 30% TBP solution pre-equilibrated with SHLW at 1M HNO₃.

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<tr>
<th>Reductant</th>
<th>Dₚ₃</th>
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<tr>
<td>0.3M HAN</td>
<td>0.11 (0.08)</td>
</tr>
<tr>
<td>0.6M HAN</td>
<td>0.09</td>
</tr>
<tr>
<td>0.3M HAN + 0.2M HN</td>
<td>0.10</td>
</tr>
<tr>
<td>0.6M HAN + 0.2M HN</td>
<td>0.11</td>
</tr>
<tr>
<td>0.3M DEHAN</td>
<td>0.06 (0.02)</td>
</tr>
<tr>
<td>0.5M DEHAN</td>
<td>0.042 (0.01)</td>
</tr>
<tr>
<td>0.8M DEHAN</td>
<td>0.029</td>
</tr>
<tr>
<td>1.0M DEHAN</td>
<td>0.02</td>
</tr>
</tbody>
</table>

(Values in bracket refer to 0.5M HNO₃)

There was a gradual decrease in Dₚ₃ value with increase in DEHAN concentration [0.06 (0.3M) to 0.02 (1M) at 1M HNO₃]. At 0.5 M HNO₃, even 0.3 M DEHAN was found to be effective for the scrubbing of Pu (Dₚ₃: 0.02). Distribution ratio values for uranium (Dₚ₃) under scrubbing conditions at 0.5M HNO₃ and 1M HNO₃ were 7 and 10 respectively suggesting little uranium loss towards the aqueous raffinate. Np distribution ratio under the scrubbing condition (1M DEHAN at 1M HNO₃) was 0.01. Based on these studies, the proposed scrubbing solution is 1.0M DEHAN at 1M HNO₃.

N, N dialkyl amides with varying alkyl groups and chain lengths viz. dibutyl decanamide (DBDA), di(2-ethylhexyl) acetamide (D2EHAAC), di(2-ethylhexyl) propionamide (D2EHPRA), di(2-ethylhexyl) isobutyramide (D2EHIBA), dihexyl octanamide (DHOA) and dihexyl decanamide (DHDA) were evaluated as phase modifiers. At 5M HNO₃, for 0.1M TODGA + 0.5 M Amide / n-dodecane solution, the Dₐm values varied in the following order: D2EHAA (12.9) > DHOA (10.7) > DBDA (7.5) > DHDA (7.0) > D2EHPRA (6.5) > D2EHIBA (6.0). In view of higher Dₐm value, Nd loading studies (Initial Nd concentration: 0.02M-0.1M) were carried out employing 0.1M TODGA + 0.5M D2EHAA / n-dodecane solution and compared with that of 0.1M TODGA + 0.5M DHOA mixture. Fig.2 clearly shows that only 0.03M Nd could be loaded in the case of former; the corresponding loading in the case of latter was 0.035M Nd. During the Nd loading experiments, Dₐm values decreased from 2.13 to 0.42 for D2EHAA and from 3.0 to 0.54 for DHOA. Further studies were, therefore, carried out employing 0.5M DHOA as the phase modifier. Nitric acid uptake studies by TODGA suggested...
the formation of 1:1 adduct (as predominant species) and it was found more basic as compare to TRUEX and DIAMEX solvents viz. CMPO ($K_{H} = 2.0$) and DMDBTMDA ($K_{H} = 0.32$) respectively. Figs.3 and 4 show the distribution behaviour of various metal ions viz. Am(III), U(VI), Pu(IV), Fe(III), Eu(III), Sr(I) and Cs(I) as a function of acidity in absence as well as in presence of PHWR-SHLW [4]. There was a gradual increase in distribution ratio value of metal ions ($D_{M}$) viz. Am(III), Pu(IV), U(VI), Eu(III) with aqueous phase acidity up to 2M HNO$_3$ beyond which saturation behaviour was observed. In the presence of SHLW, the $D_{M}$ values were lower at all acidities as compared to those for pure tracers, which was attributed to the co-extraction of other metal ions present in SHLW. There was no significant extraction of Fe(III) and Cs(I) under both conditions ($D$: $\approx 10^{-5}$). Typically in presence of SHLW at 3M HNO$_3$, $D_{M}$ values for Am(III), Pu(IV), U(VI), Eu(III) and Sr(II) were 62, 6.2, 110, 96 and 0.08 respectively.

![Graph 1: Variation of $D_{M}$ with aqueous phase acidity](image1)

**Fig. 3:** Variation of $D_{M}$ with aqueous phase acidity
Extractant: 0.1M TODGA+0.5 DHOA in n-dodecane

![Graph 2: $D_{M}$ as the function of acidity from SHLW](image2)

**Fig. 4:** $D_{M}$ as the function of acidity from SHLW
Extractant: 0.1M TODGA+0.5 DHOA in n-dodecane
Temperature: 25°C

In conclusion, DEHAN has been identified as a suitable reductant for Pu and Np during selective removal of uranium from SHLW solution. Either 0.5 M DEHAN at 0.5 M HNO$_3$ or 1.0M DEHAN at 1M HNO$_3$ could be used as the scrubbing solution for Pu. DHOA can be used as a phase modifier during actinide partitioning employing TODGA as the extractant.

**REFERENCES**

NEW OPTIONS FOR TREATMENT OF ORGANIC COMPLEXANTS CONTAINING LIQUID RADIOACTIVE WASTE

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Introduction
Technologies for processing of the majority of large amounts of standard operational radioactive waste from such facilities as nuclear power plants (NPPs) and other nuclear fuel cycle facilities are well established and are regarded as technologically mature. However, many specific and even some routine waste streams still exist, which can be considered as "problematic". Among others, this includes waste containing different organic components. As the most typical examples of such wastes, namely NPP spent decontamination solutions and evaporator concentrates can be listed; usually, they contain the oxalic (HOx) and citric (HCit) acids. For treating such complex waste formulations, combined processes in more stages have been recently suggested to offer the most promising solutions [1]. At the CTU in Prague, significant research efforts have been devoted recently to development of new options for treatment of both the spent decontamination solutions and evaporator concentrates [2-4]. In this study, direct separation of radionuclides from the waste or a combination of organic complexants degradation followed by the radionuclides separation has been investigated. Inorganic-organic composite absorbers with a binding matrix of modified polyacrylonitrile [5] were used for radionuclidic contaminants separations. For the organic complexants degradation, heterogeneously catalysed photochemical degradation by ultraviolet radiation, gamma-ray radiolysis or degradation by the action of peroxodisulphate were considered.

Spent AP-CITROX decontamination solution
This study was performed with both model solutions and a real spent acidic decontamination solution from the AP-CITROX process. This solution was generated during the steam generator decontamination in NPP Dukovany, Czech Republic, it contained 8.2 g/L of HOx, 10 g/L of HCit and 1.1·10⁻² g/L of Fe.

A screening study of direct separation of radionuclides from this solution was performed with nine inorganic absorbers at the original pH of the solution (pH ~ 1.4), and at pH = 3.6 or pH = 7.0. The main conclusion of this study was that direct separation of radionuclides is not feasible even after the pH adjustment. In addition to the insufficient values of distribution coefficients, limited chemical stability of some of the potentially prospective absorbers in the solutions can be listed among the main reasons for such conclusion.

A study of the photocatalytic degradation of organic complexants was performed in a small immersion well photochemical reactor with a 6W low-pressure mercury lamp (wavelength 254 nm). Titanium dioxide (TiO₂-M) was used as a photocatalyst. The results obtained showed that the process was strongly influenced by the experimental parameters such as amount of photocatalyst, temperature, aeration rate (vₐ), or additions of H₂O₂. It was found that in optimum conditions (3.15 g TiO₂-M/L, T = 45°C, vₐ = 50 L/hr, 1 mL of H₂O₂ each 2 hours), all the oxalic and citric acids were quantitatively degraded within 12 hours.
In a study of separation of radionuclides from the solution, where HOx and HClt were completely decomposed by means of photocatalysis, both batch and dynamic sorption experiments were performed. The absorbers studied were the same as those tested for direct separation of radionuclides from the original solution. Batch experiments showed that the most prospective absorbers were zirconium phosphate or sodium titanate.

Two composite absorbers NaTiO-PAN/SF and ZrP-PAN/SF, containing the sodium titanate and zirconium phosphate, respectively, as active components, were prepared for the dynamic sorption study. The experiments demonstrated that all the radionuclides started to brake through the columns almost simultaneously. The NaTiO-PAN/SF absorber was found to be more effective, the maximum achievable concentration factor did not exceed 100. Another experiment, performed with a standard strongly acidic cation exchanger, revealed that the sorption cycle of such absorber is significantly longer. Practical concentration factors of several hundred to one thousand should be achievable with this material.

**Spent electrochemical decontamination solutions**

This study was performed with a model solution simulating the real spent electrochemical decontamination solution. The solution was prepared by electrolysing 10 g/L of HOx and 5 g/L of HClt solution in the electrolyser made of the NPP primary circuit equipment steel. The same conditions as in the operational electrochemical decontamination were used (current density 130 mA/cm² of the anode surface, total charge per volume unit of electrolyte 44 C/mL and the ratio between the volume of electrolyte and the decontaminated area ~ 31.5 mL/cm²).

A screening study of direct separation of radionuclides from this solution, performed in a similar way as described above for the AP-CITROX solution, yielded also similar results. The main conclusion was that direct separation of radionuclides is not feasible from this solution, either. Contrary to the experiments with AP-CITROX solution, the chemical stability of most of the absorbers tested was relatively good, however, the KD values measured for the majority of radionuclides of interest were generally low (mean log KD < 2).

A study of the photocatalytic degradation of organic complexes, performed in a similar way as described above for the AP-CITROX solution, revealed that the degradation of both HOx and HClt proceeds faster in this solution. This effect was confirmed to be a consequence of a different mechanism of the reaction – in the presence of relatively high concentration of iron, Fenton-like reactions take place under UV irradiation of a system containing semiconductor photocatalyst. Under the optimised conditions (3.15 g TiO₂·M/L, T = 22°C, v₀ = 50 L/hr, 1 mL of H₂O₂ each 2 hours), all the oxalic and citric acids were quantitatively degraded within 4 or 10 hours, respectively.

Again, a study of separation of radionuclides from the solution, where HOx and HClt were completely decomposed by means of photocatalysis was performed. The absorbers tested behaved similarly as described above for the AP-CITROX solution. However, the distribution coefficients of the radionuclides of interest measured for the best performing materials were about 3 to 8 times lower in the electrochemical decontamination solution. Based on the distribution coefficients for ⁵⁴Mn, ⁵⁹Fe, and ⁶⁰Co, the Na–Y absorber (synthetic zeolite) was chosen for the dynamic experiments.

NaY–PAN/SF composite absorber was prepared for the dynamic sorption study. Similarly to the results obtained for the AP-CITROX solution, the maximum achievable concentration factor was found to be about 100. In a parallel experiment, performed with a standard strongly acidic cation exchanger, practical concentration factor of more than 200 was achieved.

Demonstration of the developed process, comprising photocatalytic degradation of organic complexes followed by the separation of the radionuclides onto a standard cation exchanger
OSTION KS806, was performed in NPP Jaslovské Bohunice, Slovakia. The data obtained with real hot solution were in full agreement with the above described results measured for model solutions. Hence practicability of the process was confirmed.

**NPP evaporator concentrate**

In addition to its much higher salinity, another main difference between the decontamination solutions and the evaporator concentrate is in its high pH. In such conditions, photocatalytic degradation of organic substances is not effective. Therefore, other options were tested.

In a study aimed at the degradation of organic complexants, efficiency of radiolysis ($^{60}$Co gamma radiation) and degradation by the action of peroxodisulphate was tested. The results showed that the radiolytic degradation of organic substances does not depend on pH of the solution. High concentration of salts was found to reduce the degradation of the complexants. Degradation by the action of peroxodisulphate was found to be more efficient. In the solutions of pure organic substances, both the citric and oxalic acids were completely decomposed in one hour under optimised conditions, similar results were obtained even for the simulated and real evaporator concentrate solution.

Direct selective separation of $^{137}$Cs and $^{85}$Sr radionuclides from the original non-treated evaporator concentrate was demonstrated to be achievable by a (TiO+FC212)-PAN composite absorber containing a mixture of titanium dioxide and potassium-cobalt hexacyanoferate as active components. Because of its unclear and complex speciation, separation of cobalt turned most complicated. A study of the influence of the degradation of organic substances on the efficiency of cobalt separation with 11 inorganic absorbers and charcoals was performed with the original concentrate and the concentrate treated by radiolysis (300 kGy). Sorption of cobalt from both the concentrates was the most effective on the samples of active carbon. The influence of the degradation of organic complexes of cobalt onto its separation was not clear, most probably because in saline alkaline solution the cobalt released from the complexes forms other neutral species, like hydroxycomplexes or pseudocolloids, which are not readily sorbed on ion-exchangers.

**Conclusions**

This study demonstrated the efficiency and applicability of a processes combining degradation of organic complexants with subsequent sorption separation of radionuclides for treatment of some organic complexants containing waste, e.g. spent decontamination solutions. The process developed is not effective for alkaline saline wastes such as NPP evaporator concentrates or Hanford-type waste. The prospective research directions seem to be waste minimisation by regeneration of the spent decontamination solution, and boric acid recycling from the evaporator concentrates and separate treatment of the residual solution with decreased salinity and pH.

**References**

TECHNOLOGICAL DEVELOPMENT FOR LIQUID RADIOACTIVE WASTE MANAGEMENT IN ORDER TO CEASE DISCHARGE INTO OPEN STORAGES

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The problem of low-level liquid waste management is very pressing among all radiochemical works since the basic amount of resulting radioactive waste accounts for this very category. In accordance with the process flowsheet now in operation, such waste is discharged and stored in open storages. During discussions on the safety of available techniques of radioactive waste management from the point of deep protection it has been discovered that the first protection level is not met during operation of open pond-storages, namely there are no physical barriers isolating waste from the environment. Radionuclides aerosol entrainment from the pond surface is possible more or less even during normal operation. Thus, in compliance with modern requirements for safety, open storages of liquid radioactive waste should be taken out of service.

At the Siberian Group of Chemical Enterprises (SGCE) the concept of low-level liquid waste management has been adopted in which the basic stages of work on open storages decommissioning and their further permanent closure are indicated. The primary task is to take out of service two open storages: pulp storages (PS 1,2) and then pool B-25. The existence of deep disposal sites has influenced the choice of this very technique as an alternative to the waste discharge into open storages PS-1,2 listed above.

The implementation of such variant demands research and development of a new process flowsheet which would provide fulfilling basic principles of the deep geological disposal technique. The basic postulate of this method is to create conditions of satisfactory compatibility for waste of a new composition with the bed material. The notion "compatibility" provides for absence of processes which substantially affect geochemical equilibria existing in the subsurface bed. Such processes as deposit formation and gasification can be related to these processes as well as considerable change of reductive-oxidative parameters etc. Another postulate of this deep geological disposal technique is to keep stability of rocks forming storage since these very rocks fulfill the role of a natural barrier which isolates waste from other aquifers.

As disposal sites long-term exploitation has shown, the compliance of conditions listed above provides for waste pumping satisfactory regime and safety parameters of their long-term localization in underground storage. However, a series of particularly economic requirements
exists for the process flowsheet. First of all, waste coming for preparation should be completely disposed, i.e. the share of secondary waste remaining on the surface must be minimum.

On basis of the results obtained during experimental investigation with the use of model systems and real liquid waste from SGCE, schemes of liquid waste mixing from SGCE plants, correlations of flows and standardized factors have been worked out. The conditions of liquid waste preparation, salt composition and several most reactive liquid waste components influence on reservoir bed rocks and processes of solid phases formation in pore space have been studied. These very rocks play the function of the basic barrier which localizes waste in a specified volume and isolates the storage from other aquifers. To keep rocks integrity when contacting waste is one of the requirements defining the safety conditions of the deep geological disposal technique.

It was found out that under alkaline environment (pH 8-10) and low temperatures (down to 20 °C) minerals under study possess substantial stability up to fluorides concentration of 0.3 g/l. This particular value has been set as a temporary limit for fluoride ions content in waste to be disposed. To achieve such value there has been provided for integration of fluorine-content flow with fluorides free liquid waste from the Radiochemical plant. The discharge modes have been estimated which prevent holes mudding.

The elaborated process flowsheet of low-level liquid waste preparation for direct disposal bypassing temporary storage in pulp storages PS-1,2 has passed through the experimental testing with real waste samples. Presently a new process flowsheet has been under development to allow the discharge into deep storage of approximately 99% low-level liquid waste by volume coming annually to pulp storages PS-1,2.

Works on pool B-25 (another SGCE open storage) decommissioning is at the stage of justification of most acceptable methods for coming waste processing. On the basis of parameters detailed investigation it has been decided to estimate the possibility of uranium waste deep geological disposal since the largest intake volume accounts for such waste. A technique has been developed for including such waste into the scheme in service today of Radiochemical plant acid waste preparation and disposal into the deep storage. The experimental-industrial testing has been conducted which proved that suggested variant has prospects and it will be recommended for commercial implementation after certain modifications. The performed research of other waste discharged into pool B-25 has determined the necessity of additional waste conditioning prior to discharging into the deep storage together with other waste from the Siberian Group of Chemical Enterprises.
LIQUIDATION OF THE SURFACE STORAGES FOR LIQUID MID-LEVEL RADIOACTIVE WASTES AT THE SIBERIAN GROUP OF CHEMICAL ENTERPRISES

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At the Radiochemical Plant of the Siberian Group of Chemical Enterprises (SGCE) liquid radioactive wastes are buried in deep seated reservoir beds. Initially wastes were accumulated in surface B-1 and B-2 ponds of the open type. Application of the liquid radioactive wastes direct pumping technology allowed to start the liquidation of the storages of the open type, as accumulate sludges and liquid phases posed hazard to the environment.

At present, the most acceptable variant (from economic and technical point of view) of the liquidation of the storages of the open type for liquid radioactive wastes is their conversion into the near surface storages of the closed type by means of filling ponds with the local soil. Development work on the abandonment of the open type storages is carried out on the territory of B-2 pond.

B-2 storage was put in operation in 1964 and has been used for mid-level liquid radioactive wastes accumulation, their averaging and defecation before deep disposal. The total volume of the pond is 150,000 m³, useful capacity is 135,000 m³, slope ratio is 1:4, precipitation sedimentation area is 8000 m², free surface vaporization area is 53300 m². In the pond there is a clay screen of thickness 1.1 - 1.3 m. During the screen construction the clay was rolled to the density of 1.48-1.56 g/cm³. Above the clay screen there is a protective layer made of sand and clay sand; its capacity along the pond bottom is 1.2 m and on the slopes is 1.0 m. In order to control salts and radionuclides output into the first (from surface) aquiferous stratum, 36 observation wells have been drilled around the pond. Annually, groundwater samples are taken from these observation wells.

During the operating period, various solutions were discharged to the pond. They were different in chemical composition and radionuclides content:
- alkali – nitrate aluminium solution;
alkaline liquid phases after settling of waste technological solutions, containing sodium acetate and sodium nitrate, sodium aluminate and sodium silicate, sodium chromate;

vat residue after acetic acid regeneration. The vat residue contain up to 380 g/l of sodium nitrate, 20 g/l of nitric acid, 10 g/l of acetic acid;

drainage – desorbent solutions, which have variable composition and contain manganese, iron, chrome, nickel etc.

highly active raffinates (in small quantities), recovered from extraction reprocessing of non-standard solutions, were periodically released to the pond. These solutions contained high quantity of hydrolyzing impurities (iron, chromium, nickel, manganese, aluminum, silicic acid) and were of high specific activity of beta-emitting nuclides (up to 40 Ci/l).

Before entering the pond, solutions' pH was not less than 8. In the pond, solutions were mixed, averaged, pond liquid phase pH was 11-11.5; sodium nitrate content was 60-80 g/l. As a result of interaction of different solutions, hydroxide precipitations layer was generated at the bottom of the pond. Multiple sampling of the sludge and its analysis during operating and conditioning period until the pond abandonment operations showed that basic elements of solid phase (50 – 80%) are aluminium compounds. Besides, solid phase contains iron, chrome, nickel, manganese, silicon hydroxide compounds. After coprecipitation on hydroxide precipitation, zirconium, niobium, strontium, rare earth elements, ruthenium radioactive nuclides concentrated in solid phase. Its β-activity is 1 – 5 Ci/l. There were 5 washing stages after the stop of solutions discharge into the pond in 1983. At a point when the pond abandonment operations were finished, liquid phase pH was 9 – 9.5. Sodium nitrate concentration was 20 – 30 g/l. By that time short-lived beta-emitters (\(^{103,106}\)Ru, \(^{95}\)Zr, \(^{97}\)Nb, \(^{141-144}\)Ce etc.) decayed; liquid phase and sludges beta activity was basically determined by \(^{90}\)Sr – \(^{90}\)Y, \(^{137}\)Cs.

Radiochemical Plant’s decommissioned liquid wastes storages (B-1 pond and B-2 pond) pose hazard to environment. That’s why experimental preservation of B-2 pond was brought into effect. It was made by means of covering its water area with the local sandy soil. During the pond preservation technology development, which provided safe long-term storage of immobilized sludges, physicochemical assessment of this variant was performed. This physicochemical assessment included evaluation of magnitude of thermal heating of radioactive precipitations as a degradation result of heat-removal, gas release intensity, speed of radionuclide migration with subsoil waters, magnitude of the liquid phase capillary rise. Clay screen reliability evaluation was performed by comparing field examination results with data of mathematical simulation of the protective layer and impervious screen condition.

For evaluation of the allocation of radionuclide and some microelements content in depth of bottom sediment protective layer and impervious screen, migration modeling has been performed by means of software simulator. Geophysical monitoring results show that the impervious screen, under the filled part of the B-2 pond, is undisturbed and demonstrates the reliability of clay screen and its characteristics retention after the soil covering. Penetration depth of salt solutions into impervious screen is 0.4 – 0.6 m, non-sorbing waste components over the pond operating period (about 40 years) penetrated deep into the screen only by 50%.

The whole pond water area was covered in February 2001. The total area of covered surface was 64000 m². The drainage system construction operations were finished in the same year.
The 2002 spring showed its good operational integrity. In February 2002 the filling of the entire pond surface with crushed rock (layer thickness was 0.4 m) was over. Now the construction activity of 40 inspection wells around the pond and installation of the detectors with data output is in progress.

The results of experimental-industrial activities, concerned with the covering of B-2 pond with the sandy soil showed that this method is reliable. Liquid phase is removed from the pond and buried in the underground wastes disposal ground. The pond is filled with approximately 200 thousand m³ of sandy soil. Radioactive sludges are immobilized in the soil. There is no soil subsidence and release and extrusion of immobilized sludges. There are precipitations between the clay screen and the protruding dyke. At the same time the impervious screen integrity is retained. Subgrade radioactivity is at the background magnitudes level. Radiation environment within the pond area improved significantly. Activities concerned the covering of B-2 pond with sandy soil did not cause radionuclides wind dispersal from the pond water area. Ponds preservation provides their environmental safe existence. The obtained results allow the continuation of the B-2 pond liquidation activities in accordance with the project.

All activities related to filling of the open type storage allowed to get experience in this matter and to work out necessary radionuclides and salts allocation inspection methods. The inspection reliability is provided for by application of different methods:
- direct dosimetric measurement of radionuclides concentration in the air, dyke surface pollution and exposure dose rate along the dyke height;
- dyke soil sample analysis, protective layer analysis and inspection well water test analysis;
- geophysical method of clay screen condition inspection and salts spread;
- mathematical modeling of processes and forecasting assessment of radionuclides and salts allocation.

Experience gained from B-2 pond abandonment operations can be used also for other surface storages, including B-1 pond. It will provide better radiation environment within territory of the Siberian Group of Chemical Enterprises.
SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF PYROCHLOR-E-TYPE MATRICES FOR IMMOBILIZATION OF ACTINIDES

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Self-propagating High-temperature Synthesis (SHS) [1-4] is proposed as an alternative for the conventional methods [5-7] of preparation of the mineral-like matrices for immobilization of actinides. In comparison with these methods SHS-method has a number of advantages: simplicity of equipment, high synthesis rates and minimum volumes of secondary wastes.

SHS consists of local inducing strong exothernal reaction by interaction of the metal and oxidizer in a charge consisting of a mixture of powders of chemical elements and mineral additions. The heat released as a result of this reaction induces exothermic reaction in adjoining layers of the substance, resulting in a rapid self-propagating process. In such a process chemical reaction (combustion) proceeds in a narrow zone moving spontaneously along the substance with a linear speed of 0.1-15 cm/sec at 2000-3000°C. Such a high temperature initiating rapid proceeding of the reaction is produced as a result of liberation of chemical energy of the initial batch mixture.

The formation of pyrochlore analogue occurred according to redox reaction:

\[(2-x)\text{Ti} + x\text{TiO}_2 + \text{Y}_2\text{O}_3 + \frac{2(2-x)}{3} \text{MoO}_3 = \text{Y}_2\text{Ti}_2\text{O}_7 + \frac{2(2-x)}{3} \text{Mo}_x\]

where Ti – reducing agent and MoO3 – oxidizing agent.

Because of large activity of the actinides the mixing of their compounds with a batch mixture should be carried out in alcohol solution followed by filtration of the suspension, using water-jet pump. The filtration was performed through special funnel, assembled with the use of cylindrical press mold, paper filter “white tape” and PTFE spinneret. After filtration the press mold was taken from the funnel and dried for 5 hours at T=90°C in drying box. After that the mixture was pressed, using massive clamp and plunger of stainless steel. The tablet was placed on a layer of incendiary mixture situated on a support of fire brick and covered with safety quartz beaker. SHS was initiated by applying electrical firing supplied from below, and the tablet was burned out (burning time - 2-3 sec). Produced by SHS samples of actinides-containing mineral-like matrices are presented in Table I.

SEM/EDS and X-ray analysis were used for the structure examinations of the samples. SEM microphotographs of the samples #1,2 are shown in Fig. 2. It is seen that the dominating
phase is pyrochlore (gray colored; content of the actinides is higher in lighter central part). The lighter phase is molybdenum and, possibly, molybdenum dioxide and rutile.

X-ray diffraction patterns of the samples are shown in Fig. 1 (Py = pyrochlore, Mo = molybdenum). Roentgen characteristic of the compound with pyrochlore structure proved to be identical to those of standard Y$_2$Ti$_2$O$_7$ phase. Proper phase of actinide oxides was not revealed. Therefore solid final products - analogous to natural pyrochlore containing up to 10 wt.% actinides incorporated owing to isomorphic insertion - were produced as a result of SHS from initial mixtures of reagents, mineral additions and actinides.

The study on chemical stability was carried out according to the MCC-1 standard. The samples under study were placed into PTFE containers. Twice-distilled water (pH = 5.80) was used as leaching agent. The containers were placed into drying box with established temperature 90±2°C. The concentrations of Np, Pu and Am in the solutions after leaching were determined by α-spectrometry, U by fluorimetric analysis.

The results of analyses of the solutions after leaching were used for calculation of leach-rates of the actinides ($R_\alpha$, g/(cm$^2$-day)). The data obtained on hydrolytic stability of the samples under study are presented in Table I. The produced matrices have good hydrothermal stability: leach-rates of the actinides lie within the limits of $10^{-7}$–$10^{-9}$ g/(cm$^2$-day).

Table I. Summary table of the matrices containing the actinides produced by SHS and the data obtained on hydrolytic stability of the samples

<table>
<thead>
<tr>
<th>sample, ##</th>
<th>Oxides contents, wt. %</th>
<th>m, g</th>
<th>$p_\alpha$, g/cm$^3$</th>
<th>$R_{237}$Np</th>
<th>$R_{239}$Pu</th>
<th>$R_{243}$Am</th>
<th>$R_{244}$Am</th>
<th>$R_{238}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 (NpO$_2$)</td>
<td>1.87</td>
<td>3.7</td>
<td>1.1·10$^{-7}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>7 (UO$_2$) + 3 (PuO$_2$)</td>
<td>1.78</td>
<td>3.5</td>
<td>-</td>
<td>4.1·10$^{-7}$</td>
<td>-</td>
<td>-</td>
<td>5.4·10$^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>9.7 (UO$_2$) + 0.3 (Am$_2$O$_3$)</td>
<td>1.84</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
<td>7.0·10$^{-8}$</td>
<td>-</td>
<td>8.1·10$^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>10 (PuO$_2$) + 0.2 (Am$_2$O$_3$)</td>
<td>3.16</td>
<td>3.0</td>
<td>-</td>
<td>2.0·10$^{-8}$</td>
<td>-</td>
<td>9.0·10$^{-9}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2. SEM microphotographs of the samples ##1,2
Fig. 1. X-ray diffraction patterns of the matrix samples

References


DISSOLUTION OF URANIUM, NEPTUNIUM, PLUTONIUM AND AMERICIUM OXIDES IN TRI-n-BUTYL PHOSPHATE SATURATED WITH NITRIC ACID.

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The extraction and purification of uranium and plutonium from spent nuclear fuel (SNF) is a key chemical process in nuclear industry. The PUREX (Plutonium Uranium Reduction Extraction) process is most widely used on a commercial scale for this purpose. Nevertheless, the generation of large volumes of aqueous and organic high-level radioactive wastes (HLW) is the main drawback of this process. A search for new alternative techniques for SNF reprocessing, which minimize waste generation, is a major challenge in nuclear industry.

The use of supercritical fluid carbon dioxide (SC-CO₂) as a solvent for SNF reprocessing was proposed [1]. Of particular interest is the direct dissolution of SNF in supercritical carbon dioxide with a suitable complexing agent forming SC-CO₂ soluble complexes with the main SNF components (U and Pu). Previously, we investigated the dissolution of actinide oxides and demonstrated that uranium dioxide is quantitatively dissolved in SC-CO₂ containing the TBP-HNO₃ complex and efficiently separated from plutonium, neptunium and thorium by supercritical fluid extraction (SFE) from a mechanical mixture of their oxides [2, 3]. The interaction of actinide dioxides with SC-CO₂ presaturated with TBP-HNO₃ complex in the ligand cell was conducted in a special extraction cell.

This process in the actinide dioxide/TBP-HNO₃ complex heterogeneous system in the absence of SC-CO₂ was of particular interest. It is known that the interaction of TBP with an aqueous nitric acid solution results in the formation of TBP-HNO₃ complex, whose composition depends on the initial HNO₃ concentration. An 8 M HNO₃ solution was experimentally found to be optimum. In this case, the TBP-HNO₃ (1:1) complex is formed [4], [5]. Commercial UO₂, NpO₂ and PuO₂ samples, as well as their mechanical mixtures, were used. In addition, the solid solutions of U-Np, U-Pu, and U-Pu-Am-Eu were prepared by the calcination of their mixed oxalates at 850°C for 8 h in an atmosphere of Ar + 10% H₂. The results of their X-ray diffraction analysis showed that UO₂ (there are no reflexes of other uranium oxides, namely, U₂O₈ and UO₃) is the matrix of the solid solutions prepared, in the crystal lattice of which Np and Pu in the oxidation state 4⁺ are distributed [6].

A known volume of the TBP-HNO₃ complex prepared according to the published procedure [5] was introduced into a centrifuge tube containing a known amount of the test sample. The tube was placed in a thermostat and heated at 60°C for about 1.5 h, as in the case of SFE [2]. After mixing and centrifuging the solution, the liquid phase was analyzed for radionuclides: Np, Pu and Am were determined by a-radiometry, and U was determined as described below. First, it was back extracted from the organic phase with 0.1 M HNO₃. The back extract was
evaporated to a wet salt and then re-evaporated with 4 M HCl to dryness for the removal of HNO₃ traces. The residue was dissolved in 4 M HCl, and U⁶⁺ was reduced to U⁴⁺ using Zn amalgam. Uranium concentration was determined by spectrophotometry using an absorption band at 650 nm (ε 63 dm³ mol⁻¹ cm⁻¹). Europium concentration was determined by γ-radiometry. The composition of the oxide samples and data on the dissolution of individual actinide oxides, their mechanical mixtures and solid solutions of mixed actinide oxides are presented in Table 1.

Table 1. Direct dissolution of actinide oxides using the TBP-HNO₃ complex. Vsamples=1 ml.

<table>
<thead>
<tr>
<th>Oxide type</th>
<th>Oxide</th>
<th>Oxide content (%)</th>
<th>Metal added, mg.</th>
<th>Metal found in liquid phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual</td>
<td>UO₂</td>
<td>100</td>
<td>9.60</td>
<td>98.4</td>
</tr>
<tr>
<td>Individual</td>
<td>NpO₂</td>
<td>100</td>
<td>6.40</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Individual</td>
<td>PuO₂</td>
<td>100</td>
<td>1.50</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Mechanical mixture</td>
<td>PuO₂</td>
<td>39.8</td>
<td>3.70</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Mechanical mixture</td>
<td>UO₂</td>
<td>60.2</td>
<td>5.60</td>
<td>98.9</td>
</tr>
<tr>
<td>Mechanical mixture</td>
<td>NpO₂</td>
<td>46.3</td>
<td>5.70</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Mechanical mixture</td>
<td>UO₂</td>
<td>53.7</td>
<td>6.60</td>
<td>96.9</td>
</tr>
<tr>
<td>Solid solution</td>
<td>AmO₂</td>
<td>10.7</td>
<td>0.55</td>
<td>92.0</td>
</tr>
<tr>
<td>Solid solution</td>
<td>UO₂</td>
<td>89.3</td>
<td>4.56</td>
<td>98.2</td>
</tr>
<tr>
<td>Solid solution</td>
<td>NpO₂</td>
<td>5.0</td>
<td>0.25</td>
<td>84.0</td>
</tr>
<tr>
<td>Solid solution</td>
<td>UO₂</td>
<td>95.0</td>
<td>4.70</td>
<td>93.6</td>
</tr>
<tr>
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<td>PuO₂</td>
<td>5.0</td>
<td>0.67</td>
<td>89.0</td>
</tr>
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<td>Solid solution</td>
<td>UO₂</td>
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</tr>
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<td>PuO₂</td>
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<td>2.15</td>
<td>86.1</td>
</tr>
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<td>69.95</td>
<td>6.14</td>
<td>94.4</td>
</tr>
<tr>
<td>Solid solution</td>
<td>Eu₂O₃</td>
<td>5.0</td>
<td>0.43</td>
<td>93.6</td>
</tr>
<tr>
<td>Solid solution</td>
<td>AmO₂</td>
<td>0.05</td>
<td>0.004</td>
<td>86.0</td>
</tr>
</tbody>
</table>

Figure 1. Absorption spectra of the liquid phase resulting from the dissolution of actinide oxides in the TBP-HNO₃ complex: (1) UO₂, (2) solid solutions of UO₂ (5% NpO₂) and (3) UO₂ (25% PuO₂).
UO$_2$ is practically (93.3-98.4%) quantitatively dissolved in the phase of the TBP-HNO$_3$ complex. Its dissolution proceeds owing to the oxidation of U$^{4+}$ to U$^{6+}$ (Figure 1, spectrum I) with the formation of the complex UO$_2$(NO$_3$)$_2$(TBP)$_2$ which is highly soluble in a SC-CO$_2$ phase [7].

The data obtained suggest that in the case of SFE the TBP-HNO$_3$ complex should be introduced into the extraction cell along with the solid sample for the full dissolution of the sample and effective consumption of a complex. Then, the solute may be removed from the cell using SC-CO$_2$ and trapped in a suitable collection system.

As can be seen in Table 1, contrary to UO$_2$, both NpO$_2$ and PuO$_2$ are insoluble in the phase of the TBP-HNO$_3$ complex. These oxides are also insoluble while they are in the mechanical mixture with UO$_2$, which quantitatively dissolves in the test system and can be separated from NpO$_2$ and PuO$_2$.

Unlike mechanical mixtures of actinide oxides, solid solutions of neptunium, plutonium, americium and europium oxides with UC$_2$ practically quantitatively dissolve in the TBP-HNO$_3$ complex. Spectra 2 and 3 in Figure 1 indicate that Pu and Np in the phase of the TBP-HNO$_3$ complex are in the oxidation state 4+, whereas U is in the oxidation state 6+. Most likely, the difference in the behaviours of mechanical mixtures and solid solutions of actinide oxides is that, on the contact of the TBP-HNO$_3$ complex with the phase of U-Pu and U-Np, solid solutions of U$^{4+}$ are easily oxidized to U$^{6+}$. As this takes place, the crystal lattice of the solid solution collapses and the formation of Pu$^{4+}$ and Np$^{4+}$ complexes with TBP-HNO$_3$ is initiated.

Thus, we found for the first time that TBP saturated with HNO$_3$ can dissolve solid UO$_2$, which provides the basis of nuclear fuel. In so doing, the new possibilities are opened up for the replacement of the stages of SNF dissolution in HNO$_3$ followed by solvent extraction of the main fuel components with the stage of the direct dissolution of SNF in TBP-HNO$_3$ complex. It may result in minimizing environmentally hazardous aqueous and organic HLW generation. Further management of the TBP-HNO$_3$ complex containing dissolved SNF components may be performed using supercritical or liquid CO$_2$, which, however, do not preclude other alternative approaches.

References

RADIATION AND CHEMICAL STABILITY OF TITANATE CERAMICS INTENDED FOR PLUTONIUM IMMOBILIZATION

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Introduction

The paper presents the results of investigation of radiation and chemical (hydrolytic) stability of model specimens of the titanate ceramics that was chosen in USA as candidate material for immobilization of surplus plutonium. Isotope $^{238}$Pu ($T_{1/2} = 87.7$ years) introduced into the ceramics isomorphically at the production stage was used for accelerated accumulation of radiation defects.

Description of the actual work

By the middle of 90s of the last century as a result of the changed international situation USA and Russia accepted that accumulated quantities of weapon-grade plutonium were surplus. Different approaches were proposed for disposition of the surplus plutonium. The USA concept anticipated to immobilize plutonium into strong ceramic matrices of the mineral-like type followed by its disposal in the geological formations. The USA experts had chosen titanate of complicated chemical and mineral composition based on the cubic phase of the pyrochlorine mineral type as the first immobilization barrier.

Results

The production technology of the compact ceramics included cold pressing of the mixed oxide charge of initial components followed by high-temperature sintering.

The study of the synthesis conditions showed that ceramics of the bulk chemical composition $(Ca_{0.76}Gd_{0.23}Hf_{0.23}U_{0.44} Pu_{0.22})Fe_2O_4$ was easy to reproduce as for the phase composition, pyrochlorine being always the dominating phase on thermal treatment of the initial oxide charge($T = 1350$-$1400^\circ$C) in air. More often brannerite and rutile, rarely fluorite, were observed as minor phases.

Accumulation of radiation defects in the ceramic specimens containing isotope $^{238}$Pu ($\approx 8.7\%$ by mass) leads to deterioration of the crystal structure of the basic pyrochlorine phase. After six-month exposure at an accumulated dose of $44 \times 10^{23}$α-decay/m$^3$ a sharp decrease of the pyrochlorine diffraction pattern (beginning of amorphisation) is observed. Complete x-ray amorphization is accompanied by disappearance of strong reflexes and it ends at a dose of about $120 \times 10^{23}$α-decay/m$^3$. The initial stage of the defect accumulation ($\approx 180$ days) is accompanied by swelling of the crystal cells with a relative increase of the volume by 1.2-1.6%. By the end of the observation period, macroscopic swelling of the ceramic pellets achieved about 5% at an accumulated dose of $190 \times 10^{23}$α-decay/m$^3$. 

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The study of chemical stability (test MCC-1, 90°C, in distilled water) demonstrated that freshly-prepared ceramics retains strongly the main chemical components and it is characterized as chemically stable material. Complete amorphous ceramics (160·10^23 α-decay/m³ dose) demonstrates a significant decrease in the chemical stability as compared to the crystal state. So, in the three-day experiment a 170-fold increase in the leaching rate of plutonium and 70-fold increase in the leaching rate of uranium was registered. At the same time, with increasing time of the specimen contact with water (up to 28 days) the leaching rates of plutonium and uranium decrease and corresponding estimations decrease as well: 30 times – for plutonium and 7 times - for uranium.

Neutron absorbers (Gd and Hf) have much slower yield rates from the amorphous ceramics in comparison with plutonium that is, obviously, favorable for prevention of nuclear criticality in case of possible contact of ceramics with subsoil water.

The study performed and the analysis of literature data [1-4] give an evidence of the fact that on complication of the chemical composition and on transition from Gd_2Ti_2O_7 to (Ca, Hf, Gd, U, Pu)Ti_2O_7 the ceramics radiation stability decreases markedly (approximately by 30%). In this case the critical dose of x-ray amorphization of the candidate material (120·10^23 α-decay/m³) is equivalent to about 360 years of ceramics storage at 10% loading of 239Pu under real storage conditions.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References
DYNAMIC LEACHING OF SPENT UO₂ FUEL UNDER OXIDISING CONDITIONS

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The long-term interaction between spent nuclear fuel and groundwater has to be understood in order to guarantee its safe disposal in a final repository. A final repository consists of multiple barriers against release of radionuclides into the biosphere, for a time span longer than the half-life of the most long-lived radiotoxic nuclides. When engineered barriers surrounding the spent fuel have failed, groundwater can penetrate into the repository and begin corroding the spent fuel matrix; radionuclides will then be released as a function of the chemical stability of the spent fuel. This process is strongly influenced by the existing repository conditions, e.g. Eh, pH, ground water composition etc. and the rate of the spent fuel dissolution is a very important parameter for repository performance assessment.

The processes of the reaction mechanism in spent fuel under repository conditions can be efficiently studied if some of the more important parameters (e.g. redox conditions) are controlled. Such information, i.e. concerning the dissolution processes occurring at the interface between solid and groundwater, can be obtained by using a continuous-flow through reactor.

The aim of the reported work is the determination of the dissolution rates of radionuclides from spent fuel in the absence of precipitation phenomena. A continuous flow-through reactor was specially designed at UPC and adapted for hot cell use at ITU, allowing the determination of dissolution rates following the mixed flow reactor method (continuously stirred tank reactors). Our experimental set-up avoids the formation of secondary phases by precipitation phenomena because these products are being swept out of the experimental device by the flow before the dissolution becomes saturated.

The results from a leaching test of spent fuel carried out under oxidising conditions in bicarbonate water at room temperature have been compared with literature values. Figure 1 shows a schematic diagram of the mixed flow reactor system used. The reaction vessel has a total volume of 70 mL. In order to avoid direct interaction between the sample and the stirring system, the sample is placed between two 50μm quartz filters in a quartz basket in the centre of the reaction vessel. The feed solution is introduced at the bottom of the reaction vessel by a dosing pump and is stirred in the region of the sample to ensure good mixing while the leached solution leaves the reaction vessel at the top. This concept assures that all of the leaching solution is in contact with the spent fuel. The top of the reactor is designed in a conical form to avoid bubble retention.
Fig. 1. Schematic diagram of the mixed flow reactor used. a) dose pump, b) redox electrode, c) pH electrode, d) sample holder, e) leachate sampler, f) waste, g) stirring system.

In order to have a representative specimen with a sufficient surface area, the leaching sample was prepared by milling and sieving slices of irradiated UO₂ fuel (53 MWd/kg U) to a 150-250 μm particle size fraction. 1.1 g of the milled fuel having a surface area of approx. 150 cm² was introduced in the reactor. The dynamic leaching was carried out during 6 months at hot cell ambient temperature (25 ± 2° C) under air oxidising conditions. The leaching solution was made up of 1mM NaHCO₃ and 19mM NaCl in ultra pure water and the flow rate was set to 0.06 mL/min. Aliquots of approx. 5mL of leachant were taken at regular intervals until a steady-state concentration of all measurable radionuclides was reached. Samples obtained were then filtered through 0.2 μm membrane filters, acidified with 2% HNO₃ and analysed by a glove-box based HR-ICPMS, and gamma spectrometry.

Dissolution rates were high enough to determine the concentration of U, Np, Pu, Sr and Cs. The concentrations of the remaining fission products and minor actinides were at such a low level that they could not be determined with the existing HR-ICPMS nor gamma techniques. The evolution of the radionuclides concentration with time is shown in Table 1. The dissolution of all radionuclides reached steady state conditions in less than 120 days.

Congruency between the dissolution of uranium with the other elements was studied by determination of dissolution rates for each radionuclide taking into account their inventory in % in the spent fuel, which was calculated using the ORIGEN program. The results are shown in Figure 2.

As can be seen, there is congruency of Np with U, while the dissolution rate of Pu is 15 times smaller, and fission products Sr and Cs 2 to 5 times higher than U. This shows that at least under these conditions Sr would not be a good indicator for matrix dissolution. Similar results were obtained in other studies [1,2].
Table 1. Elemental concentrations in ppb (ng/g) resulting from the dynamic leaching of spent fuel (burn-up ca. 53 MWD/kg U).

<table>
<thead>
<tr>
<th>Flow-rate (mg/min)</th>
<th>Time (days)</th>
<th>Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.05</td>
<td>Sr: 0.12 Cs: 0.38 U: 59.7 Np: 0.20 Pu: 0.05</td>
</tr>
<tr>
<td>0.20</td>
<td>0.84</td>
<td>Sr: 11.7 Cs: 6.72 U: 4050 Np: 10.6 Pu: 0.35</td>
</tr>
<tr>
<td>0.10</td>
<td>0.94</td>
<td>Sr: 9.07 Cs: 8.03 U: 2490 Np: 7.94 Pu: 0.36</td>
</tr>
<tr>
<td>0.06</td>
<td>1.04</td>
<td>Sr: 8.08 Cs: 8.42 U: 2540 Np: 7.45 Pu: 0.29</td>
</tr>
<tr>
<td>0.06</td>
<td>1.13</td>
<td>Sr: 8.41 Cs: 9.36 U: 2750 Np: 7.20 Pu: 0.34</td>
</tr>
<tr>
<td>0.07</td>
<td>1.76</td>
<td>Sr: 7.06 Cs: 13.4 U: 2430 Np: 4.14 Pu: 0.35</td>
</tr>
<tr>
<td>0.06</td>
<td>1.95</td>
<td>Sr: 5.39 Cs: 14.6 U: 2240 Np: 3.50 Pu: 0.31</td>
</tr>
<tr>
<td>0.06</td>
<td>3.94</td>
<td>Sr: 3.29 Cs: 15.2 U: 917 Np: 1.39 Pu: 0.35</td>
</tr>
<tr>
<td>0.07</td>
<td>9.72</td>
<td>Sr: 0.74 Cs: 9.37 U: 188 Np: 0.20 Pu: 0.22</td>
</tr>
<tr>
<td>0.06</td>
<td>57.72</td>
<td>Sr: 0.43 Cs: 3.23 U: 112 Np: 0.12 Pu: 0.11</td>
</tr>
<tr>
<td>0.16</td>
<td>86.71</td>
<td>Sr: 0.41 Cs: 4.48 U: 283 Np: 0.28 Pu: 0.22</td>
</tr>
<tr>
<td>0.12</td>
<td>93.74</td>
<td>Sr: 0.19 Cs: 4.30 U: 201 Np: 0.19 Pu: 0.13</td>
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<tr>
<td>0.05</td>
<td>113.75</td>
<td>Sr: 0.33 Cs: 2.18 U: 127 Np: 0.12 Pu: 0.09</td>
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<tr>
<td>0.07</td>
<td>164.84</td>
<td>Sr: 0.22 Cs: 1.55 U: 86.7 Np: 0.09 Pu: 0.06</td>
</tr>
</tbody>
</table>

Fig. 2. Elemental dissolution rates (mg·m⁻²·d⁻¹), normalised to their calculated inventory in spent fuel, and obtained from the dynamic leaching of spent fuel (burn-up ca. 53 MWD/kg U) vs time in days.

References

DEVELOPMENT OF A SIMPLE REPROCESSING PROCESS USING N-CYCLOHEXYL-2-PYRROLIDONE AS SELECTIVE PRECIPITANT FOR URANYL IONS

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\textsuperscript{d} Mitsubishi Materials Co., 1-3-25 Koishikawa, Bunkyo-ku, Tokyo 112-0002, Japan

In most of commercial reprocessing plants, spent nuclear fuels have been treated by Purex method\cite{1}. This method is an effective one for separating U and Pu from most of fission products (FPs) and other transuranium elements (TRU). However, such separations have been performed using the extractant (30\% tributyl phosphate/n-dodecane). Hence, facilities of extraction processes and amounts of extractant are relatively large. This results in complexity of processes and an increase in amounts of radioactive wastes. If a large portion of UO\textsubscript{2}\textsuperscript{2+} can be selectively separated from HNO\textsubscript{3} solutions of spent nuclear fuels using simple methods, subsequent extraction processes should be extremely simple or useless.

On the basis of such a viewpoint, we have investigated simple reprocessing processes based on precipitation methods\cite{2-4}, and found out that N-cyclohexyl-2-pyrrolidone (NCP, see Fig. 1) can selectively precipitate UO\textsubscript{2}\textsuperscript{2+} as UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}(NCP)\textsubscript{2} in 1 − 7 M (M = mol/dm\textsuperscript{3}) HNO\textsubscript{3} solutions containing UO\textsubscript{2}\textsuperscript{2+} and other metal ions\cite{5, 6}. Thus, we proposed the concept of simple reprocessing process for spent FBR fuels using the specific property of NCP as shown in Fig. 2\cite{7}. In the first step of this process, an appropriate amount of NCP is added to HNO\textsubscript{3} solutions of spent FBR fuels to precipitate only UO\textsubscript{2}\textsuperscript{2+} ion, followed by filtration, washing, and calcination for producing blanket fuels. The resulting filtrate contains UO\textsubscript{2}\textsuperscript{2+}, Pu (mostly Pu\textsuperscript{4+}), most of FPs, and other TRU species. In the second step, Pu\textsuperscript{4+} species in the filtrate are oxidized to PuO\textsubscript{2}\textsuperscript{2+} by using an oxidant (e.g. O\textsubscript{3}), and then NCP is added to the filtrate to precipitate PuO\textsubscript{2}\textsuperscript{2+} and the remaining UO\textsubscript{2}\textsuperscript{2+}. The resulting mixed
NCP precipitates of U(VI) and Pu(VI) are converted to MOX fuel for FBR by calcination.

![Diagram of reprocessing process for FBR fuels using NCP](image)

Fig. 2. Concept of a simple reprocessing process for FBR fuels using NCP as the selective precipitant for UO$_2^{2+}$.

In order to develop such a simple reprocessing process, we have examined the precipitation mechanism, the optimal conditions for precipitating UO$_2^{2+}$, the decontamination factors (DFs) for FP components, the radiation-resistibility of NCP, the precipitation behaviors of Pu$^{4+}$ and PuO$_2^{2+}$ species, and the calcination conditions of precipitates. As a result, it was found that the specific precipitation ability of NCP is due to its hydrophobic cyclohexyl group, that the precipitation ratio of UO$_2^{2+}$ can be controlled by changing [NCP]/[UO$_2^{2+}$] as shown in Table 1, that the DFs of most FP component are more than 100, that NCP has relatively high radiation-resistibility, and that the precipitates are completely converted to oxides with thermal treatment. Furthermore, it was suggested that the recovery of Pu and U mixture becomes possible by adjusting valence of Pu species. From these results, it is expected that

<table>
<thead>
<tr>
<th>[UO$_2^{2+}$] (M)</th>
<th>T(°C)</th>
<th>[NCP]/[UO$_2^{2+}$]</th>
<th>Precipitation ratios (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>25</td>
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<td>61.4</td>
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<td>81.0</td>
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</tr>
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</tr>
<tr>
<td>0.1</td>
<td>25</td>
<td>2.8</td>
<td>97.5</td>
</tr>
<tr>
<td>0.1</td>
<td>25</td>
<td>3.8</td>
<td>99.2</td>
</tr>
</tbody>
</table>
the proposed processes shown in Fig. 2 should be applied to the reprocessing of spent FBR fuels.

Acknowledgement
This research has been performed with supports from the Development of Innovative Nuclear Technologies Project organized by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References
STUDY OF KINETICS OF GAS GENERATION FROM MOISTENED PLUTONIUM DIOXIDE POWDER

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Introduction

In accordance with the 2000 Disposition Agreement between the Governments of the Russia and USA, Russia shall utilize 34 metric tons excess weapons-grade plutonium including about 9 metric tons weapons-grade plutonium dioxide now stored at Russian nuclear sites. Taking into account the time it takes for plutonium to be disposed of (presumably it will last from 2008 to 2020) plutonium dioxide shall be safely stored and then transported to the site of disposition, i.e. plutonium conversion and MOX fuel fabrication facility.

If plutonium dioxide powder contains water vapors, pressurization of the container might occur. The reason of gas generation inside a sealed container with PuO₂ is the radiolysis of water due to plutonium alpha-emission [1]. An in-depth and contemporary insight of all the aspects of plutonium-bearing materials storage is given in the USA DOE standard [1] and in the review [2]. The USA DOE standard DOE–STD-3013-2000 “Stabilization, Packing, and Storage of Plutonium-Bearing Materials” strictly specify the content of water in plutonium dioxide and design of a storage package. One in particular it is specified that the package shall sustain the inside pressure of gases 699 psig (4927 kPa). At the conference “Pu Futures-The Science 2000” held in Santa Fe (USA) a few scientific publications devoted to the research of PuO₂ properties have been presented. This suggests that processes occurring on long storage of plutonium dioxide invite comprehensive studies presents peculiar interest for science community. In our opinion, research findings [2-5] make it possible to suggest that the USA DOE standard DOE–STD-3013-2000 with regard to plutonium dioxide preparation and package design seems to be too stringent.

Results of investigations

Our research used weapons-grade plutonium oxide fabricated by oxalate and ammonium precipitation procedures (PuO₂ powder). The content of water adsorbed into the PuO₂ powder was 1 and 3 % wt. The process of gas accumulation was investigated by means of the P-V-T method. The pressure of gases in the reaction vessel at the start-up of experiments was less than 1 Torr (~0.02 psia). A glassy reaction vessel was equipped with a U-type mercury manometer. The volume of the reaction vessel was ~200 cm³ (0.2 l). The experiments were carried out at temperatures of 30, 50 and 100 °C during ~110 days.

Figure 1 gives the kinetics of alteration of the pressure of gases at 100 °C in the reaction vessel with PuO₂ powder synthesized by means of oxalate precipitation. Similar data were obtained for PuO₂ samples synthesized by means of ammonium precipitation.

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Figure 1. Kinetics of the overall gas pressure growth at 100°C in a reaction vessel containing PuO₂ (oxalate) with adsorbed water.

- Plutonium dioxide with 1 wt% water
- Plutonium dioxide with 3 wt% water

The table given below presents the rate of gas generation in experiments with PuO₂ powder at 100°C. Experimental findings allowed us to suggest that notwithstanding the radiolysis of water in the system, the quantity of water vapors adsorbed onto plutonium dioxide does not decrease below a fixed value. The processes of water radiolysis and synthesis, being run simultaneously, shall result in dynamical equilibrium.

Table. Gas generation from PuO₂ samples at 100°C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Precipitation method</th>
<th>Sample weight, g</th>
<th>Water content, % wt.</th>
<th>Overall pressure, torr (10 days of testing)</th>
<th>Gas accumulation rate (20-110 days) mole/(day*g PuO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxalate</td>
<td>3</td>
<td>1</td>
<td>12</td>
<td>$3.2 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>Oxalate</td>
<td>2.5</td>
<td>3</td>
<td>35</td>
<td>$10.5 \times 10^3$</td>
</tr>
<tr>
<td>3</td>
<td>Ammonium</td>
<td>3</td>
<td>1</td>
<td>14</td>
<td>$3.4 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>Ammonium</td>
<td>2.5</td>
<td>3</td>
<td>37.5</td>
<td>$11.6 \times 10^4$</td>
</tr>
</tbody>
</table>

The synthesis of water from oxygen and hydrogen can occur not onto the whole surface, but, from our point of view, onto active centers of the metal surface (container case walls) and plutonium dioxide. However, these centers could be accessible for reagents only under
specific conditions. In our case, one of the provisions for this effect would be a low concentration of adsorbed water corresponding to two monolayers of chemisorbed water filling the plutonium dioxide surface. The depth of this layer corresponds to a dynamical equilibrium between water decomposition and synthesis processes.

Let’s evaluate the content of water corresponding to the two water monolayers. For the first one, the content of water has been assessed to be within 0.11 mg/m², for the second one - ~ 0.23 mg/m² [6]. It means that the effect of filling up the plutonium dioxide surface by the two water monolayers corresponds to the concentration of water in plutonium dioxide ~ 0.34 % wt. (at a powder specific surface area ~ 10 m²/g). According to the USA DOE standard STD-3013-2000 the maximum content of water in PuO₂ is 0.5 % wt. Therefore, only a few adsorbed water molecules will be subject to radiolysis with the formation of oxygen and hydrogen. The maximum gas pressure inside the sealed container with weapons-grade PuO₂ must be evaluated based on both water content and a powder specific surface area. If one uses a new modification of the well-known equation by J.M. Haschke, presented in the attachment B to the USA DOE standard DOE–STD-3013-2000 [1], gas pressure values could be determined. These data are in good agreement with work [2].

References

RADIOACTIVE WASTE AND NUCLEAR FUEL CYCLE BACK-END

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Radioactive waste management is one of the most pressing problems facing the world today. The term radioactive waste implies nuclear materials and radioactive substances which cannot be used in future. Spent unprocessed fuel is represented by reactor fuel elements removed from the core after a set time for the generation of energy and the buildup of fission products. The latter contain both fertile and fissile actinides, and fission products. Heat is generated by the radioactive decay. There are two types of fuel cycle: the open-ended fuel cycle when the spent nuclear fuel unloaded from a reactor is not processed and is considered as radioactive waste; and the closed nuclear fuel cycle, when the prepared spent fuel is transported to the spent fuel reprocessing plant. The processing of spent nuclear fuel with the purpose of extraction of U and Pu for repeated manufacturing nuclear fuel also is accompanied by formation of radioactive waste. Radioactive waste is divided in liquid, solid and gaseous ones. Liquid high-level radioactive waste creates serious problems because of powerful thermal emission and radiation. Therefore the following scheme of the management with liquid waste is accepted:

- storage in the liquid form up to a decrease of thermal emission (radioactive decay short-life isotopes); • solidification and storage under controllable conditions; • a final disposal of solid radwaste in geological formations.

Now a disposal of radwaste in stable geological formations is the only real technology of isolation of these dangerous materials from biosphere. Therefore the choice of a site with the geological conditions guaranteeing long-term isolation of radionuclides, is the key moment to provide the safe radioactive waste repository. The geological environment is the natural barrier preventing a migration of radionuclides to the biosphere. That is why isolated properties of the geological environment are in the centre of attention, as well as negative processes which can break integrity of a burial ground and lead to outflow of radionuclides in the environment. As noted [Laverov et al., “Geological aspects of a problem of a repository of radioactive waste”, Geocology, 1994, no. 6, 3-20], the problem of disposal of radioactive wastes is, first of all, a geological problem.

In order to choose an optimum place for disposal, sociopolitical and economic factors should be taken into account, and the environment of the disposal should be estimated by means of geological criteria. The analysis of safety includes a definition of the set of natural reasons (geological conditions) capable to cause a failure in the system and an estimation of consequences of these failures. In such complex system as a repository, environmental contamination can result from a chain of events and processes of both geological and technological origin, e.g., heat generation by high-level radioactive waste–accumulation pressure in containing rocks in connection with overheating–cracking these rocks–activation entering underground waters to radwaste–extraction of radionuclides from radwaste–involving radionuclides in movement of underground waters and their carrying out in an environment. An analysis of this chain leads to some conclusions on the features of geological environment providing safe
radwaste disposal: i) rocks suitable for disposal of radwaste should possess certain thermal physical properties, ii) the environment of a repository should include low water content, iii) underground waters should be nonaggressive in relation to radioactive waste solidification and poorly dissolve a radionuclide, iv) the stream of underground waters should not unload on a surface. At underground isolation of the radwaste by the basic technological loading the thermal emission which changes filtrational characteristics of a file of rocks, essentially influences the sizes and design features of a burial place.

Actions on decrease in temperature in a burial ground demand additional material inputs. In this situation use of the geological environment, capable effectively to allocate superfluous heat due to special heat-physical properties can be a possible decision of a problem. From rocks the greatest heat conductivity stone salt differs. This property of stone salt is taken for a basis of the present research.

Historically, bedded salts deposits have received a great deal of consideration as potential waste repository sites. The basic arguments for the favorable consideration of these rocks include extremely low water content, extremely low porosity and permeability, high thermal conductivity and the ability of salt to anneal after fracturing (i.e. should faulting occur, the fault would self-seal, thus preventing radionuclide escape) among others.

For objectivity it is necessary to point on the possible negative effects intrinsic only in salt. It is predilection of salt depositions and, for some sources, there is a capability of "up-floating" of the chamber of repository in layer of salt.

Essential elements of an estimation of long-term behavior of a burial place are the mathematical models forecasting physical and chemical processes which are flowing past in a repository, geosphere and biosphere. Pricaspian depression – the largest sedimentary basin of Russia and Kazakhstan. Salt domes are distributed in all territory of the Pricaspian depression. Their total reaches 2000. Every one 1000 km² on the average there are three-four domes. We build thermal non-steady model for calculation of temperatures in conditions of long-term dumping of the radwaste (see Fig.1). For simulation the following parameters were used:

<table>
<thead>
<tr>
<th>parameter</th>
<th>the purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Data of seismic sounding of eastern part Pricaspian depression.</td>
<td>construction of geologic pattern of a salt dome Kenkijak</td>
</tr>
<tr>
<td>2. Data of measurements of values of a heat flow</td>
<td>a task of boundary conditions</td>
</tr>
<tr>
<td>3. Value of energy release of highly active waste with residual quantity U, Pu, Am, Cm 0.1%; Sr, Cs, Te, I 1%</td>
<td>a task of heat release from a source (chamber of repository)</td>
</tr>
<tr>
<td>4. Estimated time</td>
<td>10.000 years - advisable IAEA period of guaranteed safety of a radwaste repository.</td>
</tr>
<tr>
<td>5. Software package TERMGRAF</td>
<td>mathematical calculation of temperatures</td>
</tr>
</tbody>
</table>
The boundary conditions in model were organized as follows: on lower boundary the reduced heat flow was set, i.e. that flow, which one is peer measured minus a fraction of radiogenic heat a modeled layer, i.e. in a 10-km zone; on high bound temperature of a neutral layer, defined by M.D. Khutorskoy for eastern part Pricaspian depression [Khutorskoy M.D. A heat flow in the field of structural - geologic heterogeneities. M.: Science, 1982]. Heat conduction and heat diffusivity over saline, saline and under saline of complexes were measured by us directly on the formation samples, selected for it.

Fig.1. Temperature distribution into Kenkijak salt dome, thick line is the dome boundaries (see text)

The simulation has shown, that visible heating of containing environment can be watched in 10 000 years. It allows to speak that saliferous structures, especially salt domes, are capable to allocate heat allocated at decay of radioactive elements, and, at the initial stage of research, to predict a favorable thermal mode of a repository.

CONCLUSIONS

In the nature there are no situations theoretically suitable for radwaste repository. The geologic requirements by environment of repository are multiple and have a miscellaneous significance; therefore solution on suitability of a particular environment will be foregone to wear nature of the compromise between substantial combination of separate geological conditions and requirements, shown to these conditions. It speaks that the isolation in the nature "of materials and matters, further usage which one is envisioned" is an optimum solution of a problem. The bases of the ecological approach to any kind of activity - minimum environmental impact and co-evolution with her that becomes possible only at entrainment in a turnover (natural or anthropogenesis) all products of production. In relation to a radioactive waste it means necessity of their maximum salvaging. The structure of the radwaste, as a rule, is enriched with chemical members, the consumer demand for which increases. Besides the radioactivity itself - valuable consumer quality, and rate of growth of needs in radionuclide of commodity in medicine, agriculture, industry is higher, than in the other raw. Radioactive waste can be esteemed as secondary resource - perspective raw material of a nuclear complex. It is necessary to remark, that the idea of greatest possible usage of matter, inclusive in the radwaste (fuel, radionuclides) is not new and is embodied in many projects (for example, in the programs of obtaining chemically pure products from spent nuclear fuel).

On the basis of above-stated it is possible to draw a conclusion, that a cardinal solution of the problem of radioactive waste will be waiving the concept "waste" for the benefit of concept «secondary raw ». It can become a breakthrough, which will convert a present problem in ecological reasonable, cost-effective practice.
\[^1\text{\textsuperscript{132}}\text{Te}, \text{\textsuperscript{95}}\text{Zr}, \text{\textsuperscript{99}}\text{Mo AND \textsuperscript{103}}\text{Ru} \text{ TRACE LEVEL FISSION PRODUCTS SPECIATION AND ADSORPTION ON INORGANIC MATERIALS AS A FUNCTION OF pH VALUES}\]

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Introduction

The hydrous oxides are effective materials for treatment of waste radioactive liquids because they have affinity for certain ions or groups of ions from both acidic and alkaline solution. They also show high selectivity and resistance to high temperatures and high levels of radiation. Sorption behaviour of trace amounts of \(^{235}\text{U}\) fission products present in aqueous solution was investigated under static conditions. TiO\(_2\), MnO\(_2\) and SnO hydrous oxides, were the sorbents chosen for this study. A variety of anions, cations and neutral species of \(^{132}\text{Te}, \text{\textsuperscript{95}}\text{Zr}, \text{\textsuperscript{99}}\text{Mo and \textsuperscript{103}}\text{Ru}\) in aqueous solutions at different pH values (1, 3, 5, 7 and 10) formed in solution were identified by high voltage electrophoresis. Fission products retention values on the solids are discussed.

Experimental

Analytical grade hydrous oxides (Merck) were used without further purification. The fission products were obtained by irradiating \(\text{UO}_2(\text{NO}_3)_2\) solution with neutrons for 5 hours in a TRIGA Mark III nuclear reactor with an approximate neutron flux of 10\(^{12}\) n.cm\(^{-2}\).s\(^{-1}\). Afterwards, the sample was diluted with distilled water to obtain a final 5 x 10\(^{-4}\) M uranyl nitrate solution and pH was adjusted with \(\text{NH}_4\text{OH}\) or \(\text{HNO}_3\) aqueous solutions using a calibrated potentiometer. The \(^{235}\text{U}\) fission products studied were identified by gamma ray spectrometry. Chemical species of the trace level \(^{235}\text{U}\) fission products were surveyed by using high voltage electrophoresis and gamma ray spectrometry as described by Serrano et al. [1]. Batch experiments were carried out at room temperature by mixing, in closed glass vials, portions of 100 mg of the inorganic sorbent and 10 mL of \(^{235}\text{U}\) fission products solution at different pH values (1, 3, 5, 7 and 10). Samples were stirred for 72 hours until equilibrium was reached. The liquid was separated from the solid by centrifugation (5 minutes at 3000 RPM).

Results and discussion

Surface areas values of hydrous oxides are found to be in the range of those given in the literature [2-4]. The chemical species of \(^{235}\text{U}\) fission products were identified with the help of MEDUSA program [5], Baes and Mesmer [6].
Fig 1a) shows that TiO\textsubscript{2} has a good sorption capacity for \textsuperscript{132}Te with a maximum sorption at pH 9, 83.9±1.1%. However MnO\textsubscript{2} and SnO are not good sorbents for \textsuperscript{132}Te. It reached a maximum sorption of 33.4±1.4% on MnO\textsubscript{2} and 25.9±0.5% on SnO in alkaline media. This sorption behaviour can be explained on the basis that metal oxides in aqueous solution usually carry a surface charge, which is very dependent on the pH of the solution and the zero point charge (zpc) of the solids. At lower pH values (below zpc) the oxide surface is strongly positive and has very weak affinity for cations, and for high pH values there is affinity for anions. The percentages of \textsuperscript{132}Te sorption were very different on TiO\textsubscript{2}, MnO\textsubscript{2} and SnO sorbents. This behavior is due to the different average pore radius for alkaline conditions, TiO\textsubscript{2} and MnO\textsubscript{2} were the best sorbent materials for \textsuperscript{132}Te sorption.

Figure 1b) shows \textsuperscript{95}Zr sorption on inorganic materials; TiO\textsubscript{2} was found to be a good material for \textsuperscript{95}Zr uptake, 80.1±0.7% in acid pH values, while \textsuperscript{95}Zr sorption on MnO\textsubscript{2} and SnO was very low. Figure 1b) shows that the form of the \textsuperscript{95}Zr sorption curve for TiO\textsubscript{2} is not similar to those found for MnO\textsubscript{2} and SnO. The maximum of \textsuperscript{95}Zr sorption on TiO\textsubscript{2} was observed at acid pH values. \textsuperscript{95}Zr sorption on MnO\textsubscript{2} is higher than in SnO because of the larger pore radius of MnO\textsubscript{2}.

Fig. 1. a) \textsuperscript{132}Te and b) \textsuperscript{95}Zr sorption on inorganic materials at different pH values (pH\textsubscript{f} = final pH).

Fig. 2. a) \textsuperscript{99}Mo and b) \textsuperscript{103}Ru sorption on inorganic materials at different pH values (pH\textsubscript{f} = final pH).
Figure 2a), shows that $^{99}$Mo was adsorbed very efficiently on some of the inorganic materials studied. The high $^{99}$Mo retention on TiO$_2$ (91.4±0.8%) at all pH values is probably due to the precipitation of MoO$_3$ and the other non-identified species on the pores of the TiO$_2$. $^{99}$Mo sorption on MnO$_2$ was 59±0.9%, at pH 1. At higher pH values the amount sorbed decreased to 19.8±0.3% at pH 9.6. $^{99}$Mo sorption on MnO$_2$ was better in acid pH values than in all alkaline solutions. $^{99}$Mo sorption on SnO was very low, following the same pattern than on MnO$_2$ but with slightly lower retention values. These $^{99}$Mo species are retained with less efficiency on MnO$_2$ and SnO probably because of the small pore radius. As mentioned before, fission products solution were dissolved in HNO$_3$, therefore $^{103}$Ru was probably present as nitrosyl nitrate complexes, the difficulty of $^{103}$Ru sorption on inorganic materials is characterized by the large number of chemical species and their complex forms present in aqueous solution [7]. Little is known about ruthenium solution chemistry, but it can be conjectured that the capacities of $^{103}$Ru sorption on inorganic materials, reflect the presence of complex ruthenium species in solution. According to 3lasius [8] ruthenium nitrosyl complexes in aqueous solution are converted into one another quickly. It can be seen from Figure 2b), that $^{103}$Ru sorption on TiO$_2$, MnO$_2$ and SnO was low, specifically on SnO. These poor results show only a sorption of 17.6±0.8% in alkaline media. On both, TiO$_2$, and MnO$_2$, $^{103}$Ru sorption was higher for higher pH values. It can be seen on Figure 2b) that the uptake of $^{103}$Ru chemical species increases on each solid with a rise with pH values, being higher the sorption on TiO$_2$ because of the larger pore radius. $^{103}$Ru, in the fission fragments solution at pH 1, is sorbed on MnO$_2$ apparently mainly due to the attraction of the negatively charged $^{103}$Ru species on the positively charged surface of MnO$_2$ (zpc= 4.5). However at higher pH values, the negatively charged $^{103}$Ru species are not so well attracted because of the competition between the uranium species, which are retained in the oxide at pH values between 2 and 5. At pH values above 4.5 the retention decreased because of the few positively charged $^{103}$Ru species [($^{103}$RuNO(OH)$_3$(H$_2$O)$_2$]$^{2+}$ and probably of the neutral species ($^{103}$RuNONO$_2$(OH)$_2$(H$_2$O)$_2$), which is poorly adsorbed on the MnO$_2$.

Acknowledgment. The authors would like to thank the financial support of CONACYT, project 39893-Q

References

INFLUENCE OF $\beta$ RADIATION ON THE UO$_2$ DISSOLUTION AT DIFFERENT pH

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$^b$ Dept. Nuclear Engineering, UPC, Barcelona, Spain  
$^c$ Dept. Nuclear Fission, CIEMAT, Madrid, Spain

If a failure of the spent nuclear fuel container is assumed to occur during the first 1000 years after the final disposal, $\beta$ radiation has to be considered in the conceptual model [1]. However, the influence of $\beta$ radiation separated from $\alpha$ or $\gamma$ radiation on the dissolution of the spent nuclear fuel has not been extensively studied. The study of the effect of $\beta$ radiation on the UO$_2$ dissolution will help to understand the results obtained in spent fuel leaching experiments and might be useful to improve the databases of the radiolitical models. For this reason, we have studied the dissolution of non irradiated uranium dioxide, as a chemical analogue of the spent nuclear fuel, under external $\beta$ irradiation using a sequential methodology.

The experiments were carried out using specially designed reactors. The solid used was a non irradiated uranium dioxide with a particle size of 100-320 $\mu$m, which specific surface area was determined by the BET method. Uranium concentration in solution was measured by ICP-MS to determine UO$_2$(s) dissolution rates. Hydrogen peroxide concentration was measured by chemiluminescence to determine the oxidant formed due to water radiolysis as well. In addition, both the pH and the redox potential of the solutions were continuously monitored. In all the cases, parallel blank experiments were performed.

A $^{90}$Sr source with an activity of 7 mCi has been used. The dose rate to the solution was calculated taking into account the geometry of the system. The reliability of this calculation was determined using a SIEMENS EPD-MK2 dosimeter, obtaining a value of 5 Gy/hour. We studied the effect of $\beta$ radiation on pure water measuring pH, redox potential and hydrogen peroxide concentration. We could detect an increase of about 60-80 mV on the redox potential on the experiment under $\beta$ radiation and a hydrogen peroxide concentration of $10^{-7}$ mol·dm$^{-3}$ was measured after 5 days.

An increase of the redox potential was also observed in the experiments in the presence of UO$_2$, as it can be seen in Figure 1. In this experiment the pH of both blank and irradiated experiments was 3.5 and did not vary during the experimental time. Figure 2 shows the variation of the uranium concentration in solution with time. After 10 days, the uranium concentration in the blank experiment seems to start to decrease with time while in the $\beta$ irradiated experiment continues increasing. Similar results were obtained in non-sequential experiments [2]. The higher dissolution rates can be related to the increase of the measured hydrogen peroxide concentration in solution.
Figure 1. Evolution of the redox potential with time in the presence of UO$_2$.

Figure 2. Uranium and H$_2$O$_2$ concentrations measured in the experiments with UO$_2$.

The MAKSIMA code has been used to model the generation of radiolytical products, both molecular and radical species. This program allows the modelling of complex kinetics in radiolytic processes with pulse trains.

ELECTROCHEMISTRY AND SPECTROELECTROCHEMISTRY OF NEPTUIUM IONS IN AQUEOUS SOLUTION

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Electrochemical reactions of neptunium ions have been studied extensively in acidic and alkaline solutions and reduction mechanisms have been proposed. Plocek measured the formal redox potential for Np(VI)/Np(V) at a glassy carbon (GC) electrode in HClO₄ solution by using cyclic voltammetry (CV)[1], and confirmed that the redox system is reversible. Casadio et al. investigated the Np(VI)/Np(V) couple by CV at a pyrolytic graphite electrode[2]. Niese et al. characterized the charge transfers of Np(IV), Np(V), and Np(VI) in HClO₄, HNO₃, and H₂SO₄ by CV with a GC electrode[3]. They observed one one-electron reduction wave of Np(VI) in HClO₄ and HNO₃ instead of three one-electron reduction waves, which had been observed in cyclic voltammogram using the pyrolytic graphite electrode in 1M HNO₃ by Casadio et al. [2]. The electrochemical data on Np redox system are still uncertain particularly at different concentration of HNO₃. Based on these backgrounds, we have investigated the electrochemical and spectroscopic properties of Np(VI) ions in concentration 1-8 M HNO₃ solutions by using CV and spectrophotometer equipped with an optical transparent thin layer electrode (OTTLE) cell, because the data on redox potentials of Np(VI) ions are very important for considering valence adjustment in separation processes of spent fuel reprocessing.

Experimental
Cyclic voltammograms were measured at 25 ± 1 °C under nitrogen atmosphere with a BAS CV-660A voltammetric analyzer. A three-electrode system utilized, i.e., a BAS 002012 GC working electrode(surface area: 0.07 cm²), a BAS 002020 reference electrode (SSE), and a BAS 002233 Pt auxiliary electrode. The spectroelectrochemical experiments were performed using Shimadzu UV-4100 spectrophotometer equipped with a quartz OTTLE cell, which has Pt minigrid electrode as an optical transparent working electrode. The optical pathlength was ca. 1 mm and calibrated spectrophotometrically for every measurement. Other conditions for spectroelectrochemical measurements were the same as those for CV measurements.
Results
The CV measurements of Np(VI) in 1 M HNO₃ solution were carried out in the potential range from +1.20 to +0.60 V at the different scan rates. The results are shown in Fig. 1. Redox coupled peaks (Pₑ and Pₒ) are observed at around +0.826 (Eₑₒ) and +0.985 V (Eₒₒ). The values \( \Delta E_p \) (= \( E_p - E_o \)) increase from 0.135 to 0.181 V with an increase in \( v \). The values of \( (E_p + E_o)/2 \) (= \( E^0 \)) are constant, +0.906 V, with independent of \( v \). This result is consistent with that of Niese et al.[3] and suggests that the electrochemical reduction of Np(VI) at GC electrode proceeds quasi-reversibly as follows.

\[
\text{NpO}_2^{2+} + e^- = \text{NpO}_2^{+} \quad (1)
\]

![Fig. 1. Cyclic voltammograms for the reduction of Np(VI) (6.97 × 10⁻³ M) in 1 M HNO₃ solution measured in the potential range from +1.2 to +0.6 V at different scan rates.](image)

![Fig. 2. Change in electronic absorption spectra measured at the applied potentials in the range from +1.05 to +0.65 V for Np(VI) (7.75 × 10⁻³ M) in 3 M HNO₃ solution.](image)

To evaluate the validity of suggestion that the electrochemical reaction (1) is a quasi-reversible electron transfer reaction, the standard rate constant (\( k_r \)) was estimated by using Nicholson’s equation (\( \psi = k_r/D_n(D_{red})^{1/2} \)) based on the assumption that the diffusion coefficient of oxidant (\( D_{ox} \)) is equal to that (\( D_{red} \)) of reductant. The electrochemical data of Np(VI) ions in concentration 1-8 M HNO₃ solutions are presented in Table 1. The results indicate that the redox reaction of Np(VI)/Np(V) at GC electrode is quasi-reversible. For more detail discussion of the electrochemical reaction mechanism in this system, the spectroelectrochemical measurements were carried out for the 3 M HNO₃ solution containing Np(VI) (7.75 × 10⁻³ M). Electronic spectra were measured at any applied potentials in the range from +1.05 to +0.65 V on the basis of the redox potentials determined from the cyclic voltammograms. The results are shown in Fig.2. It is found that with the gradual reduction of
Np(VI), the absorption bands in the range from 300 to 500 nm and at 1224 nm, which are characteristics for the absorption of Np(VI) ions, decrease and those at 617, 980 and 1094 nm, which are characteristic for the absorption of Np(V) ions, increase. In addition, the isosbestic point is observed at 1124 nm. These results indicate that Np(VI) ions are reduced to Np(V) in the potential range from +1.05 to +0.65 V and the resulting Np(V) undergoes no subsequent reactions.

Table 1 Electrocatalytic data for neptunium ions in varying concentration of HNO₃

<table>
<thead>
<tr>
<th>[HNO₃]/M</th>
<th>( E_{pa}/V )</th>
<th>( E_{pa}/V )</th>
<th>( E^0/V )</th>
<th>( D_0/(10^6 \text{ cm}^2/\text{s}) )</th>
<th>( k_2/(10^3 \text{ cm/s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.826</td>
<td>0.985</td>
<td>0.906</td>
<td>2.40</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>0.836</td>
<td>0.980</td>
<td>0.908</td>
<td>2.03</td>
<td>1.32</td>
</tr>
<tr>
<td>3</td>
<td>0.847</td>
<td>0.971</td>
<td>0.909</td>
<td>4.77</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>0.855</td>
<td>0.949</td>
<td>0.902</td>
<td>3.83</td>
<td>4.37</td>
</tr>
<tr>
<td>5</td>
<td>0.853</td>
<td>0.939</td>
<td>0.896</td>
<td>3.73</td>
<td>5.64</td>
</tr>
<tr>
<td>6</td>
<td>0.852</td>
<td>0.939</td>
<td>0.895</td>
<td>3.69</td>
<td>5.72</td>
</tr>
<tr>
<td>7</td>
<td>0.845</td>
<td>0.931</td>
<td>0.888</td>
<td>3.24</td>
<td>5.63</td>
</tr>
<tr>
<td>8</td>
<td>0.844</td>
<td>0.923</td>
<td>0.844</td>
<td>3.60</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Summary

The results of the present study are listed in Table 1. It is found that the \( E^0 \) values become negative in order of neptunium ions with HNO₃ solution, and that the \( D_0 \) values are almost constant and the \( k_2 \) values increase when HNO₃ solution varies from 1 to 8 M. The spectroelectrochemical experiments shows that the absorption spectra measured at the applied potentials in the range from +1.05 to +0.65 V have isosbestic point at 1124 nm and that the evaluated electron stoichiometry is 0.93. These results support that the reduction product of Np(VI) is only Np(V) and the resulting Np(V) does not undergo any subsequent reactions.

Acknowledgements

This study was carried out by Japan Atomic Energy Research Institute(JAERI) under the auspices of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

EFFECT OF ALKYL SUBSTITUENTS ON EXTRACTION PROPERTIES AND SOLUBILITY OF PHOSPHORYLATED CALIX[4]ARENES

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One of the promising methods for extractant modification is attachment of phosphoryl groups to rigid calixarene platform. In this case the extraction efficiency considerably increases due to optimal disposition of extractant donor centers around metal cation. Previously we found [1] that phosphorylated calix[4]arenes (Fig. 1, \( R = \text{CH}_3\text{P(O)Alk}_2 \)) afford the combined recovery of lanthanide, actinide, technetium and palladium from acidic HLW.

![Phosphorylated calix[4]arene](image1)

Fig. 1. Phosphorylated calix[4]arenes.

![Europium extraction](image2)

Fig. 2. Europium extraction by 0.01 M solutions of calixarenes in m-nitrobenzotri fluoride (NBTF) [1].

In contrast to common phosphinoxides, the length of alkyl substituents at phosphorus atom of calixarenes strongly affects their extraction properties. By decreasing the length of \( R \)-substituents in a row of dibutyl (CIP-2), dipropyl (CIP-67), diethyl (CIP-45) and dimethyl (CIP-57) - methylenphosphinoxides the extraction maximum is displaced into more acidic region (Fig. 2).
The main reason for such anomalous alkyl effect is unexpected high solubility of calix[4]arenes methyl (CIP-57) and ethyl (CIP-45) substituents at phosphorus atom in diluted HNO₃. In two-phase aqueous-organic systems CIP-45 passes into aqueous phase to a considerable degree, its concentration in organic phase decreases, which results in decreasing the metal extraction from diluted acid. The degree of calixarene transfer from organic phase into aqueous phase depends on diluents type (Table 1). CIP-45 passes from p-xylene into aqueous phase much better than from NBTF. From dichloethane (DCE) CIP-45 goes only into water. Calixarene with propyl substituents at phosphorus atom (CIP-67) does not pass even into diluted acid from the investigated diluents.

<table>
<thead>
<tr>
<th>Calixarene</th>
<th>Solvent</th>
<th>Concentration HNO₃, M</th>
<th>Calixarene content in aqueous phase, % of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP-45</td>
<td>NBTF</td>
<td>0.3</td>
<td>35</td>
</tr>
<tr>
<td>R = CH₃P(O)Et₂</td>
<td>DCE</td>
<td>1.0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>R' = Pr</td>
<td>Water</td>
<td>0.3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td></td>
<td>p-xylene</td>
<td>0.3</td>
<td>&gt; 90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>CIP-67</td>
<td>NBTF</td>
<td>0/3</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

The degree of calix[4]arene CIP-45 transfer from organic phase into aqueous phase also depend on HNO₃ concentration (Fig. 3).

Fig. 3. Distribution of CIP-45 (0.01 M solution in NBTF) between aqueous and organic phases
In IR-spectrum of CIP-45 solution in water the anomalous decrease of v(P=O) frequency at 73 cm\(^{-1}\) is observed (Table 2). Other frequencies of the spectrum, including v(COC), remain identical to those for non-aqueous solutions. Spectrum of water associated with CIP-45 varies as well: absorption in the region of valence OH vibrations is broadened, especially from low-frequency side; as well as the band of deformation vibrations at 1640 cm\(^{-1}\), a wide absorption appears in the region of 1600-980 cm\(^{-1}\). This points to a strong binding of water with CIP-45. Similar strong binding of P=O groups of CIP-45 with water molecules, having no effect on the remaining portion of calixarene molecule, is not known for other phosphinoxides.

In diluted solutions of HNO\(_3\) this hydrate weakly interacts with HNO\(_3\) molecule and remains strongly hydrated (Table 2). Therefore, CIP-45 partly goes from organic into aqueous phase under these conditions.

Table 2. Value of low-frequent shift v(P=O) of CIP-45 molecules in aqueous solutions and in DCE

<table>
<thead>
<tr>
<th>Solvent</th>
<th>v(P=O)</th>
<th>Δv(P=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Free</td>
<td>Hydrated</td>
</tr>
<tr>
<td>DCE</td>
<td>1177</td>
<td>1164</td>
</tr>
<tr>
<td>Water</td>
<td>1104</td>
<td></td>
</tr>
<tr>
<td>0.3 M HNO(_3)</td>
<td>1104</td>
<td>1094</td>
</tr>
</tbody>
</table>

In strongly acidic solutions (3 M HNO\(_3\)) CIP-45 is protonized by HNO\(_3\) to form an insoluble in water non-hydrated complex [CIP·2H\(^+\)]\([\mathrm{O}_2\mathrm{NO-H-ONO}_2]\)^\(^{-}\), which does not practically pass from organic into aqueous phase.

The work was performed within the joint Russian-Ukrainian project supported by ISTC (grant 2068) and STCU (grant Rus-09).

Reference
SEPARATION OF ACTINIDES FROM LANTHANIDES BY ELECTROLYSIS - A COMPARISON BETWEEN MOLTEN BI AND SOLID AL CATHODES

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Electrolysis in high temperature molten salts (chlorides or fluorides) is envisaged for the reprocessing of spent nuclear fuel [1,2]. The dissolved actinides (An) chlorides or fluorides (U, Pu, Am, Np,...) are recovered from the bulk by reduction onto a cathode leaving the fission products (mainly lanthanides, Ln) into the molten salt phase. The actinide/lanthanide separation by electrorefining is here studied in molten chloride media using two cathodic materials, Bi and Al, to collect selectively the actinides. The reduction of An\(^{3+}\) and Ln\(^{3+}\) onto Bi and Al electrodes leads to the formation of alloys (M\(_2\)Bi\(_x\) or M\(_2\)Al\(_y\), with M: An or Ln). Cyclic voltammetry on molten Bi electrode and solid Al working electrodes was carried out to evaluate the reduction potentials of actinides and lanthanides onto these materials. Electroseparation tests were then carried out under different current densities in order to optimise the separation efficiency.

![Cyclic voltammogram](image)

**Figure 1.** Cyclic voltammetry of Pu\(^{3+}\) and La\(^{3+}\) ions in LiCl-KCl.

Temperature: 733K Scan rate: 100 mV/s. [Pu\(^{3+}\)] = 0.98 wt%. [La\(^{3+}\)] = 0.96 wt%

(−) on Al electrode.

(−) on molten Bi electrode.

Figure 1 shows cyclic voltammmograms recorded from a LiCl-KCl salt containing both LaCl\(_3\) and PuCl\(_3\) on Al and Bi. The PuCl\(_3\) containing salt solution was prepared by a chemical reaction between Pu-metal (in Bi) and BiCl\(_3\). Addition of LaCl\(_3\) salt was then done in order to
obtain salts containing Pu\(^{3+}\) and La\(^{3+}\) in different ratios. It can be seen that the difference in reduction potentials between Pu\(^{3+}\) and La\(^{3+}\) is larger on Al compared to Bi. The separation of these two elements is thus expected to be more efficient on Al than on Bi.

![Graph showing cathodic potential vs. electrolysis time](image)

**Figure 2. Pu/La separation test on liquid Bi electrode.**  
Temperature: 733K. Starting composition: [Pu\(^{3+}\)] = 0.85 wt%, [La\(^{3+}\)] = 0.18 wt%

The separation of plutonium from lanthanum has been performed by electrolysis on unstirred molten bismuth electrode (S ~ 5 cm\(^2\)) starting with a solution of LiCl-KCl eutectic containing PuCl\(_3\) and LaCl\(_3\) salts. The experiments were carried out under constant current using the dissolution of a metallic Pu rod as anodic reaction. Assuming that the electrochemical oxidation of the metallic Pu rod proceeds at 100% faradic yield and that only Pu is reduced during the electrolysis, i.e. 100% of the reduction’s current is used for the conversion of Pu\(^{3+}\) to Pu metal, the concentration of Pu\(^{3+}\) in the salt phase should be constant (electrotransport) during a separation test. During the experiment, salt samples were taken to monitor the Pu and La concentrations.

Fig. 2 shows the Pu and La concentrations as a function of the time of electrolysis as well as the evolution of the cathodic potentials during an electroseparation experiment with a LiCl-KCl salt having a Pu\(^{3+}\)/La\(^{3+}\) ratio (in wt%) of approximately 5. At low current density (10 mA/cm\(^2\)) the anodic (\(E_a = -1.55\) V) and cathodic potentials (\(E_c = -1.1\) V) are both stable. The cathodic potential corresponds to the reduction potential of Pu\(^{3+}\) obtained on Bi electrode in the cyclic voltammograms shown in Fig. 1. At this current density only Pu is reduced on the Bi cathode and the concentration of La in the salt phase, during electrolysis, stays constant (see Fig. 2 dotted line). The concentration of Pu in the salt phase is, however, not constant but somewhat reduced. This can be explained if the faradic yield of anodic oxidation of the Pu rod is less than 100%.

The same starting solution was used for a second separation test at higher current density (30mA/cm\(^2\)). Also in this case the electrolysis proceeded under stable anodic potential (\(E_a = -1.37\) V). The cathodic potential dropped from \(E_c = -1.2\) V in the beginning to about \(E_c = -1.45\)
V in the end of the electrolysis which is a more negative potential compared to the previous experiment at low current density. In this potential range, the reduction of La should occur, according to the cyclic voltammetric curve obtained on liquid Bi, see Fig. 2 bold line. This is confirmed by the concentration of lanthanum in the salt phase which decreases from 0.19 wt% to about 0.10 wt% (see Fig. 2), i.e. half of the amount of La was reduced at this current density. In addition, the Pu concentration salt phase concentration shows an increasing trend which can be explained when a part of the cathodic current is used for the reduction of lanthanum (and maybe also of lithium) causing a decrease in the faradic yield of Pu$^{3+}$ reduction.

For comparison, an electroseparation of Pu from Nd was carried out by applying a constant current between a Pu rod and an Al foam cathode. Nd was selected since it is slightly easier reduced than La and also because of its multiple valency (Nd$^{3+}$ and Nd$^{4+}$) in chloride salts which makes the separation more difficult. Stable cathodic and anodic potentials (~1.2 V and ~1.45 V, respectively) were obtained during the experiment. The electrolysis was stopped after an exchange of 400 C at 10 mA/(cm$^2$·wt% of Pu), still at a stable cathodic potential of ~1.2 V, corresponding to Pu$^{3+}$ reduction onto solid Al.

Table 1. Results of Pu/Nd electroseparation on solid Al foam

<table>
<thead>
<tr>
<th>Pu and Nd concentration in the salt phase (wt%)</th>
<th>∆m (g)</th>
<th>m$_{th}$ (g)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>After</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu</td>
<td>1.39</td>
<td>Pu</td>
<td>1.26</td>
</tr>
<tr>
<td>Nd</td>
<td>0.51</td>
<td>Nd</td>
<td>0.50</td>
</tr>
<tr>
<td>0.325</td>
<td>0.330</td>
<td>98.5</td>
<td></td>
</tr>
</tbody>
</table>

The results are shown in Table 1 where concentrations of Pu and Nd in the salt phase before and after the experiment as well as the faradic yield are listed. As expected, the Pu$^{3+}$ concentration remained almost constant during the electrolysis, as it was balanced by close to 100 % faradic anode and cathode processes. Also the Nd$^{3+}$ concentration remained unchanged in the salt phase during the electrolysis as the cathode potential (~1.2 V compared to ~1.4 V for Nd$^{3+}$/Nd$^{4+}$(Al)) was not negative enough to allow its reduction. It can thus be concluded that an efficient separation of Pu from lanthanides can be performed onto solid Al with a faradic efficiency close to 100%.

Conclusions

Efficient separation of Pu from La by electrolysis on an unstirred molten Bi electrode is obtained below 15 mA/(cm$^2$·wt% of Pu). At higher current density, co-reduction of La occurs. Electroseparation of Pu from Nd is achieved onto Al electrodes with a faradic yield close to 100%. Cyclic voltammetric curves clearly indicate that Al appears to be a more suitable cathodic material to perform An/Ln separation compared to Bi or Cd. The larger difference of reduction potentials between An and Ln obtained on Al, leads to a more efficient separation of minor actinides elements (Am and Cm) from Ln.

References

DEVELOPMENT OF A REGENERABLE STRIP REAGENT FOR TREATMENT OF ACIDIC, RADIOACTIVE WASTE WITH THE UNIVERSAL SOLVENT EXTRACTION PROCESS

Jack D. Law¹, R. Scott Herbst¹, Dean R. Peterman¹, Terry A. Todd¹, Valeriy N. Romanovskiy², Vasily A. Babain², Igor V. Smirnov² and Vyacheslav M. Esimantovskiy²

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As a collaborative effort between the Khlopin Radium Institute (KRI) in St. Petersburg, Russia and the Idaho National Engineering and Environmental Laboratory (INEEL), amine carbonate solutions were proposed for stripping such metals as Cs and Sr from CCD-based solvents (CCD, CCD + PEG or UNEX solvent), transplutonium and rare earth elements from CMPO solutions in a suitable diluent (TRUEX process), or uranium from solutions of TBP or phosphine oxides (PUREX or TRPO process) [1]. It was shown that methylamine carbonate solutions, perhaps with complexant addition, act as effective metal stripping reagents. The advantage of such solutions is the possibility for regenerating the bulk of the organic component, methylamine carbonate.

Regenerated methylamine carbonate can be re-used, thereby reducing the consumption of the organic compound by several orders of magnitude (calculated per mole of radionuclide). The regeneration process is simple and safe. Decreasing the organic substance content in the strip product results in simplification, acceleration, and reduction or elimination of organic destruction in the process.

In this work results of two dynamic tests of the UNEX process are presented. These tests were performed at the INEEL and at KRI to further evaluate the effectiveness of using and recovering MAC as a stripping reagent. Dissolved surrogate HLW calcine was used as a feed solution. UNEX solvent (0.08 M ChCoDiC + PEG-400 + diphenyl-N,N-dibutylcarbamoylphosphine oxide in trifluoromethylphenyl sulfone - was used as extractant.
A schematic of the process flowsheet with strip reagent regeneration is indicated in Fig. 1. The resultant strip product containing the radionuclides can be evaporated with 93-95% MAC are recovery. The distillate is methylamine carbonate that can be regenerated and re-used in the strip process. The flowsheet test was conducted for five hours using fresh MAC. The process was shutdown, the MAC regenerated, and testing continued for an additional five hours using the regenerated MAC.

In the course of bench tests the following was established:

- Recovery degrees of target radionuclides into extract as calculated from their content in raffinate constituted for Cs-137 – 99.74%, Sr-90 – 99.92% and Eu-154 – 99.96%; in accordance with the existing standards, this enables to assign the process raffinate to low-level waste class A.
- Strip solution on the basis of methylamine carbonate and nitrilotriacetic acid affords efficient stripping of target radionuclides. In this case, recycle extractant washing from methylamine carbonate, in contrast to guanidine carbonate, is attained even at the second stage of extraction zone, where cesium extraction coefficient exceeds 1.
- Yield of Cs, Sr and Eu into strip product was practically equal to 100% relative to their content in strip product.
- The following purification of target elements was attained: Al - 411, B – 26, Mg – 147, Hg – 45, Ca – 4, Fe – 5, Na – 4.
- The losses of target elements with raffinate were as follows: Cs – 0.26%, Sr – 0.08% and Eu – 0.04%.

![Fig.1. Extraction process flowsheet with recovery and re-use of the stripping reagent.](image-url)
In the course of experiment extractant made more than 12 cycles without any visible damage of extraction properties.

Reference
SORPTION OF AMERICIUM FROM COMPLEXONE SOLUTIONS IN DENSE CO₂

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Many laboratories of the world are engaged in development of decontamination technology in media of liquid or supercritical carbon dioxide [1,2,3,4]. Implementation of this technology should drastically reduce volume of the secondary liquid radioactive waste [5]. The drawback of the technology is complicated regeneration of extractants. One of the possible ways for their regeneration may be radionuclide sorption on ionites immediately in liquid CO₂ medium. It has been demonstrated in the present work that only strongly acidic cationites are suitable for efficient purification of extractants. Total ion-exchange capacity towards Eu is calculated for cation-exchange resin KY2-8 (analog of DOWEX-50*8).

Demonstration of possibility of complexone recycle on cation-exchange resins.

Experiments were conducted on a laboratory setup, the block-diagram of which is shown in Fig. 1. The setup involves a high-pressure syringe pump, bubbler, three extraction 3.5 ml cells and extract receiver. Experimental conditions: 25 °C, pressure 70 atm, Volume of liquid CO₂ pumped though the extraction cells·35 ml.

![Block-diagram of laboratory setup for sub- and supercritical decontamination](image)

Fig. 1 - Block-diagram of laboratory setup for sub- and supercritical decontamination

Initially, possibility of radionuclide sorption on cationites and solid acids immediately from liquid carbon dioxide was investigated. For this purpose two extraction cells were used. Samples and complexones were placed into cell 1, cationite being investigated - into cell 2. Following ion-exchange resins were used as cationites: KY2-8 (C₄H₆SO₃H, pK=1,4), AHKB-35 (C₃H₆RN(CH₃COOH)₂, pK1=2, pK2=3,8); КФ-2в (C₄H₆PO(OH)₂), pK1=3,4, pK2 = 7,1), Kβ-4 (RCOOH, pK=6,5), as well as zeolite A and oxalic acid (H₂C₂O₄·2H₂O, pK1=1,4, pK2=4,2). Mixtures of hexafluoroacetylacetone (HFA) - tributylphosphate (TBP) - water and dioctfluoroamylphosphoric acid (DOFAPA) - TBP -
octanol - water dissolved in carbon dioxide were subjected to purification. The experimental results show that the required purification degree of extractant may be attained only by using the strongly acidic cationites KY2-8, oxalic acid (Table 1).

**Table 1 – Cs$^{137}$ and Am$^{241}$ Sorption by cationites from complexone solutions in liquid carbon dioxide (25°C, 70 bar., 35ml CO$_2$)**

<table>
<thead>
<tr>
<th>Amount of complexes in cell</th>
<th>Cationite amount</th>
<th>Element</th>
<th>Recovery, %</th>
<th>Am content in solution, %</th>
<th>Am distribution over cationite, %</th>
<th>Balance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KY2-8, 1 g</td>
<td>Am</td>
<td>63$_{53}$</td>
<td>11$_{52}$</td>
<td>40$<em>{53}$ 17$</em>{52}$ 4$_{51}$ &lt;1</td>
<td>63$<em>{53}$ 45$</em>{55}$</td>
</tr>
<tr>
<td></td>
<td>KY2-8, 2 g</td>
<td>Am</td>
<td>56$_{54}$</td>
<td>2$_{51}$</td>
<td>46$<em>{50}$ 7$</em>{52}$ 3$<em>{51}$ 1$</em>{51}$</td>
<td>57$<em>{51}$ 45$</em>{55}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$C$_2$O$_2$H$_2$O, 1 g</td>
<td>Am</td>
<td>44$_{53}$</td>
<td>&lt;1</td>
<td>28$<em>{51}$ 17$</em>{50}$ 1$_{51}$ &lt;1</td>
<td>46$<em>{51}$ 63$</em>{53}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$C$_2$O$_2$H$_2$O, 2 g</td>
<td>Am</td>
<td>57$_{51}$</td>
<td>&lt;1</td>
<td>37$<em>{51}$ 6$</em>{55}$ 1$<em>{51}$ 1$</em>{51}$</td>
<td>45$<em>{55}$ 57$</em>{57}$</td>
</tr>
<tr>
<td></td>
<td>KY2-8, 1 g</td>
<td>Cs</td>
<td>75$_{52}$</td>
<td>3$_{51}$</td>
<td>65$<em>{52}$ 7$</em>{53}$ 2$_{52}$ &lt;1</td>
<td>31$<em>{51}$ 102$</em>{54}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$C$_2$O$_2$H$_2$O, 1 g</td>
<td>Cs</td>
<td>85$_{54}$</td>
<td>&lt;1</td>
<td>80$<em>{55}$ 3$</em>{54}$ 1$_{51}$ &lt;1</td>
<td>85$<em>{55}$ 99$</em>{54}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$C$_2$O$_2$H$_2$O, 2 g</td>
<td>Cs</td>
<td>91$_{55}$</td>
<td>&lt;1</td>
<td>38$_{50}$ &lt;1 &lt;1 &lt;1</td>
<td>41$<em>{59}$ 63$</em>{58}$</td>
</tr>
</tbody>
</table>

The obtained data have confirmed in principale the possibility of radionuclide sorption directly from complexone solutions in liquid CO$_2$, opening the way to recycle both carbon dioxide and complexones. In order to demonstrate such possibility some additional experiments were conducted with the use of three extraction cells of the laboratory setup. Samples being decontaminated were placed into extraction cells 1 and 3. Into extraction cell 2 between them cationite was placed. Complexones were added only into cell 1; this allows modeling the decontamination process of sample in the third cell by complexone solution purified on cationite in liquid carbon dioxide. The results obtained are presented in Table 2.

**Table 2 – Decontamination by recycled extractant (25°C, 70 atm., 35 ml CO$_2$)**

<table>
<thead>
<tr>
<th>Amount of complexes</th>
<th>Amount of cationite</th>
<th>Element</th>
<th>Recovery of element, %</th>
<th>Element content in solution, %</th>
<th>Distribution of elements over cationites, %</th>
<th>Balance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30µl HFA 30µl TBP 10µl H$_2$O</td>
<td>KY2-8, 1 r</td>
<td>Am</td>
<td>91$<em>{51}$ 75$</em>{55}$</td>
<td>solution, % 38$<em>{52}$ 71$</em>{55}$ 16$<em>{53}$ 3$</em>{51}$ 1$_{51}$</td>
<td>92$<em>{51}$ 91$</em>{52}$</td>
<td></td>
</tr>
<tr>
<td>30µl DOFAPA 30µl C$_2$H$_2$OH 30µl TBP 10µl H$_2$O</td>
<td>KY2-8, 2 r</td>
<td>Am</td>
<td>93$<em>{53}$ 50$</em>{54}$</td>
<td>29$<em>{54}$ 91$</em>{53}$ &lt;1 &lt;1 &lt;1</td>
<td>93$<em>{53}$ 91$</em>{51}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cs</td>
<td>88$<em>{52}$ 54$</em>{54}$</td>
<td>26$<em>{52}$ 71$</em>{53}$ &lt;1 &lt;1 &lt;1</td>
<td>73$<em>{55}$ 63$</em>{53}$</td>
<td>581</td>
<td></td>
</tr>
</tbody>
</table>
Thus, the possibility of using the cationites for complexones recycle has been demonstrated; in such a manner the consumption of reagents may be reduced 10-20 times and the volume of liquid radioactive waste may be reduced as well.

**Determination of ion-exchange capacity of KY2-8 resin**

One of the most important parameters of cationite is its total ion-exchange capacity. The total ion-exchange capacity of cationite resin KY2-8 was determined with the use of setup consisting of two cells and bubbler. Into cell 1 a weighed amount of europium (Am) oxide was placed, into cell 2 - a weighed portion of KY2-8 with known mass, and complexones were introduced into bubbler. After experiment the resin was divided into five equal portions and in each of them the amount of sorbed europium was determined. It was established from the results obtained that the fist layer of KY2-8 resin is saturated with europium at a maximum and, reasoning from these data, the total ion-exchange capacity of KY2-8 under above conditions was assessed as 0,06 mg-equiv/g.

**Conclusion**

The possibility of regenerating the complexones for subcritical decontamination in carbon dioxide with the use of cationites has been demonstrated. Recycle of complexones should reduce their consumption by a factor of 20. The strongly acidic cationite KY2-8 and solid H₂C₂O₄·2H₂O are shown to be suitable for efficient purification of extractants. The total ion-exchange capacity of KY2-8 was assessed as 0,06 mg-equiv/g towards europium.

The work was carried out under financial support of ISTC (Project 2055).

**References**

GRAPHITE AND PYROCARBON CORROSION IN WATER AND SALT BRINES

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The proposed solution for HTR spent fuel management is their storage in deep geological repository, for example salt domes. The long term safety of repository depends on the integrity of fuel element consisting of coated particles embedded into a graphite matrix.

As an accident scenario the water ingress into repository, accompanied with the highly concentrated salt brines formation, and its interaction with the protective barriers graphite and the pyrocarbon coatings should be taken into account. In this scope, the behaviour of graphite and pyrocarbon in repository relevant conditions is important.

The objective of this work was to determine the corrosion rates and investigate the behaviour of graphite and pyrocarbon in different aquatic phases.

In the present work the graphite powder from graphite pebbles without fuel and pyrocarbon coatings from unirradiated BISO coated particles were used for investigations. As aqueous media deionised water, MgCl₂-rich (brine-2) and NaCl-rich (brine-3) solutions were used [1]. All experiments were performed in sealed glass tubes under argon or oxygen atmosphere at 90°C. Some experiments were performed under γ-irradiation in AVR cooling pool to investigate the influence of water radiolysis process on carbonaceous material corrosion. The integral γ-dose over the period of 2 months amounts to approximately 2.2 M Gy. Gas phase of vessels was analysed by gas chromatography. The CO₂ content measured was used for the corrosion rate calculation. All experiments were corrected to blanks.

Results and discussion

Corrosion experiments under argon atmosphere without the irradiation source lasted over two years. For different graphite fractions in MgCl₂-rich brine the average corrosion rate obtained is in the order of magnitude 10⁻⁵ g/m²·d. The gas phase composition revealed the absence of carbon monoxide and hydrogen, which indicates, that corrosion is not caused by the interaction of graphite and water. Therefore, the reaction of graphite with the trace amount of dissolved oxygen and oxygen absorbed on the surface was considered.

To investigate the influence of dissolved oxygen on the graphite corrosion rate, additional short term experiments under pure oxygen atmosphere were performed. The switch from argon to oxygen atmosphere leads to one order of magnitude increased corrosion rates. Such exaggerated conditions had been used for the estimation of upper limit of the graphite corrosion rate 10⁻⁷ g/m²·d.

In the final repository aqueous phase will be irradiated from spent fuel elements and oxidising reagents, as products of water radiolysis will be present. The experiments under γ-irradiation showed its dramatic impact on the graphite stability in aquatic phases. The corrosion rates of graphite and pyrocarbon in MgCl₂-rich solution are similar amounting to 1.5·10⁻⁷ g/m²·d. As can be seen from the results of experiments under pure oxygen atmosphere, such a significant increase of corrosion rate can not be caused only by oxygen produced by water radiolysis but...
mainly by the different radical species. It can be seen in chloride ion rich media under irradiation that the corrosion rate is higher than in water. The obtained values are $10^2$ g/m$^2$d and $10^6$ g/m$^2$d correspondingly. The possible reason for such behaviour is significant contribution of chloride ions to radical formation, leading to increasing aggressiveness of salt brines under irradiation.

The summary of the main experiments carried out is presented in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fraction, mm</th>
<th>Aquatic phase</th>
<th>Atm.</th>
<th>Duration, d</th>
<th>$O_2$, vol%</th>
<th>$H_2$, vol%</th>
<th>$N_2$, vol%</th>
<th>CO$_2$, vol%</th>
<th>Corrosion rate, g/m$^2$d</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>0.15-0.25</td>
<td>brine-2</td>
<td>Ar</td>
<td>770</td>
<td>–</td>
<td>–</td>
<td>0.8</td>
<td>0.1</td>
<td>1.4E-08</td>
</tr>
<tr>
<td>graphite</td>
<td>&gt;0.8</td>
<td>brine-2</td>
<td>Ar</td>
<td>770</td>
<td>–</td>
<td>–</td>
<td>0.6</td>
<td>0.1</td>
<td>2.2E-08</td>
</tr>
<tr>
<td>graphite</td>
<td>0.15-0.25</td>
<td>brine-2</td>
<td>Ar</td>
<td>770</td>
<td>0.4</td>
<td>–</td>
<td>1.8</td>
<td>0.1</td>
<td>1.6E-08</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>Ar</td>
<td>770</td>
<td>0.2</td>
<td>–</td>
<td>0.7</td>
<td>0.2</td>
<td>1.4E-08</td>
</tr>
<tr>
<td>graphite</td>
<td>&lt;0.05</td>
<td>brine-2</td>
<td>Ar</td>
<td>790</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>0.2</td>
<td>1.9E-08</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>$O_2$</td>
<td>92</td>
<td>98.9</td>
<td>–</td>
<td>0.3</td>
<td>0.5</td>
<td>2.9E-07</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>$O_2$</td>
<td>92</td>
<td>96.4</td>
<td>–</td>
<td>0.9</td>
<td>0.8</td>
<td>2.7E-07</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>$O_2$</td>
<td>60*</td>
<td>2.6</td>
<td>44.5</td>
<td>n.d.</td>
<td>17.1</td>
<td>1.3E-05</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>$O_2$</td>
<td>60*</td>
<td>2.9</td>
<td>44.1</td>
<td>2.4</td>
<td>17.0</td>
<td>1.5E-05</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-3</td>
<td>Ar</td>
<td>60*</td>
<td>6.0</td>
<td>39.6</td>
<td>0.6</td>
<td>10.5</td>
<td>6.6E-06</td>
</tr>
<tr>
<td>graphite</td>
<td>0.05-0.15</td>
<td>brine-3</td>
<td>Ar</td>
<td>60*</td>
<td>6.1</td>
<td>37.4</td>
<td>3.5</td>
<td>10.2</td>
<td>6.7E-06</td>
</tr>
<tr>
<td>pyrocarbon</td>
<td>0.05-0.15</td>
<td>brine-2</td>
<td>Ar</td>
<td>60*</td>
<td>2.7</td>
<td>40.1</td>
<td>–</td>
<td>13.8</td>
<td>2.6E-05</td>
</tr>
<tr>
<td>pyrocarbon</td>
<td>0.05-0.15</td>
<td>water</td>
<td>Ar</td>
<td>60*</td>
<td>0.7</td>
<td>2.9</td>
<td>0.4</td>
<td>0.9</td>
<td>8.5E-07</td>
</tr>
</tbody>
</table>

symbol (*) indicates experiments under $\gamma$-irradiation

Conclusions

The investigations carried out have showed the high stability of both graphite matrix and pyrocarbon coatings in the absence of $\gamma$-irradiation, which increases the corrosion rate significantly. However, even under such aggressive conditions the materials investigated are still much more stable than some other materials considered for waste isolation [2].

Based on the results obtained and assuming the constant and uniform corrosion, the lifetimes of pyrocarbon coatings and graphite layer free of kernels can be estimated. The thickness of pyrocarbon coating and outer graphite layer was assumed to be about 40 $\mu$m and 0.5 cm respectively. The estimations for corrosion in brine-2 under $\gamma$-radiolysis with dose rate of 1.5 KGy/h give us the approximate lifetime in the range of 9 thousand years for pyrocarbon layer and 1.5 million years for graphite. It should be mentioned that it is the upper limit estimation because the dose rate used is conservative relevant to final repository condition.

References


EXTRACTION OF AMERICIUM AND EUROPIUM BY CARBAMOYL-SUBSTITUTED ADAMANTYLICALIXARENES

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3 M. V. Lomonosov Moscow State University, 119892, Moscow, Russia

The management of high-level nuclear waste requires the separation of long-lived radionuclides and their concentration in small volumes of solutions for further vitrification and storage. To minimize the waste volume, it is of high importance to choose compounds which are capable of removing the radionuclides with a high degree of efficiency and selectivity from acidic or strongly salted media. The TRUEX-process is known for the recovery of transplutonium actinides. It is based on (N,N-di-isobutylcarbamoylethyl)octylphenylphosphine oxide (CMPO) as organic extractant. Attachment of four CMPO-like functions on the wide or narrow rims of calix[4]arenes gave extractants, which are not only more efficient, but also exhibit considerably higher selectivity towards actinides than to lanthanides under acidic conditions [1].

It was the aim of the present work to synthesise novel ligands based on adamantylcalixarenes with CMPO functions on the wide or narrow rim and to study their extraction properties. p-Adamantylated calixarenes have been chosen as molecular platforms for several reasons: (i) these compounds can be easily obtained on a multi-gram scale from p-H-calix[4/6]arenes and 3-R-1-hydroxyadamantanes (R = H, alkyl, aryl, or other functional groups) [2]; (ii) the presence of a bulky and lipophilic adamantane nucleus promises to improve the solubility and the extraction efficiency of the desired ligands and (iii) the adamantyl unit provides several positions for the introduction of additional substituents which open the road for further development of this type of ligands (possible fine-tuning of selectivity, creation of new binding sites at the wide rim, etc.).

The CMPO-substituted adamantylcalix[4]arenes summarized in Table 1 were synthesised and their extraction properties towards Am and Eu were investigated. It was shown that the cooperative effect (the ratio of the distribution coefficients for metal extraction by the solution of a substituted adamantyl calixarene and by the solution of the corresponding monomeric CMPO) depends on the spacer between the CMPO function and the adamantylcalixarene backbone. The americium/europium selectivity was evaluated as well.

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Adamantylcalixarenes C1, C3 with CMPO functions attached to the adamantyl residues at the wide rim via a direct linkage and via a single methylene group showed significant differences in extraction properties between themselves and in comparison to the corresponding monomers C2 and C4. While the extraction abilities of the compounds C2 and C4 are practically identical and low, the introduction to the same ligating functions to the wide rim of the calixarene platform leads to a considerable growth of the extraction efficiency: e.g. the distribution coefficient of americium for calixarene C1 (concentration 0.01 M) is 1.6, and the distribution coefficient for C2 (concentration 0.04 M) - 0.18; hence, the cooperative effect is about one order of magnitude. For substances C3 and C4 (same conditions applied) the cooperative effect manifested by the calixarene C3 comes to $10^3$. For the narrow rim CMPO-substitution of the adamantylcalixarenes we prepared three novel calixarene ligands in which four CMPO functions are attached via ether linkers of three or four methylene groups. Tetra-CMPO derivatives C5-C7 were synthesized by O-alkylation of p-adamantylcalixarene by N-(3-bromopropyl)- and N-(4-bromobutyl)-phthalimide respectively (one step for C5 and C7, two subsequent alkylation steps for C6)
followed by hydrazinolysis and acylation of the tetraamines by an active ester (p-nitrophenyl-diphenylphosphoryl) acetate.

The cooperative effect shown by calixarenes C5 and C7 with four identical spacers, as compared to N,N-diethylcarbamoymethyl)diphenylphosphinoxide C8, is approximately $10^3$. For the substance C6 involving two different ether groups in the alternating sequence, extraction ability increases by ten times as compared to C7, but decreases twice as compared to C5.

![Figure 1. Extraction of americium by dichloromethane solutions of various ligands from the 3M HNO$_3$ solution](image)

To evaluate the quantity of ligand molecules involved in the formation of the complex with a metal ion, solvate numbers (SN) of extractants were determined. Monomeric compounds (C2, C4, C8) showed SN higher than 2 (from 2.3 to 3); for the calixarene derived chelators C1, C5-C7 SN varied from 1.4 to 1.5 and for C4 SN was 1.9.

Financial support by INTAS, Project, No 01-2044, is gratefully acknowledged.

References


COMPLEX RADIOCHEMICAL AND ACTIVATION ANALYSIS OF MINOR ACTINIDES TRANSMUTATION IN FAST REACTORS AND IN THE BEAMS OF HIGH ENERGY ACCELERATORS

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Joint Institute for Nuclear Research, Dubna, Russian Federation

The results of radiochemical and nuclear physical research of specimens with individual minor actinides (Np-237, Pu-240, Am-241) irradiated in BN-350 reactor for a long time are presented.

The research results include determination of a burnout of each isotope, change of its isotopic composition, accumulation of actinides, determination of a residual concentration of the parent radionuclide after the reactor irradiation. The research diagram was as follows: a batch of minor actinides (Np-237, Pu-240, Am-241, Cm-244) highly purified from radionuclide impurities was produced, every batch composition was certified, every batch was loaded into capillaries made of stainless steel, capillaries were placed in the reactor fresh assembly, the assembly with capillaries was established in BN-350 reactor, the assembly was irradiated in reactor during 6 micro-runs (80 effective days on average adjusted to the reactor power 1000MW), capillaries were removed.

Next radiochemical investigations included: capillary dilution together with the cladding, solution analyzing by alpha- and gamma- spectroscopy, recovery of the objective actinide by chemical methods, analysis of the actinide recovered by alpha- and gamma- spectrometry methods.

Results of radiochemical research of every specimen are presented in the report.

The experimental results have been compared with the calculation data obtained using TRIGEX codes (BNAB-93 constants) with the following cross section compressing into 18 groups and ORIGEN codes (kinetics calculation). For this purpose the calculation models of BN-350 reactor have been developed, neutron fields have been calculated in multi-group approach in 3D hexagonal geometry for all micro-runs in the places of capillary location, calculation values of the actinide burnout and secondary nuclide accumulation in corresponding capillaries have been defined. Comparison results of calculation and experimental data are presented in the report. General data on the sample burnout parameters are given in the Table:

<table>
<thead>
<tr>
<th>Cell</th>
<th>Irradiation time, days</th>
<th>Fluence $10^{23}$ cm$^{-2}$sec$^{-1}$</th>
<th>Burnout of the main isotope</th>
<th>Accumulation of secondary actinides</th>
<th>Total burnout, % of heavy metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
<td>89</td>
<td>781</td>
<td>2.0</td>
<td>35%</td>
<td>25%</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>89</td>
<td>781</td>
<td>1.8</td>
<td>31%</td>
<td>8%</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>110</td>
<td>781</td>
<td>1.7</td>
<td>11%</td>
<td>0.5%</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>89</td>
<td>781</td>
<td>1.9</td>
<td>35%</td>
<td>25.5%</td>
</tr>
</tbody>
</table>
The complete evaluated neutron data files for $^{240}$Pu, $^{237}$Np and $^{241}$Am have been created at the IPPE in the energy range up to 150 MeV during the last years in the frame of the Project.

The coupled-channel optical model has been used to calculate the neutron total, elastic, and reaction cross sections and the elastic scattering angular distributions. The parameters of the optical model have been determined on the basis of available experimental data including the recent precise measurements of the total cross sections for $^{232}$Th and $^{238}$U. The calculations based on these parameters describe consistently the available data on neutron and proton absorption cross sections in a wide energy range and enable to evaluate the total and elastic scattering cross sections for actinides with higher accuracy than previous evaluations. Analysis of data has been performed both below and above 20 MeV neutron energy.

Evaluations of the fission cross sections, the secondary neutron multiplicities and spectra, as well as the charged particle production cross sections are performed in the frame of the statistical model that includes direct, pre-equilibrium and equilibrium mechanisms of nuclear reactions. For neutron energies above 20 MeV the evaluation of fission cross sections was obtained using statistical optimization with rational functions. Such approach allows us not only to provide the critical selection of experimental data, but also to determine uncertainties of evaluations together with the corresponding covariance matrix. The description of multiplicity and spectra of secondary neutrons was realized separately for the events with and without fission. The Kalbach parameterization of angular distributions has been used to describe the double-differential cross sections of emitted neutrons and charged particles in ENDF/B-V1 format. The recently published experimental data have been used to estimate more precisely model parameters for charged particle production. The direct and pre-equilibrium pick-up and knock-out mechanisms were taken into account for the cluster emission.

The created files are intensively used now for the comparative analysis of developing accelerator-driven systems.

In order to study the minor actinide transmutation in the high-energy accelerator beams a facility consisting of a lead target surrounded with four sections of uranium blocks has been assembled for neutron flux generation, detecting and control and measuring systems of facility have been prepared, sessions of the lead target irradiation in the proton beam with paraffin moderator have been performed, neutron spectra generated in uranium-lead assembly have been investigated with the help of a set of threshold activation detectors as well as their spatial and energy distribution, the targets with $^{237}$Np, $^{239}$Pu, $^{239}$Pu and $^{241}$Am isotopes have been irradiated by the secondary neutrons produced during the facility irradiation by protons, gamma-spectrometric research of irradiated targets has been carried out in order to measure the mass composition of these isotopes under the influence of the secondary neutron beam, the uranium-lead target experimental conditions have been simulated and comparison of theoretical and experimental results has been presented.

The results mentioned have been obtained when implementing the ISTC Project #1372.
PENETRATION AND LEACHING STUDIES OF RADIONUCLIDES IN CONCRETE AND HARDENED CEMENT PASTE

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2Verein für Kernverfahrenstechnik und Analytik e.V. Rossendorf, Bautzner Landstraße 128, 01314 Dresden, Germany
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Introduction
Decommissioning of nuclear facilities and their conversion into “green fields” entails the accumulation of enormous amounts of building materials, concrete being the major component. Safety aspects impose the need to consider it as nuclear waste, thus placing it within the operative frame of national and international radiation protection guidelines. A costly process for appropriate disposal is strictly dictated for such materials. According to recent investigations, the huge part of nearly 92% of these rest concrete masses from nuclear plants is free of contamination and can be unrestrictedly released for further use [1]. A smaller slightly contaminated part of roughly 6 - 7% is liable to a restricted release but can be modified into an unrestrictedly free subject after proper decontamination. The conception of recycling valuable aggregate from dismantled concrete gains more and more acceptance, since it will save natural resources on the one hand and considerably decrease the high costs of waste disposal on the other. The objective of the present research project is to clarify processes associated with contamination of concretes through water paths and to delineate certain leaching options. Acquisition of basic experimental data will support the development of a regulation framework to establish activity limits after decontamination.

Penetration of radionuclides in concrete
The usual construction material used in nuclear power plants (NPPs) is concrete of the strength class C 30/37. For the investigations in this work, concrete specimens of cylindrical geometry (diameter 10 cm, length 30 cm) having the same compression strength were therefore produced. All pertinent physicochemical properties (porosity, permeability etc.) of the material and transport coefficients were preliminarily characterized. Manufacturing of specimens and experimental setup are extensively described in previous papers [2, 3].

From three principal transport mechanisms in concrete, permeation, diffusion and capillary suction, the latter is a consequence of pressure gradients within the pore system of hardened cement paste and leads to a fast and efficient solution transport in deeper peripheral zones. Capillary suction ceases normally after some weeks and diffusion processes can follow due to concentration differences in the pore solution. The radionuclides utilized in this work were Co-60, Sr-85, I-131, Cs-137, natural uranium and Am-241. After completion of the capillary suction process, the loaded concrete samples were gradually ground up to 10 mm deep and the specific activity in each removed layer was measured. Gamma emitters (Co-60, Sr-85, I-131, Cs-137 and Am-241) were assessed by means of gamma ray spectrometry. For uranium, analysis with an ICP-MS instrument was the preferable way.
The determined activity profiles up to now exhibit a drastic descent within the first 4 mm depth for all elements. Between 4 and 10 mm, specific activity declines slowly one order of magnitude farther (Figure 1). Compared to the other species, caesium profiles in concrete and more significantly in hardened cement paste are notably flatter. Adsorption of caesium on pure quartz aggregate as it is used in this work should be negligible. Besides, potassium shows four orders of magnitude higher concentration in the pore solution and poses the main competitive occupant for active adsorption sites in the hardened cement paste. Stronger interactions of cobalt, strontium, uranium and americium with the cement matrix in concrete lead to a pronounced steeper depth profile [3, 4]. Capillary suction with uranium was performed with two solutions of different concentration. Precipitation of mixed Ca/U compounds adhering on the concrete samples caused rapid decrease of the uranium concentration in the solution and its moderate penetration. Uranium traces detected in 10 mm depth are five times higher than the natural background of non-contaminated concrete.

An exceptional behaviour was observed in the case of iodine with a concentration maximum at 0.7 – 3.0 mm depth. We strongly assume a reverse movement of pore solution during the drying process of the loaded specimens which leads to a concentration build-up in that region. A forthcoming paper will be devoted to the work with uranium, iodine and americium reporting all the experimental details and results.

![Graph showing activity profiles in concrete after three weeks of capillary suction](image)

**Figure 1:** Activity profiles in concrete after three weeks of capillary suction

**Leaching behaviour of radionuclides from contaminated concrete of NPPs**

By processing of dismantled concrete for recycling purposes as it is industrially applied i.e. breaking, sieving and classification, a different activity distribution is anticipated in any collected fraction. There are not yet values available related to an acceptable level of contamination (restricted release) for concrete, as they are for metal scrap. A complete release of radioactive contaminants is therefore assumed as the worst case. Only a thorough
investigation of radioactivity release under conditions prevailing in a permanent disposal site could provide information permitting to revise the above attitude.

Concrete used for the present experiments was contaminated with Co-60 (1.0 Bq/g) and Cs-137 (0.4 Bq/g) and was acquired by a German NPP. Elution procedures of recycled concrete fractions and their conformity with environmental requirements are described by the German norms DIN 4226 and DIN 38414-4. The separated fractions were treated with deionised water and also with aggressive waters (Figure 2) according to the European norm EN 206 (3 g/l Mg\(^{2+}\) and 2.5 g/l SO\(_4^{2-}\)). The leachable amount of Co-60 was estimated between 0.4 and 2.3% and the relative release was observed to be the highest from the 2 - 4 mm fraction. The activity of Co-60 in the eluates is in good correlation with the cobalt content primarily originating from hardened cement paste.

The release of Cs-137 varied between 1.0 and 3.4%. The effect of aggressive waters is significantly stronger in this case. Some fractions seem to be more susceptible to leaching agents as we can see for the fraction >16 mm, where values up to 10% were observed. Cs-137 concentration in the wash solution correlates with the potassium concentration. Despite considerable attack of the concrete matrix by leaching agents, a complete release of radionuclides could not be achieved. Investigations with stronger contaminated concrete and its leachability with weak acidic solutions are underway.

![Graph showing eluted amounts of radionuclides from classified concrete fractions](image)

Figure 2: Eluted amounts of radionuclides from classified concrete fractions

**References**


SORPTION OF TECHNETATE ON MG-AL-LAYERED DOUBLE HYDROXIDE

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Introduction
Due to political decision that there should be no reprocessing of fuel elements in Germany, the direct disposal of spent fuel elements has to be investigated. A possible repository under consideration is a salt mine and the accident scenario for long-term safety analysis is a hypothetical water ingress. Different leaching experiments with (MTR-FE) 1 in high concentrated salt brines at 90 °C showed that the radionuclides were mobilised quickly but then trapped by the corrosion products [1]. Investigations of these secondary corrosion products as a near field barrier to radionuclide migration showed, that one component is a Mg-Al-Cl-LDH, also referred as hydrotalcite[2].

Hydrotalcite-like compounds can be structurally characterised as containing brucite-like layers in which some divalent cations have been substituted by trivalent ions to form positively charged sheets. The cationic charge created in the layers is compensated by the presence of anions in the interlayer. In the free space of this interlayer crystalline water is present too. Layered double hydroxides (LDHs) have received considerable attention in recent years because of their unique layered structures and high anion exchange capacities. Technetium-99, formed in nuclear reactors with a fission yield of ca. 6%, is a long time hazardous radionuclide (half-life = 2.13E+5 years) and like I is of serious environmental concern because it is retarded poorly by geochemical barriers. In the present work, the solid-liquid interactions of TcO4 with a Mg-Al-Cl-hydrotalcite is investigated and the potential of man-made near-field barriers against radionuclide migration.

Experimental
Deionised water was boiled and stored under argon atmosphere to minimise CO2 2 in solution. Chemicals were purchased from Merck and used without further treatment. The pertechnetate solutions used were prepared from a stock solution (0.01M ammonium hydroxide containing 740 μg of 99mTc per mL as ammonium pertechnetate and 1 mg of formaldehyde per mL). All experiments were performed under an argon atmosphere.

For the preparation of Mg-Al-Cl-hydrotalcite 250 ml water was placed in a three necked glass flask and a pH of 10 was adjusted using 2 M NaOH. A mixed aqueous solution of MgCl2·6H2O (0.3M) and AlCl3·6H2O (0.1M) in 250 ml water was added over a time period of three hours while the pH was maintained at 10 by addition of 2 M NaOH. The temperature

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1 The MTR-FE of the DIDO type contains 20 wt% U-Al alloy with an initial enrichment of 80% in 235 U. The fuel alloy plates with a thickness of 0.6 mm (meat) are covered on both sides with aluminium claddings of 0.38 mm, the total thickness is then 1.36 mm. The spent fuel element is disposed in a cast iron POLLUX container.
was maintained at 70°C. After the addition was complete the temperature was raised to 90 °C and stirring was continued for 18 hours. After cooling to room temperature the formed precipitate was filtered and then dialysed at 60 °C. For dialysis a dialysis hose was filled with the substance and placed in 2 L vessel containing deionised water. The water was changed till free of chloride (Chloride measurements were performed with the cuvette test LCK 311, DR.LANGE). The precipitate was filtered and dried in a desiccator. The obtained substances were characterised by photometry, XRD, BET, FTIR and ICP-AES. For XRD and FTIR measurements dry samples were milled to powder. For photometrical and ICP-AES measurements the solid samples were dissolved in 2 M HNO₃.

Time-dependent adsorption processes were studied as follow: To 10 ml water, 100 μl TcO₄⁻ solution (3.99E-07 mol/L) and 0.1g Mg-Al-Cl-hydrotalcite were added in that order. Samples were taken at different time intervals. Adsorption isotherms were carried out by the batch technique. To 10 ml water, 100 μl TcO₄⁻ solution (concentration of TcO₄⁻ ranged from 3.99E-09 to 3.99E-07 mol/L) and 0.1g Mg-Al-Cl-hydrotalcite were added in that order. The effect of pH on the adsorption of TcO₄⁻ was evaluated too. To 10 ml water, 100 μl TcO₄⁻ solution (3.99E-07 mol/L) was added, the pH was adjusted and 0.1g Mg-Al-Cl-hydrotalcite was added. After two days all samples were filtered (450 nm) and the pH was measured. Aliquots of the solutions were analysed with ICP-MS and the concentration of TcO₄⁻ was determined radiometrically by LSC (Packard 2200 Tri-carb). The solids were washed, dried and analysed by XRD and FT-IR. Blank experiments were performed, indicating that the adsorption of TcO₄⁻ on the glass walls was negligible.

Result and discussion

For the synthesised hydrotalcite a Mg/Al mole ratio of 3:1 was determined. Chloride was detected photometrically and the water content obtained by heating at 250 °C was 13.71%. From these results the formula of the Mg-Al-Cl-hydrotalcite can be given as: Mg₃Al(OH)₂C₆H₆₈ (CO₃)₀.₆₃ 2.₄·H₂O. The X-ray diffraction patterns show only sharp 003,006,009,110 reflexes. The obtained lattice parameters c (d003:8.055) and a (d 110: 1.53) agree well with the values found in literature the [3]. The specific surface was found to be 30 m²/g.

![Fig. 1. SEM of the Mg-Al-Cl-hydrotalcite.](image1)

![Fig. 2. Time dependence for TcO₄⁻ adsorption.](image2)

In the IR-spectra, strong bands at 3400 cm⁻¹ and 1635 cm⁻¹ (hydroxylation and hydration) are observed. The Al-O and MgO vibration bands appear in the region 1090 cm⁻¹ to 550 cm⁻¹. A
very weak carbonated vibration band at 1352 cm⁻¹ is present, indicating only a small amount of carbonate. The morphology of the Mg-Al-Cl-hydrotalcite was investigated by SEM (Fig. 1). The sand rose crystal structure, typical of hydrotalcites, is clearly seen. In Fig. 2 the time dependence for TeO₄²⁻ adsorption on the Mg-Al-hydrotalcite is shown. Equilibrium is reached within one day. The pH of equilibrium is 6.5. In the pH range between 4 and 8 the adsorption is not effected by pH (Fig. 3). In Fig. 4 an adsorption isotherm for TeO₄²⁻ adsorbed at pH 5.5 and 25 °C is shown. The isotherm is defined as L-type that characterises a system where the monofunctional adsorbate is strongly attracted by the adsorbent, generally by ion exchange interactions. Furthermore the X-ray diffraction pattern of the complex with TeO₄²⁻ was investigated. There were no significant peak changes, suggesting that the exchange with chloride occurs only at the edges of the layers and that chloride has a higher affinity to Mg-Al-Cl-hydrotalcite. To confirm this consideration first experiments using diluted MgCl₂ solutions were performed. No TeO₄²⁻ adsorption was observed.

![Fig. 3. pH dependence for TeO₄²⁻ adsorption.](image3.png)

![Fig. 4. Adsorption isotherm for TeO₄²⁻.](image4.png)

**Conclusion**

A synthesis of a Mg-Al-Cl-hydrotalcite was performed. The hydrotalcite obtained was pure and all analytical data were determined. Further it was shown, that TeO₄²⁻ adsorbed and equilibrium was reached within one day. The adsorption isotherm can be described as L-type. In the pH range between 4 and 8 the adsorption was not effected by pH. Further investigations including the effect of competing anions are in progress.

**Acknowledgement**

This work is funded by the BMWi (Förderkennzeichen: 02E9803).

**References**


METHODS OF PROCESSING OF Am-INCLUSIVE WASTE
FORMED AT THE CONVERSION OF METALLIC PLUTONIUM

D.G. Kuznetsov, A.A. Minaev, I.B. Popov, V.V. Ivanov, S.M. Baranov

Institute of Physical Chemistry of Russian Academy of Science, Moscow, Russia

The work was conducted under the Project of ISTC №2037p and was concerned with investigation of methods of processing of Am - inclusive waste formed at conversion of plutonium of different genesis in pyroelectrochemical technology. Thus there is a capability re-use saline melts, for example, for extraction of americium allocation. The given technology is waterless, and for this reason can not create any amount of low level radioactive secondary waste, typical for water technologies. This circumstance, according to our reckoning, creates the essential advantages of pyroelectrochemical technology in contrast to water one. Therefore in the present work the preliminary data on the immobilization of the radioactive waste formed in the indicated process are reported. Depending on the origin of plutonium going to processing, three types of phosphate waste are possible.

The type 1 - waste which is obtained in processing of power plutonium. It represents a mixture of iron and REE orthophosphates, approximately 26% and 40%wt., respectively, and the rest are Al, Cr, Mn, Cu, Zn, alkaline and alkaline-earth metals phosphates. In waste there is also B₂O₃. The content of Am in them is 2%wt. The type 2 is the waste obtained at processing of weapon plutonium. They have the following composition: Am – 62%wt., Ga – 34%wt., Pu – 4%wt. The type 3 is the waste obtained as a result of gallium extraction from waste such as 2. It is individual americium phosphate.

In the present work Na - phosphate, Na – fluorine- phosphate, Na –boron- phosphate and Na – boron-fluorine-phosphate matrixes were studied. Besides the methods of the immobilization of actinide waste in different mineral-like and glassy matrix compositions was investigated. The investigation results of phosphate glasses are given in Table 1.

Obviously, the leaching rates of obtained samples on the base of phosphate glassy matrixes, lie within the limit 10⁻⁵ – 10⁻⁶ g/cm² day. Though the phosphate glasses allow including sufficient quantity of Am phosphate - inclusive waste, nevertheless the leaching rate of these glasses is insufficiently low. For this reason in future we shall research the basalt-like matrixes. The researches of matrices were conducted also on the basis of the stone casting (SC) with the addition of boric anhydride.

The leaching rate of boron-basalt matrices for all given compositions has value ~ 10⁻⁷ g/cm² day, that is quite reasonable for the purposes of the immobilization of radionuclides in them. Temperature of synthesizing for obtaining homogeneous glasses of all given compositions, was approximately 1250°C.

These matrices are capable to include up to 40%wt. of phosphate waste. It is quite enough from the point of view of technology. We work furthered with waste obtained from pyroelectrochemical technology of conversion of metallic plutonium (waste 2). In this system glasses containing calcined waste 20-30%wt. and leaching rate ~ 1x10⁻⁷ g/cm² day are obtained. Besides a study was done of the boron-basalt matrices including only americium oxide as waste, for investigation of radiation - physical and chemical properties of the obtained materials. In the present work the chemicals of americium oxide with specific α-activity 2.5. 10¹⁰ Bq/g was used. The calculated power of the α -radiation absorbed dose by samples equals approximately 0.5 MGy/day, average energy of α -particles 5.5 MeV, the
average weight of samples ~2.5 g, geometrical surface ~ 5 cm². The leaching rate of samples, determined radiometrically during 120 day, equals ~ 1x10⁻⁷ g/cm² day.

Table 1. Aggregate state and leaching rate of samples, 10⁻⁶ g/cm² day (conductometry)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Synthesizing temperature, °C</th>
<th>Leaching rate at T syn., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂O P₂O₅ mol.</td>
<td>Na₂O P₂O₅ +B₂O₃ mol.</td>
</tr>
<tr>
<td>15</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>35</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>35</td>
<td>1.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Note: gl – glass; hcf – homogenous crystal fusion; gsc – glass with surface crystallization; cf – crystal fusion; ns – non synthesizing.

Table 2. The leaching rate of samples determined by radiometric measurements, g/sm² day*10⁻⁷

<table>
<thead>
<tr>
<th>Sample, #</th>
<th>Leaching time, day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>5.5</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Essential nuclear - physical feature of boron- containing system, distinguishing it from all others, with the exception of fluorine one, is the considerable flow of fast neutrons generated on boron nucleus through the reaction (α, n). The given circumstance is important enough, since it concern not only radiation safety of technology of waste handling, but also nuclear safety of depository of the radioactive waste inclusive of the fissionable materials. Besides the high neutron flux is also capable to cause activation of materials and equipment of depository, in particular, containers. An estimation of all these circumstances is not a subject of the present activity. Here attempt is made only to obtain the specifications of the possible subsequent analysis. The results are given in Table 3.

It was shown that the neutron flux obtained on boron nucleus is approximately one order higher, than on the other components of boron-basalt matrix nucleus. Last flux basically is determined by interplay of alpha particles with oxygen, silicon and aluminum nuclei and, thus, it is peculiar to any silica-alumina system.

Boron-silicate matrix on the basis of the stone casting but not inclusive boron may be
use as an alternative matrix. The generated neutron flux at application point rather decreases in comparison with boron -inclusive systems. Technological lack of non-boron matrices is more heat indispensable for fusion of components of the mixture (the stone casting + HAW oxides) resulting in homogeneous stony melt. It is approximately 1400°C. It is necessary in technology of the immobilization of the special equipment, for example, "cold" crucible (IFCC).

The stability of the obtained materials to thermal effect (annealing) is also investigated. It was shown that the crystallization temperature of boron-basalt matrixes insignificantly increases the leaching rate of samples. For rather fusible matrices (up to 1200°C) the method of compacting by melting and casting in the forms was applied. For high-melting matrices the method of cold pressing with the subsequent sintering, or the method of hot pressing permitting essential to lower the temperature of compacting process were applied.

The researches conducted earlier in IPC of RAS showed the possibility of the essential decrease of the compacting temperature of ceramic matrices with the help of the addition in the mixture of the fusing components on the basis of the basalt-like materials. The possibility of increase of matrices hydrolytic stability (slowing down of radionuclides leaching from fragments of matrices material in water) by creation of the additional protective barrier at the expense of screening of fragments by a layer of "cold" chemically stable glass-crystalline or glass basalt-like melt of the material was shown.

In connection with a large volume of experimental material in report we present summaries table of optimal compositions and their properties.

<table>
<thead>
<tr>
<th>Composition, % wt.</th>
<th>Wastes (type 1)</th>
<th>Wastes (type 2)</th>
<th>Wastes (AmO₃)</th>
<th>Stone casting</th>
<th>B₄O₃</th>
<th>T synthesis, °C</th>
<th>State of example</th>
<th>Leaching rate, 10⁻⁷ g/sm² days</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>65</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>55</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>-</td>
<td>45</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>20</td>
<td>-</td>
<td>65</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>25</td>
<td>-</td>
<td>60</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>30</td>
<td>-</td>
<td>55</td>
<td>15</td>
<td>1250</td>
<td>Glass</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>20</td>
<td>65</td>
<td>1250</td>
<td>Glass</td>
<td>2.0</td>
<td>Crystal melt</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>20</td>
<td>80</td>
<td>1350</td>
<td>Crystal melt</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Relative neutron fluxes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative neutron flux</th>
<th>Yield, n/Cu per s</th>
<th>Yield, n/Cu-kg. calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AnO₃ (type 3 waste)</td>
<td>1.0</td>
<td>10³</td>
<td>2. 10⁶</td>
</tr>
<tr>
<td>7</td>
<td>60 ± 20</td>
<td>10³</td>
<td>2. 10⁶</td>
</tr>
<tr>
<td>8</td>
<td>8 ± 4</td>
<td>10³</td>
<td>2. 10⁷</td>
</tr>
</tbody>
</table>

Table 4. Temperature of synthesis and properties of various examples
INVESTIGATION OF MATRICES FOR IMMOBILIZATION OF SOME FRACTIONATED RADIOACTIVE WASTE

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Recently in many countries the concept of fractionation of the radioactive waste is accepted. It involves isolation of the ecologically most dangerous long-lived α-active actinide, REE, cesium - strontium fractions etc. It is possible to transfer all remaining radioactive waste in less dangerous middle - and low active waste category.

In this work the immobilization of the ecologically most dangerous fraction of RAW (Cs - Sr) in glassy and mineral-like matrices possessing high chemical stability at reasonable synthesizing temperatures was studied.

As glassy matrices the following systems were investigated: natrium - phosphate, natrium – fluorine-phosphate, natrium – boron-phosphate and natrium – boron- fluorine- phosphate matrix, and also different silica-alumina and lead-silicate compositions with a number of additives.

The systems on the basis of basalts and stone casting from them were investigated. The conducted preliminary researches have shown that the stone casting can be the initial material for creation of the matrix for inclusion of the RAW, and it has definite advantages as contrasted to other rocks.

The influence of various additions on the melting point, viscosity and leaching rate was conducted. As the additions were studied: PbO, NaF, B₂O₃, Fe₂O₃, NaPO₃, CaO, Na₂O, CeO₂ in quantity - 5 – 20 % wt.

On the basis of the earlier conducted numerous researches it was shown, that the concentration of the boric anhydride about 15 % wt. for boron-silicate systems is optimum, from the point of view of the ratio of synthesizing temperature and chemical stability. For this reason an investigation of the system CaO-Na₂O-SiO₂-Al₂O₃-B₂O₃-Ce₂O₃ was conducted at given and identical in all cases contents of the boric anhydride. Its contents varied in limits 5-15 % wt. in matrices CaO and Na₂O. Its contents, for the reasons, mentioned above, were 15-25 % wt. in matrices Cs₂O. This system at 1250°C has the glass forming area at the contents of adamant 20-25 % wt. and silicon oxide of 25-35 % wt. in it. Also it is possible to include up to 25 % wt. of cesium oxide. The leaching rate of obtained glassy matrices lies within the limits 10⁻⁶-5·10⁻⁷ g/cm²·day. In the investigated system glasses will not be obtained at lower temperatures. The increase of the synthesizing temperature up to 1350°C results in obtaining glassy materials with some lower leaching rate, about 5·10⁻⁷ g/cm²·day.

An investigation of the system Cs₂O-PbO-SiO₂-Na₂O-CeO₂ was conducted with identical PbO contents. Its concentration in matrices CaO and Na₂O varied in limits 5-15 % wt. Its contents in matrices Cs₂O, for the reasons, mentioned above, were 15-25 % wt. The given matrix allows inclusion of not less than 20 % wt. of cesium oxide and leaching rate of the obtained materials was 10⁻⁶ g/cm²·day at the contents Cs₂O 20 % wt. The inclusion of cerium oxide in the matrix in quantity ~ 1 % wt. notably increases the chemical stability of the obtained materials.
The investigation of the system SC- $\text{B}_2\text{O}_3$-$\text{Cs}_2\text{O}$ was conducted at a little bit smaller contents of the boric anhydride than in the previous cases, and the introduction of stone casting (SC) instead of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ allows obtaining practically maximum chemical stability.

System SC-$\text{B}_2\text{O}_3$-$\text{PbO}$-$\text{Cs}_2\text{O}$ differs from the previous ones by the addition of the lead oxide in quantity 18-25 % wt., and, in a number of cases, large contents of the boric anhydride. The results are given in Table 1.

Table 1. Composition and state at synthesizing temperature and leaching rate of samples in the system SC-$\text{B}_2\text{O}_3$-$\text{PbO}$-$\text{Cs}_2\text{O}$.

<table>
<thead>
<tr>
<th>Composition, % wt.</th>
<th>State at synthesizing temperature, °C</th>
<th>Leaching rate g/cm² day, $10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>$\text{B}_2\text{O}_3$</td>
<td>$\text{PbO}$</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>35</td>
<td>15</td>
<td>20</td>
</tr>
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<td>40</td>
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<td>45</td>
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<td>35</td>
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<td>25</td>
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<tr>
<td>30</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

In this system, as against previous, observation at synthesizing temperature 1250°C the inclusion of up to 25 % wt. of cesium oxide with formation of glassy matrix is possible. It is reached mainly owing to increase of the boric anhydride content up to 20 % wt. However the leaching rate of the obtained material was $5 \times 10^{-6}$ - $10^{-5}$ g/cm² day.

In the system $\text{SrO}$-$\text{PbO}$-$\text{SiO}_2$-$\text{Na}_2\text{O}$-$\text{CeO}_2$, (see Table 2) as well as in case of the system $\text{Cs}_2\text{O}$-$\text{PbO}$-$\text{SiO}_2$-$\text{Na}_2\text{O}$-$\text{CeO}_2$, glassy matrix is synthesized already at 1100°C. It creates considerable advantages from the point of view of implementation of the manufacturing process. The given matrix allows including ~ 20 % wt. of strontium oxide, and the leaching rate of the obtained materials was about $10^{-6}$ - $10^{-7}$ g/cm² day. The introduction in the matrix of ~ 1% wt. cerium oxide notably increases the chemical stability of obtained materials.

Replacement $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ by the stone casting as well as in case of cesium systems improve the characteristics of the system. On the basis of the investigations, presented in this work, it is possible to make a conclusion, that for the purposes of the immobilization of Cs - Sr fraction of RAW the most reasonable are sodium-lead-silicate and boron-basil system.

In sodium-lead-silicate system the glassy matrix is synthesized already at 1100°C. It creates considerable advantages from the point of view of realization of their synthesizing manufacturing process. The given matrix allows inclusion 20 % wt. of strontium or cesium oxide, and the leaching rate of the obtained materials were $10^{-6}$ - $10^{-7}$ g/cm² day. The results are given in the Table 3.
Table 2. Composition and state at synthesizing temperature and leaching rate of samples in the system SrO-PhO-SiO₂-Na₂O-CeO₂.

<table>
<thead>
<tr>
<th>Composition, % wt.</th>
<th>State at synthesizing temperature, °C</th>
<th>Leaching rate, g/cm² day 10⁻⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100 °C</td>
<td>1200 °C</td>
</tr>
<tr>
<td>SrO</td>
<td>PhO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>55</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>55</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>55</td>
</tr>
<tr>
<td>SrO</td>
<td>PhO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
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</tr>
<tr>
<td>20</td>
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</tr>
<tr>
<td>SrO</td>
<td>PhO</td>
<td>SiO₂</td>
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<tr>
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</tr>
<tr>
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<td>20</td>
<td>53</td>
</tr>
</tbody>
</table>

Cerium oxide in quantity 1 % wt. in the matrix notably increases the chemical stability of the obtained materials. In this system the materials possessing the least leaching rate, are synthesized at 1250°C. The decrease of synthesizing temperature due to change of the ratio SrO or CeO₂ and Na₂O in the system results in a noticeable decrease of hydrolytic stability of matrices, which is their weakness. Probably, further investigations of these systems will allow eliminating this drawback.

Table 3. Composition and state at synthesizing temperature and leaching rate of samples in the system SC·B₂O₃·PhO·SrO.

<table>
<thead>
<tr>
<th>Composition, % wt.</th>
<th>State at synthesizing temperature, °C</th>
<th>Leaching rate, g/cm² day 10⁻⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1050</td>
<td>1150</td>
</tr>
<tr>
<td>SC</td>
<td>B₂O₃</td>
<td>PhO</td>
</tr>
<tr>
<td>60</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>50</td>
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FABRICATION AND CHARACTERIZATION OF INERT MATRIX AND THORIA FUEL FOR ACTINIDES TRANSMUTATION

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In using nuclear energy in the uranium fuel cycle, Plutonium (Pu) and so-called minor actinides (MA) such as neptunium (Np), americium (Am) and curium (Cm) are produced in addition to the fission products. The strategies currently pursued involve the partitioning of uranium and plutonium by the reprocessing of spent fuel elements for use as Pu/U-mixed oxide fuel (MOX) or the direct final disposal of the spent fuel elements after interim storage. In contrast to the predominantly short-lived fission products (<300 years), the long-lived MAs as well as Pu dominate the toxicity potential of the waste over long periods (>10^5 years). The selective partitioning of MAs from the fission products and separate treatment can considerably improve long-term safety. At present, strategies are being discussed world-wide to “burn” the MAs as well as Pu in special reactors, i.e. using thorium based fuels, or accelerator-driven subcritical systems and thus transmute them into short-lived fission products.

Many different types of fuels or targets for transmutation of actinides have been suggested in recent years, mainly depending on fuel cycle strategy considerations. One of the most interesting is the use of dedicated fuels/targets, which have a high content of MAs and are free of uranium. In this case, the production of actinides is limited; a non-fissile (inert) matrix may so be advantageous as support or diluent of the actinides phase.

A limited number of compounds can be used as a host phase for the actinide oxides in so-called inert-matrix oxide fuels (IMMOX), such as ZrO₂ [1-3]. The attractive properties of this material are the small neutron capture cross sections of the components, the high melting point, the high radiation stability and the high chemical stability. Yttria-stabilised zirconium oxide is considered because with the addition of Y₂O₃ the cubic fluorite lattice of ZrO₂ can be partially or completely stabilised down to room temperature. Moreover, the addition of yttrium increases the actinides solubility[1].

A ThO₂ based ceramic also seems to be promising from the waste minimisation point of view. In fact by using thorium as support for burning of plutonium in PWR, the actinides production is very low and so the consumption rates of plutonium are much higher than in MOX. [4]

In this context, simulated fuel pellets have been produced and characterized to investigate the possibility of fabrication of zirconia and thoria based fuel for transmutation and to evaluate the impact of a large addition of plutonium (simulated by Ce) and MAs in the properties of matrices.
Thus (Zr, Y, Ce)O$_2$, and (Th, Ce)O$_2$, powders, with a wide range of Ce (from 0 to 100 %), were synthesized by co-precipitation method with ammonia [5]. Thermal behavior of the powders was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The crystal structure of the powders was investigated by X-ray diffraction. After the optimization of the compaction and sintering parameter, materials have been synthesized and their morphological structure investigated by scanning electron microscopy (SEM) coupled to an Energy Dispersive X-Ray analyser (EDX). The mechanical properties of pellets were also investigated.

(Zr,Y,Ce)O$_2$$_x$ powders were dried at 110°C, calcined at 600°C and ground by attrition in acetone. Pellets with densities up to 0.97 TD have been synthesized. The SEM investigations reveal that pellets compacted from dried powder have the best microstructure. The materials have a homogeneous structure, well-formed grains and boundaries and uniformly distributed pores mainly located at triple grain boundary junctions and inside the grains. Moreover, according to EDX investigations at the surface of the pellets, it can be affirmed that the elements are uniformly distributed in the material. (Th,Ce)O$_2$ pellets have been synthesized with densities up to 0.94 TD from powders calcined at 400°C without grinding nor milling. Investigations on the structure and mechanical properties of the pellets are under way.

References

RETENTION OF ANIONIC RADIONUCLIDES
BY ORGANOPHILIC CLAYS IN AQUEOUS SOLUTIONS

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The safe disposal of radioactive waste requires a well elaborated system of barriers including technical, engineered and geological barriers. Clays have been proposed as host rock and as a principal component of barrier and backfill materials. They are characterized by high plasticity, low hydraulic conductivity, excellent sorption capabilities for cations, but they are generally ineffective in adsorbing anions. The weak sorptive capabilities of clays for anionic radionuclides (like iodine, selenium and technetium) can be improved substantially by replacing the natural inorganic interlayer cations of the clay with organic cations of certain chemical structures. The resulting organo-clays are capable of sorbing non-ionic organic compounds [1, 2, 3] as well as iodine and technetium [Bors, 1990, Riebe et al., 2001].

As different geological formations have been proposed as host rocks for waste repositories, backfill and barrier materials would be exposed to a number of impacts, which are typical for the geological formation and the type of waste under normal operation as well as under accidental conditions.

Our present work focuses on the sorption of anionic radionuclides by organophilic clays under the influence of different aqueous solutions up to high-molar saline solutions, which are adapted to naturally occurring brines in rock salt formations. Three clays are used, modified by adding certain organic cations in amounts corresponding to 200% of the CEC of the clay. The cations are hexadecylpyridinium (HDPy⁺), hexadecyltrimethylammonium (HDTMA⁺), Benzethonium (BE⁺) and 1,12-dipyrindiododecan (DPyDD⁺). Their structures are given in Fig. 1.

Fig. 1: Structures of the organic cations used for preparation of organophilic clays.
Iodide sorption experiments are performed applying the batch technique. In a first step, organo-clays are exposed to the electrolytic solution, representing a certain impact scenario, and then iodide is added to the solution simulating radioactivity releases from the corroded waste container. Sorption is quantified by the technically very practical term of a sorbed fraction of the iodide available per kg of organo-clay (relative sorption in %).

Figure 2 shows results for iodide sorption by MX-80 Wyoming-bentonite, treated with HDPy⁺ (HDPy⁺-MX-80), and exposed to different solutions: bidistilled water, synthetic ground water (SGW), sea water with half of the ionic strength (SEA/2), paragenetic equilibrium solution of a rock salt formation (IP-21) and saturated sodium chloride solution (NaCl). The sorption of radiiodide is lower with higher ionic strengths of the solutions. However, organophilic clays remain capable of sorbing iodide even in the presence of extremely high amounts of competing anions, which is an important safety feature regardless of the repository location.

![Graph showing iodide sorption by MX-80](image)

**Fig 2:** Sorption of iodide by MX-80 bentonite, treated with HDPy⁺, in solutions of different ionic strengths.

Clays modified with BE⁺, HDTMA⁺ or DPyDD⁺ exhibit a relative iodide sorption of about 35 to 75 % in IP-21 and NaCl solution, respectively. Smectites (MX-80, Bentonite TP) are more efficient, when combined with HDTMA⁺ or BE⁺, whereas the Russian vermiculite produces better results with DPyDD⁺.
References


POROUS ZIRCONIUM CARBIDE-BASED INERT MATRIX FUEL
DEVELOPED FOR FAST REACTORS TO DISPOSE OF PLUTONIUM
AND MINOR ACTINIDES

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In-pile reprocessing of radioactive waste produced from nuclear power engineering, i.e. a
closed fuel cycle, is the most attractive way of reducing waste radiotoxicity. The method is
based on utilization of plutonium and minor actinides – neptunium, americium and curium
recovered from spent fuel – as fresh fuel for fast reactors. Its advantage is an additional
electricity to be generated by burning up plutonium and minor actinides stored. Of great
interest is uranium-free plutonium inert matrix fuel (IMF).

The authors have studied a composite based on a porous zirconium carbide frame with heavy
nuclides introduced into pores as a variant of such fuel. The porous zirconium carbide-based
inert matrix fuel of frame type shows a unique combination of thermophysical, physical-
mechanical thermodynamic and radiation properties, including a high melting point of
3500°C, an increase in conductivity with increasing operating temperature as well as
chemical, thermodynamic and radiation stability. Such a fuel has its good points: easy
fabrication and versatility. Reactors operated on this fuel type are expected to have a negative
sodium void effect of reactivity, which makes it possible to introduce minor actinides in great
amounts (up to 30-40%). Requirements on characteristics of the porous zirconium carbide
frame-based IMF for the operating BN-600 fast reactor have been specified from our
calculations performed. According to the calculation, 60 kg/year $^{237}$Np can be transmuted in
the BN-600 reactor. With plutonium fuel doped with $^{238}$Pu from $^{237}$Np transmutation,
weapons-grade Pu is unsuitable for military purposes, and around 200 kg weapons-grade -Pu
can be burned up.
Fig. 1. Basic schematic for fabricating fuel composites of ZrC-PuO₂ and/or minor actinide oxides.
With these requirements in mind, a flow sheet shown in Fig. 1 has been developed for fabricating porous zirconium carbide-IMF pellets in the shape of a cylinder. Following this flow sheet, an experimental lot of cylinders containing ZrC + minor actinide imitator (CeO₂) were prepared. The parameters were as follows: cylinders 5.9 mm in diameter and 40-70 mm long, an open porosity of 60-70%, a compression strength of 11-14 MPa. The X-ray diffraction examination evidences the phase composition (fcc, a = 4.691-4.700Å) corresponding to the zirconium carbide stoichiometry.

The fissile component content of the IMF is 20 to 30 g per m of the fuel element, in good agreement with the calculated data.

In the near future a scaled-up lot of porous ZrC-IMF will be produced. It will be irradiated in the BOR-60 reactor and further examined.

References

INHIBITING THE RADIOLYSIS OF BTP-MOLECULES BY ADDITION OF NITROBENZENE

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Nuclear power production not only produces electricity but also long-lived radioactive waste. As an alternative to direct disposal of this waste, separation of the different elements coupled with manufacturing of new fuel or targets from the fissile material in the waste is given some attention. This fuel can then be burnt in reactors or special accelerator driven systems. The separation of radionuclides can be performed using liquid-liquid extraction, used in the PUREX-process, among others. Research in the field of separation of elements in the high-level waste from the PUREX-process has been conducted for instance in the PARTNEW project (2000-2003) and will continue in the EUROPART project (started 2004). One group of molecules feasible for the separation of actinides from lanthanides is derivatives of 2,6-bis (1,2,4-triazin-3-yl) pyridine, BTP [1]. The chemicals used in separation processes for radioactive material will be exposed to ionizing radiation. Therefore, it is interesting to study and develop an extraction system that can withstand relatively large doses without affecting the distribution ratios. This work focuses on the radiolysis of a specific BTP-molecule and the effect of changing the organic diluent.

Part I

Three organic solutions comprising 0.0018 mol/dm³ tetraethyl-BTP, see figure 1, were prepared.

Figure 1. Schematic picture of tetraethyl-BTP

The organic diluent was 1-hexanol in all three samples but in two of the samples 10% per volume of tert-butylbenzene and nitrobenzene were added, respectively. The solutions were transferred to glass flasks, which were sealed by a lid. These flasks were placed in a gamma-irradiating cobalt source (Gamma cell 220 from Atomic Energy of Canada Ltd) with an activity of 0.99 TBq ⁶⁰Co and an estimated dose rate to water of ~40 Gy/h. The flasks were connected via tubes to a bubble flask to avoid any pressure build up. As a reference, three vials containing solutions of the same composition were placed outside the gamma source during the irradiation time. Samples were taken during a time period of ~500 h. At each sampling two samples of 0.5 ml were taken from each of the three flasks containing BTP and only one sample of 0.5 ml from each of the three reference vials.
The samples were contacted with 0.5 ml of an aqueous phase containing trace amounts of $^{243}$Am, 0.99 mol/dm$^3$ NaClO$_4$ and 0.01 mol/dm$^3$ HClO$_4$. The contact time was 5 min, shaking vigorously by hand. After contact the phases were separated by centrifugation for 15 min at 2000 g and aliquots of 100 µl were taken from each phase for gamma measurements in a Na(Tl) detector (Intertechnique Gamma Counter 4000).

The distribution ratios (D) observed show that the extraction decreases with increasing dose to the solutions. There is also a big difference between the solution containing 10% nitrobenzene and the two other solutions, see figure 2. The solution containing nitrobenzene does not show the same rapid decrease in americium extraction, indicating that nitrobenzene somehow inhibits the degradation of BTP. None of the reference solutions shows any significant reduction in americium extraction.

![Distribution ratios of americium as a function of dose to irradiated samples.](image)

Figure 2. Distribution ratios of americium as a function of dose to irradiated samples.

*Part 2)*

Noting that nitrobenzene somehow inhibited the radiolysis a new experiment was conducted. New organic solutions were prepared, similar to those used in part 1, containing BTP dissolved in 1-hexanol with different amounts of nitrobenzene, ranging from 0 to 10% per volume, see figure 3. The organic solutions were transferred to glass vials, which were sealed with a lid and parafilm. These vials were placed in the same Co-source as was used before. Along with the vials with BTP were two vials without BTP, containing samples of pure nitrobenzene and a mixture of 10% per volume of nitrobenzene in 1-hexanol, respectively. Samples were taken during a time period of ~500 h. At each sampling two samples of 0.5 ml were taken from each of the eight vials containing BTP and one sample of 0.5 ml from each of the other two vials.

The samples containing BTP were contacted with an aqueous phase containing americium, according to the method described in part 1, and distribution ratios were measured. These measurements show that there is an impact on the BTP degradation depending on the amount of nitrobenzene added to the system, see figure 3. It is, however, unclear if there is a saturation level where any extra nitrobenzene will make no difference to the degradation.
The samples without BTP were used for spectrophotometric studies. 10 μl of each sample was taken and diluted a factor 100 000 and 10 000, for the samples containing pure nitrobenzene and 10% nitrobenzene in 1-hexanol respectively, with 10 ml with 95% EtOH. From this solution ~1 ml was withdrawn for measurements on a spectrophotometer (Perkin Elmer Lambda 19 UV/VIS/NIR using a 1 cm quartz cells).

The results from the spectrophotometer studies showed no differences in the spectra of nitrobenzene between different doses. This may indicate that the nitrobenzene is not destroyed during irradiation of the solution containing nitrobenzene and 1-hexanol.

The full mechanism behind the radiolysis of BTP and stabilisation effect of nitrobenzene is not yet fully understood but may include complexation between the -OH-radical and nitrobenzene [2]. Nitrobenzene may also act as a scavenger of the solvated electrons [2]. The influence of the aromatic ring alone seems to have little impact on the stabilisation effect since tert-butylbenzene was unable to stabilise the BTP-molecule. A more thorough explanation of the mechanism will be presented during the NRC6-conference.

References


EXTRACTION OF ACTINIDES, FISSION PRODUCTS AND CORROSION PRODUCTS FROM SYNTHETIC HIGH LEVEL LIQUID WASTE WITH DIMETHYL-DIOCTYL-HEXAETHOXY-MALONAMIDE (DMDOHEMA)

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During the last decades partitioning and transmutation (P/T) of nuclear waste has been studied rather intensively as a way to decrease the need for long term storage. In P/T the High Level Liquid Waste (HLLW) from reprocessing will be partitioned into fractions that can be burnt in nuclear reactors or specially designed accelerator facilities (e.g. Np, Am, Cm) and a fission product fraction that has a rather short half-life, thus requiring storage for less than ~1000 years. When performing these separations it is important to separate the trivalent actinides from the trivalent lanthanides because many lanthanides are neutron poisons which would severely hamper the possibility to burn the actinide fraction. Some early examples of P/T processes are the CTH-process and the TRUEX process. Since these early attempts much effort has been put into the development of new extractants. These extractants are designed to yield larger separation factors e.g. between minor actinides and other elements, and also to be completely incinerable when they have to be disposed off after use in the solvent extraction process, they i.e. contain only carbon, hydrogen, oxygen and nitrogen (the CHON principle).

One of the new processes that is evaluated for possible use to separate minor actinides from fission products in HLLW is the DIAMEX process. It is based on extraction of actinides and lanthanides using malonamides as extractants.

In this investigation, 1 M DMDOHEMA (DiMethylDiOctylHexaEthoxyMALonamide) in TPH (an aliphatic diluent) has been used to extract corrosion products, fission products and actinides from a synthetic HLLW solution. The waste solution has the same composition as the one used for cold tests of the CTH-process, and it was prepared according to Svantesson et al. [1]. It consists of about 30 elements dissolved in 6 M nitric acid. This solution was used to prepare solutions with 1, 2, 3, 4 and 5 M HNO₃ by dilution with water. To make the determination of Fe, Cr and Ni easier, ⁵⁶Fe, ⁶⁵Cr and ⁶⁵Ni tracers were added in the same chemical form as the macro amounts of these elements. In addition, trace amounts of ⁷⁵⁷Np, ²³⁸Pu or ⁹ⁱ⁹Am were added to some samples to gain additional information about actinide extraction. These elements were added as Np(V), Pu(IV) and Am(III).

Four series of extraction experiments were performed:

M1. Synthetic HLLW solutions (1,2,3,4,5,6 M HNO₃)
M2. Synthetic HLLW solutions (1,2,3,4,5,6 M HNO₃) + ⁵⁶Fe, ⁶⁵Cr, ⁹ⁱ⁹Am
M3. Synthetic HLLW solutions (1,2,3,4,5,6 M HNO₃) + ⁶⁵Ni, ⁷⁵⁷Np
M4. Synthetic HLLW solutions (1,2,3,4,5,6 M HNO₃) + ²³⁸Pu

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The contact time was 1 h in all experiments. All extractions were performed in triplicate. After extraction, the phases were separated by centrifugation for 15 min at 2000 g. After phase separation aliquots were taken and analyzed by ICP-MS or radiometrical methods in the following way:

M1: Since the ICP-MS instrument (a Perkin-Elmer Elan 6000) is less suited for measurements of organic phases, the distribution ratios were determined by comparison of the metal concentrations in the aqueous phases before and after extraction. A prerequisite for this method is that no sorption occurs on the walls of the test tubes and also that no significant amounts of material stay at the liquid-liquid interface. This assumption should be realistic under the present experimental conditions, i.e. strong acid solutions containing macro amounts of the metals. This assumption is valid also for the experiment series M2 – M4.

Before the ICP-MS analysis the aliquots were diluted using a 1 M HNO₃ (Suprapur) solution containing 5 ppb of the internal standards Cu, Nb, Ho and Th.

The 31 solutes present in the samples make them a very complicated matrix. In order to study possible interferences between mass numbers another 31 samples were prepared. These samples contained either 6 M or 1 M HNO₃ and each sample lacks one solute. In this way it is possible to estimate interferences at the mass of the missing solute.

The preliminary results are that Zr, Mo, U and the lanthanide elements are extracted with high D-values. The extraction from 1 M HNO₃ is rather low while the D-values are in the range 10 – 100 when using 6 M HNO₃ as the aqueous phase. The other elements in the HLW solution are not extracted to any significant amount.

M2: ⁵⁹Fe, ⁵¹Cr and ²⁴¹Am were all determined by γ-ray spectrometry using HPGe detectors. Both the aqueous and the organic phases were measured. The results are shown in Fig. 1.

![Figure 1. Results for ⁵³Cr, ⁵⁹Fe and ²⁴¹Am](image-url)
M3: $^{239}\text{Np}$ was measured by $\gamma$-spectrometry using a NaI(Tl) detector. Both phases were measured. Thereafter $^{239}\text{Np}$ ($t_1/2 = 2.355$ d) was allowed to decay, and the pure $\beta$-emitter $^{63}\text{Ni}$ was determined by liquid scintillation counting. The results are shown in Fig. 2.

![Graph showing log D vs log HNO3 for $^{239}\text{Np}$ and $^{63}\text{Ni}$](image)

**Figure 2. Results for $^{239}\text{Np}$ and $^{63}\text{Ni}$**

M4: $^{238}\text{Pu}$ was determined by liquid scintillation counting. The results are shown in Fig. 3.

![Graph showing log D vs log HNO3 for $^{238}\text{Pu}$](image)

**Figure 3. Results for $^{238}\text{Pu}$**

A general conclusion from the experiments is that actinides, Zr, Mo and Fe are well extracted at the higher nitric acid concentrations, while the other elements are not extracted to any significant extent. In the conference contribution, the use of ICP-MS for this type of analyses will be discussed together with the obtained results.

SEPARATION OF TRIVALENT ACTINIDES AND LANTHANIDES USING SYNERGISTIC EXTRACTION WITH PYRIDINE BASED LIGANDS

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Separation of chemical elements has during all times been an interesting topic and references may be found from ~3000 B.C., i.e. ion exchange for purification of drinking water. With increasing knowledge the separation methods have become more and more refined. There are many methods used for the separation processes, e.g. pyrometallurgy, chromatographic methods, ion exchange and solvent extraction. Of these the solvent extraction technique is widely used today due to its relative simplicity to scale up and use industrially. The solvent extraction processes have during the last 100 years been successfully used in various areas ranging from the mining industry to the reprocessing of spent nuclear fuel.

In some cases the elements that are to be separated have quite different chemical properties and a relatively simple process can be used. In the case of separation of trivalent metal ions with similar properties such as trivalent actinides and lanthanides the problem is more difficult. The separation of actinides and lanthanides is an important question when considering future alternatives to take care of waste from reprocessing of spent nuclear fuel (partitioning and transmutation/conditioning). To decrease process losses to secondary waste streams it has been suggested that only extracting agents containing carbon, hydrogen, oxygen and nitrogen are to be used (CHON-principle), which further increases the difficulty level. Often synergistic extraction is used, i.e. adding the synergist to e.g. a 2-bromodecanoic acid extraction system in order to increase the extraction and the separation efficiency. Two examples of such synergists are 2,2':6',2''-terpyridine and 2,6-bis-(benzoxazolyl)-4-dodecyloxylypyridine.

Figure 1. Left: 2,2':6',2''-terpyridine (TERPY), middle: 2-bromodecanoic acid (HA) and right: 2,6-bis-(benzoxazolyl)-4-dodecyloxylypyridine (BODO)

There are, naturally, pros and cons with both the synergists used. TERPY is relatively cheap but protonates readily and is then transferred to the aqueous phase and the extraction becomes thus less effective. BODO, on the other hand, does not protonate to any noticeable extent even in contact with ~7 mol/dm³ nitric acid but is on the other hand custom made and as such very expensive. HA contains other elements than proposed by the CHON-principle, but may be replaced by more expensive alfa-cyano acids. The separation factor (SF) is often used to describe the efficiency in separation. It is the ratio of the distribution ratios for the two metals.
studied. Using the ligands described above good separation between actinides and lanthanides can be achieved. The bond to nitrogen is of a more covalent nature for actinides than it is for lanthanides, making this separation possible. The separation factors obtained for the two synergistic systems are shown in Table 1.

Table 1. Separation factors obtained using HA as extracting agent and TERPY or BODO as synergist

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<td>SF Am/Eu</td>
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<td>SF Am/Cm</td>
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Investigating Table 1 it may seem that TERPY is as good as BODO in separation, but one must remember that the results shown there are the best obtained for the TERPY system, which has been extensively studied. For BODO it is merely a result obtained for a more or less arbitrary system and no attempts have been made to optimise this system.

Extraction experiments using a synergistic mixture of TERPY and HA indicate that there is a significant difference in distribution ratios using different organic diluents, but the separation factor is independent of the organic diluent [1].

One factor that affects the separation efficiency is the nitrate ion concentration. This is due to the fact that actinides and lanthanides form nitrate complexes of different strengths. Using stability constants obtained from [2] it has been possible to calculate the changes in separation factors as a function of nitrate concentration, see Figure 2.

![Figure 2. Separation factors as a function of nitrate ion concentration (298 K, constant ionic strength 5 mol/dm³)](image-url)
The effect of the ratio of the synergist to 2-bromodecanoic acid has also been investigated [3, 4].

![Figure 3. The effect of the ratio of the synergist and the extracting agent on the distribution ratios.](image)

From Figure 3 it is clear that the synergistic extraction is increasing with increasing HA-concentration up to a certain level, approximately 0.5 mol/dm$^3$, but decreases when a higher HA concentration is used. This might be due to some changes in the extraction mechanism, a change of the polarity of the solution, or that the influence of the extraction with only HA is starting to be more significant. Preliminary results from test at different temperatures indicate also a change of mechanism at 0.5 mol/dm$^3$ HA.

References


DETERMINATION OF STABILITY CONSTANTS OF LANTHANIDE NITRATE COMPLEX FORMATION USING A SOLVENT EXTRACTION TECHNIQUE

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For lanthanides and actinides the nitrate complex formation is an important factor when considering reprocessing of nuclear fuels and in studies connected with partitioning and transmutation conditioning. In these processes it is common that the base electrolyte is rather strong nitric acid, about 6 mol/dm³. It has been shown earlier that at these concentrations nitrate complex formation of trivalent actinides and lanthanides are abundant. The strength of the nitrate complex formation is different between lanthanides and actinides, a feature that assists in the separation of the two groups, which otherwise can be a quite difficult task. This paper deals with the nitrate complex formation of eleven different lanthanides: La, Pr, Nd, Pm, Sm, Eu, Gd, Dy, Ho, Er and Lu using custom made radionuclides in combination with a solvent extraction technique.

2,6-bis-benzoxazolyl-4-dodecyloxylypyridine (BODO) is a pyridine based nitrogen containing ligand, which extraction abilities have been tested earlier [1]. It has also been used in previous studies of nitrate complex formation [2]. The extraction of lanthanide ions into an organic phase consisting of tert-butylbenzene (TBB), 2-bromodecanoic acid (HA) and BODO as a function of nitrate ion concentration in the aqueous phase can be studied in order to model the stability constants of the nitrate complex formation. When the nitrate ion concentration is increased in the aqueous phase the nitrate complex formation starts to compete with the extraction of lanthanide ions. Thus a decrease in extraction can be measured and modelled using the stability constants of the nitrate complex formation.

The aqueous phases consisted of trace amounts of lanthanide ions, a hydrogen ion concentration of 0.01 mol/dm³ and 5 mol/dm³ salt solution (total ionic strength, either nitrate or perchlorate ions). For neutron activation of Dy, Lu, Er and Nd aliquots of the aqueous solutions were irradiated at the TRIGA Mainz research reactor for one hour at a neutron flux of 7 x 10¹⁰ cm⁻² s⁻¹ to produce suitable amounts of tracer activities of ⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶⁰⁰⁶
detectors use had efficiencies of 29.2% and 24.0% and resolutions of 1.70 and 1.69 keV (at $^{60}$Co, 1332 keV), respectively. The measurement times were adjusted to optimise the influence of statistical uncertainties.

Once the relationship between the extraction performance and the nitrate ion concentration in the aqueous phase is known it is easy to model the stability constants of the nitrate complex formation with the following equation:

$$D_M = \frac{D_0}{1 + \sum \beta_i [NO_3^-]}$$

where $D_M$ is the distribution ratio of a metal ion M, $D_0$ is a constant describing the distribution of the metal in absence of nitrate ions and $\beta$ are the stability constants. An example of an extraction curve for this system is shown in Figure 1. The stability constants obtained from the fit shown in Figure 1 are given in Table 1

![Figure 1](image)

**Figure 1.** Distribution ratios of Eu and Pm as a function of nitrate ion concentration.

<table>
<thead>
<tr>
<th></th>
<th>$D_0$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm</td>
<td>0.09±0.001</td>
<td>1.20±0.05</td>
<td>0.24±0.01</td>
</tr>
<tr>
<td>Eu</td>
<td>0.06±0.0004</td>
<td>1.33±0.05</td>
<td>0.13±0.04</td>
</tr>
</tbody>
</table>

The final results for the different lanthanides studied are not yet finished but will be presented at the conference and in the final paper.
References


EXTRACTION SEPARATION OF AMERICIUM(III) FROM LANTHANIDES(III) with N, N, N', N'-TETRAKIS(2-METHYLpyRiDYLyL)ETHYLENEDIAMINE (TPEN) AND DERIVATIVES

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It is well known that separating trivalent actinides (An(III)) and lanthanides (Ln(III)) is one of the most challenging issues because of their similarity of chemical properties. From the viewpoint of the application to practical process, it has been of great importance in the field of nuclear fuel cycle. Transmutation is a technology aimed to reduce dramatically high level waste (HLW) from reprocessing process of spent nuclear fuel. Long-lived radioactive nuclides in HLW, such as actinides, will be converted to short-lived ones by the technology using high energy neutron. However, lanthanides, whose total amount corresponds to up to 30 times that of actinides in HLW[1], adversely affects on the efficiency of the transmutation of actinides, because these elements absorb a large proportion of neutron. Therefore, the separation of An(III) from Ln(III) is one of the essential subjects to establish the transmutation technology. One rational approach for the separation of An(III) is to use a soft-donor extractant based on its preferable coordination to softer An(III). Nitrogen-based soft-donor extractants have been recently attracted attention as a means of establishing a new sustainable separation process which has the feature of secondary waste free based on the combustibility of the extractant[2]. As a result, considerable efforts have been devoted to the development of new nitrogen-donor extractants for separating An(III) from Ln(III)[3].

One of the successful example is 2,6-di(5,6-dipropy1-1,2,4-triazin-3-yl)-pyridine (BTP) and its analogues which have good selectivity between Am and Ln(III) without any co-extractant[4]. However, the chemical instability of BTP and its analogues is still a matter of concern.

Jensen et al. reported that N,N,N',N'-tetraakis(2-methylpyridyl)ethylenediamine (TPEN) demonstrates 100-fold preference for Am over Ln(III) from the difference between stability constants with these metal ions in the aqueous phase[5]. TPEN is a hexadentate ligand which has six soft-donor sites as a kind of podand type molecule and can encapsulate a metal ion.(Figure 1) We have reported that Am(III) was selectively extracted from the aqueous phase containing Ln(III) by TPEN in nitrobenzene as Figure 2[6]. From the point of view of
the application of this extraction system in the nuclear fuel cycle, an aliphatic or alcoholic solvent is more preferable to nitrobenzene because of the toxicity of the latter. Recently, we also reported that Am is separated effectively from Eu by a synergistic extraction system with TPEN and a higher fatty acid, decanoic acid, diluted with 1-octanol. Based on the results, we have been investigating Am(III)/Ln(III) separation by TPEN and some derivatives which are improved the chemical and physical characteristics, such as hydrophobicity and extraction behaviors of pH dependency. In the presentation, the structures of complexes of Am(III) and Ln(III) with TPEN and some derivatives will be shown, and extraction behaviors of Am(III) and Ln(III) by the derivatives of TPEN will be discussed.

Figure 1  \( \text{N,N',N'-tetrakis(2-methyl pyridyl)ethylenediamine (TPEN)} \)

Figure 2  The pH dependence of \( D_{\text{Am}} \) and SF \( \text{Am/Eu}^{2+} \).  
Aq.phase: 0.1MNH4NO3 spiked with \( ^{241}\text{Am} \) and \( ^{152}\text{Eu} \),  
Org.phase: 1.0mM TPEN in nitrobenzene

PRELIMINARY STUDIES ON THE REPROCESSING OF ADVANCED HEAVY WATER REACTOR (AHWR) SPENT FUEL

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A large potential exists for the resource conservation through exploitation of thorium as fertile material for nuclear fuels. This is particularly true for India as it possesses one third of the proven world thorium reserves. Advanced Heavy Water Reactor (AHWR) is being developed in India with the specific aim of introduction of thorium-based fuels. In this reactor, (Th, Pu)O₂ and (Th, ²³⁴U)O₂ with fissile content as high as ~4% are proposed to be used as the fuel material. Reprocessing of AHWR fuel would be quite challenging in view of the presence of ²³⁴U, Pu and large concentration of thorium along with fission products in the feed solution. Tributyl phosphate (TBP) has been successfully used for the reprocessing of spent fuel as well as irradiated thorium in PUREX and THOREX processes respectively. However, the chemical / radiolytic degradation, large volume of secondary waste and third phase formation due to co-extraction of Th during reprocessing of irradiated thorium puts a serious limitation on the use of TBP. High molecular weight N, N dialkyl aliphatic amides have been identified as potential alternate extractants of actinides. Apart from their desirable extraction behaviour, amides offer distinct advantages over TBP, viz. (i) their radiolytic and chemical degradation products, mainly carboxylic acids and amines, are innocuous; (ii) their complete incinerability leading to reduced volume of secondary waste, and (iii) ease of their synthesis on a larger scale [1,2]. AHWR spent fuel solution is expected to contain 200g/L Th + ~0.05 M F + 0.1M Al(NO₃)₃ at ~3.5M HNO₃.

The present paper deals with the distribution studies U, Pu and Th under simulated AHWR spent fuel conditions using TBP as extractant. In addition, N, N dialkyl amides (straight as well as branched chain) were evaluated as alternate extractants in the above-mentioned feed solution.

Fig.1 shows the extraction data of U(VI), Pu(IV) and Th(IV) obtained as a function of TBP concentration (5-30% solutions in n-dodecane) under proposed AHWR feed conditions. As expected, distribution ratio (Dₐ) values increased with TBP concentration. At 200g/L. Th₃, marginal decrease in Dₐ values was observed at all

![Graph showing variation of Dₐ with TBP concentration.](image-url)
TBP concentrations as compared to those at 100g/L Th for Th(IV) and U(VI) due to thorium loading of the organic phase (Fig.1). These studies suggested that 5% TBP could be used for selective U/Pu removal (D_U; 0.04, D_Pu; 1.4, D_Th; 2.6).

In order to optimise the conditions for selective extraction of U(VI) and Pu(IV) from the feed solution, the effect of feed acidity (1 - 6M HNO_3) on distribution behaviour of U, Pu and Th was studied employing 5% TBP / n-dodecane as the extractant. Feed solution used in these studies was 200g/L Th + 0.05 M F + 0.1M Al(NO_3)_3 at varying nitric acid (and uranium) concentration. There was negligible variation in D_Th values in the entire range of acidities (0.033±0.003). On the other hand, D_U values increased with nitric acid concentration up to 2-3 M HNO_3 and decreased thereafter. Similar behaviour was observed during Pu extraction except that maximum D_Pu was obtained between 4-5 M HNO_3 (Fig.2). There was a decrease in D_U and D_Pu values as the uranium concentration increased from 4 to 8g/L U (taken as representative of fissile materials 233U and Pu) at all acidities. This behaviour was attributed to the increased loading of the organic phase. Typically, for a feed solution containing 8g/L U and 200g/L Th at 4 M HNO_3, the D_U, D_Pu and D_Th values were 2, 1.2 and 0.035 respectively.

![Graph 1: Variation of D_U (U, Pu, Th) with aqueous phase acidity; TH: 300g/L; Extractant: 5% TBP / n-dodecane Temperature: 25°C](image1)

![Graph 2: Variation of D_Th as a function of acidity; Extractant: 5% TBP / n-dodecane; Temperature: 25°C](image2)

It appears that though D_Th value is quite low, significant amount of Th (~6-8g/L) would be extracted during the U/Pu extraction cycle from the feed solution containing 200g/L Th (D_Th; 0.03-0.04). Fig.3 shows the solvent extraction data of U, Pu and Th using tracers as a function of acidity. This study revealed that 4-5M HNO_3 could be used to scrub out Th from
the loaded organic phase ($D_{U}$: 3.6, $D_{Pu}$: 1.3, $D_{Th}$: 0.18). Stripping of U and Pu could be achieved at pH 2 solution and with reducing reagents respectively. On the other hand, 30% TBP was found suitable for co-extraction strategy ($D_{Th}$: 1.5, $D_{Pu}$: 10.4, $D_{U}$: 7.6 at 200g/L) by maintaining organic-to-aqueous phase (O/A) ratio as 7 (Fig.1).

Several N, N dialkyl amides with varying alkyl substituents were evaluated with respect to limiting organic concentration (LOC, g/L) of thorium. 1.1M solutions of amides in n-dodecane were used for this study. LOC was found to increase with (i) total number of carbon atoms, and (ii) carbon chain length on acyl side. Whereas for dibutyl oceanamide (DBOA), LOC value at 3.5M HNO$_3$ was 8.6 g/L (16 carbon atoms); the corresponding values for dihexyl derivatives of octanamide (DHOA) and decanamide (DHDA) were 34 and 48g/L.

Thorium LOC value for 30% (1.1M) TBP at 3.5 M HNO$_3$ was 26g/L. In view of relatively higher LOC of Th in the case of DHOA and DHDA, the effect of aqueous phase acidity (0.01M – 7M HNO$_3$) on Th-LOC was also investigated. Fig.4 shows a gradual decrease in Th – LOC values for both the amides as well as with TBP. Whereas for DHOA, Th – LOC (g/L) decreased from 61 (0.01M HNO$_3$) to 14 (7M HNO$_3$); the corresponding values for DHDA were 64.5 and 20 respectively. This behaviour was attributed to the increase in organic phase polarity with aqueous phase acidity. In view of significant improvement in Th-LOC values for DHOA and DHDA, it is proposed to investigate these amides more systematically.

References


EXTRACTION-ELECTROCHEMICAL SEPARATION OF RARE EARTHS

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Extraction methods based on the achievement of a chemical equilibrium traditionally have received the greatest attention. If the separation factor of the pair of two elements is approaching the value one then the number of extractors in the separation cascade increases infinitely. There is a possibility of increasing the separation factor of elements using nonequilibrium extraction under special conditions. The possibility to increase the elements separation by oscillatory nonequilibrium methods of extraction was shown in [1-5]. It is possible to use the external factors, which are capable of influencing the chemical potential to disturb equilibrium of the chemical system. For the first time in the article [6], it was reported about electrochemical displacement of oscillatory system from stationary equilibrium and from nonequilibrium state to disturb the Ce\(^{3+}\)/Ce\(^{4+}\) ratio in the aqueous phase.

A new separation extraction system was created based on an oscillatory extraction/stripping process in two extractors coupled by a bulk liquid membrane stream (0.5 M tri-butylphosphate in tetradeane). Electrochemical oxidation / reduction were used to induce the cyclic extraction-stripping process. The experimental setup consisting of two extractors is built up. The electrochemical extractor with platinum electrodes with separate cathodic and anodic compartment was used. To separate the emulsion the centrifugal separators ЭЦ33[XE "ЭЦ33"] (EC33) was applied. Absorption spectra of an aqueous and an organic phase were measuring by three diode-array spectrophotometers (two SF 2000-01, and one PMR11) on various wavelengths in a kinetic mode. Two Watson-Marlow[XE "Watson-Marlow"] 205U/CA8 peristaltic pumps, two stirrers HANNA HI313N/D (auto speed), the block of the stabilized current KBNS-4, thermostat TG-TS-01 and three IBM PC, and the assembly rack are the part of the set up. The scheme of this set up is on the Figure 1. Absorption spectra of these three phases, reduction / oxidation potential, temperature in extractors were continuously filed on the hard disks of the computers. The possibility of periodic oxidation and reduction of cerium ions was established. The possibility of using this approach to separate the rare earth elements (REE) was considered. The conditions in which the separation coefficient of the pair Pr/Nd is equal to 6.25 in an organic phase were determined. The test results of separation Pr and Nd from the model solutions and from industrial concentrate of REE from Kola Peninsula is presented.

Acknowledgements: This work was supported by CRDF-DOE grant RCO-20000-SC14.

References
Figure 1 – The schematic of experimental set up.
CHROMATOGRAPHIC SEPARATION OF ACTINIDES AND LANTHANIDES FROM FISSION PRODUCTS ON CMPO/SiO₂-P EXTRACTION RESIN

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Introduction

Since several years, IRI is developing an alternative for the PUREX process, based on chromatographic separations. Next to other advantages, this process shall allow partitioning of the minor actinides.

At SCK-CEN, previous chromatographic experiments using LWR fuel dissolved in concentrated nitric acid, showed that Am and Cm do not adsorb onto the proposed AR-01 anion exchanger and elute simultaneously with the fission products, while U, Pu, and Np are retained quantitatively and can then be further separated and purified [1]. After such a test, the fractions containing Am, Cm and fission products were pooled and loaded onto a CMPO/SiO₂-P column. IRI had prepared this silica-based extraction resin by impregnating CMPO into a styrene-divinylbenzene copolymer, which was immobilized in porous silica particles. Earlier experiments with simulated HLW solutions in nitric acid had revealed that it allows separating the trivalent actinides (Am, Cm) and lanthanides (Ce, Nd, Eu, ...) from fission products such as Cs, Sr and Ru [2]. The present hot cell experiment using real LWR fuel confirms these results.

Experiment

To the freshly conditioned column (CMPO/SiO₂-P column: 500 mm x 10 mm; packing height: 460 mm, temperature: 55°C, conditioned with 200 ml of 6 M HNO₃), the feed (pooled fractions of the AR-01 separation containing Am, Cm and fission products: 63.592 g; φ: 1.192 g/ml) was loaded at a flow rate of 1 ml/min. To avoid the formation of air bubbles during the separation at 55°C, all solutions were degassed during 15 min in an ultrasonic bath, placed in the hot cell. After the loading step, the column was rinsed successively with 50 ml of 6 M HNO₃ (58.750 g; φ: 1.175 g/ml), 150 ml of water, 150 ml of 0.5 M oxalic acid (152.700 g; φ: 1.018 g/ml) and finally with 100 ml of water. During the elution, the flow rate was 1 ml/min. Fractions of 10 ml (time controlled) were collected to obtain the elution profile. Each fraction was sampled, diluted and prepared for analysis by ICP-MS and gamma spectrometry.

Results

The elements of interest were analyzed using ICP-MS (Sr-88, Y-89, Zr-91, Zr-93, Mo-95, Te-99, Ru-101, Pd-105, Ag-109, Cs-133, Ce-140, Nd-145, Eu-153, Am-243, and Cm-244) and gamma spectrometry (Cs-134 &137, Eu-154 and Am-241). We noticed that the described chromatographic procedure separated the multi element solution (LWR fuel without U, Pu and Np) into 3 different groups of elements.
The elements in the first group (Sr-88, Cs-133) showed no interaction with the stationary phase and leaked out with the mobile phase during the loading process (fraction 3 to 8; mass: 77.034 g). More than 50 % of both isotopes were already detected in the effluent at the end of the loading step. And both elements were recuperated quantitatively during the cleaning step with 6M HNO₃.

The elements in the second group (Ce-140, Nd-145, Eu-153, Am-243, and Cm-244) were quantitatively recuperated by elution with deionized water (fraction 15 to 17; mass: 32.152 g). Y-89 eluted in fraction 14 & 15 (mass: 21.625 g).

The elements in the third group (Zr-91 & 93, Mo-95) were recuperated quantitatively in fraction 28 to 32 (mass: 54.084 g) by elution with a 0.5 M oxalic acid solution.

In the second water fraction (between fraction number 38 and 50), no elements were detected anymore, as expected. As yet unexplained results were obtained for Tc-99, Ru-101 and Ag-109.

The gamma ray spectrometric data for the radionuclides Cs-134 &137, Eu-154 and Am-241 corresponded (fraction range and profile) with the results of the ICP-MS analyses for the same elements. The profiles of both Cs nuclides confirmed that there was no interaction with the stationary phase.

**Conclusion**

After removal of U, Pu and Np from a spent fuel solution, extraction chromatography using CMPO/SiO₂-P resin allows to separate the residual solution into three groups of elements: fission products such as Sr & Cs, Am, Cm & lanthanides, and Zr & Mo.

**References**


ROLE OF IRRADIATION IN THE LEACHING OF ALKALI ELEMENTS FROM GLASSES

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The rates of alkali leaching from silicate glasses are controlled by the extent and rate of reactions between aqueous solutions and the glass network. Early stage of alkali leaching is controlled by alkali ion exchange, e.g. by Doremus’ mechanism [1-4]. The duration of the initial stage at low temperatures may be very long, exceeding many hundreds of years for high-sodium content glasses and many thousands years for durable nuclear waste glasses [4]. The Doremus’ mechanism is dominant when the glass network hydrolysis is suppressed, e.g. in silica saturated solutions [2, 4]. A model description of alkali leaching is given by the structural energy barrier model [2], which expresses the alkali exchange rate (mol/m²·s) as:

\[ r_e = \omega \exp(-E_e / RT) \]

where \( \omega \) is the exchange attempt frequency, \( E_e \) is the energy barrier to ion exchange \( M^+ \leftrightarrow H^+ \), \( R \) is the universal gas constant and \( T \) is temperature. The energy barrier is given by formula:

\[ E_e = E_b + E_s \]

where enthalpy \( E_b \) is the bond energy of the alkali M on the NBO site and enthalpy \( E_s \) associated with the distortion of the glass network is the elastic strain energy. For irradiated glasses the rate of alkali exchange can be determined from equation [6]:

\[ r_e = \omega \exp(-E_e / RT) + \phi f(q, D) \exp(-E_e / RT) \]

where \( f(q, D) \) is a function of both dose rate \( q \) and absorbed dose \( D \) of radiation. \( E_e \) is always much lower than the activation energy of thermally induced ion exchange \( E_a \). For example, \( \text{Na}_2\text{O}-25\text{SiO}_2 \) glass holds \( E_a = 33.6 \text{ kJ/mol} \), and a much lower \( E_e = 7.87 \text{ kJ/mol} \), whereas \( 38\text{Na}_2\text{O}-47\text{SiO}_2-15\text{Al}_2\text{O}_3 \) glass holds \( E_a = 48.5 \text{ kJ/mol} \) and correspondingly \( E_e = 8.58 \text{ kJ/mol} \) [2]. For X-ray and gamma irradiation \( f(q, D) \) can be expressed in terms of \( q \) and \( D \) by a fractional exponent law [6, 7]:

\[ f(q, D) = KD^b + W q^a \]

where \( b \) is the fractional exponent \( 0 < b \leq 1 \), \( K \) is a rate-depending constant, \( r \) is the characteristic relaxation time and fractional exponent \( B \) holds its values within an interval \( 0 < B \leq 1 \).

Observed behaviour of alkali leaching from irradiated glasses indicates a faster leaching rate for irradiated glasses the effect being characteristic to short term leaching [5]. New data on leaching of irradiated glasses were obtained in [8] where leaching from actual radioactive borosilicate glasses was about 5 times higher compared to non-radioactive simulants.

Define the relative ion exchange rate \( r_{re} \) by dividing the rate of alkali ion exchange of an irradiated glass to that of an un-irradiated one, e.g. dividing equation (3) by equation (1):

\[ r_{re} = 1 + f(q, D) \exp(E_b / RT) \]
Fig. 1 shows the leaching behaviour of irradiated waste glass PNL 76-68 [9] as a function of temperature.

\[ RT_N \]

Experimental data from D. Wronkiewicz.

Fig. 1. Increase of ion-exchange rate of Na after 14-days irradiation of PNL 76-68 glass (1.75 Mrad/h).

As seen the radiation-induced increase of leaching is most significant at lower temperatures and diminishes with the increase of temperature. From equation (5) we can find the critical temperature \( T^* \) and the inverse dose \((D^*)^{-1}\) below which one can observe the increase in alkali leaching:

\[
T^* = \frac{E_0}{R \ln \left( \frac{1}{f(q,D)} \right)} \quad (6)
\]

\[
(D^*)^{-1} = \frac{K^{1/\beta}}{\left[ \exp \left( \frac{E_0}{RT_{\min}} \right) - W(qr)^a \right]^{1/\alpha}} \quad (7)
\]

where \( T_{\min} \approx 0^\circ \text{C}. \) Fig. 2 shows the alkali ion exchange behaviour of irradiated glasses. It comprises two areas with different impact of irradiation at different temperatures of leaching experiments. At low doses and high temperatures (area I) there is practically no increase in the leaching rate, whereas at high doses and low temperatures (area II) there is a significant increase of ion exchange rate \((nr_{z2})\).
Fig. 2. Alkali leaching from irradiated glasses: radiation-induced effects are significant only in the area II.

As seen for every dose of irradiation there is a critical temperature above which the radiation increase of ion exchange is negligible. For every temperature there is a critical dose of irradiation below which the increase of ion exchange is negligible. Below the critical temperature and above the critical dose the increase of alkali ion exchange rate is significant.

References

PROCESS DEVELOPMENT FOR THE TREATMENT OF RADIOACTIVE WASTE USING ZIRCONIUM SALT OF DIBUTYL PHOSPHORIC ACID DISSOLVED IN 30% TRIBUTYL PHOSPHATE

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Dibutyl phosphoric acid (HDBP), which is TBP degradation product, is an effective acidic solvent when dissolved in diluted TBP and so this solution is of significant interest for application to treatment of liquid radioactive waste. Presence of zirconium in the systems leads to the formation of HDBP zirconium salt (ZHDBP) which can very effectively extract TPE, RE, Sr, Mo and some other elements (but not Cs) from neutral and acidic aqueous solutions. The results of laboratory-scale investigations on extraction equilibria in systems containing ZS HDBP [1, 2] are the basis for elaboration of a process for treatment of HL and IL radwastes. The results of process flowsheet testing are given below.

**Verification of the flowsheet for liquid radwaste treatment in centrifugal contactors**

The experimental verification of the process including joint extraction of RE, TPE and Mo, followed by joint stripping of RE and TPE was realized in the small-scale centrifugal-contactor pilot facility. A variant of process flowsheet (Fig. 1) was tested, which provided for concentrating radionuclides during their extraction, scrubbing and stripping of all the extracted elements; 0.6 mole/L ZSHDBP dissolved in 30% TBP was used as a solvent.

![Flow diagram](image)

Fig.1. Flow diagram of the process for treatment of liquid radioactive waste containing TPE, RE, Mo, Zr and Fe with the use of ZSHDBP (0.6 mole/L HDBP) dissolved in 30% TBP.

1 – extraction cascade; 2 – evaporation unit; 3 – centrifugal separator; 4 – solvent regeneration unit.
Joint stripping of all the radionuclides and accompanying elements together with HDBP was performed with the solution of ammonium carbonate in combination with a complexing agent. Completely substituted ammonium ethylenediamine tetraacetate (NH₄)₂EDTA was used as a complexing agent. The stripping product obtained was concentrated by evaporation.

The extraction of target elements and scrubbing of the solvent product, as well as stripping, were conducted in an eight-step cascade of centrifugal contactors. The feed solution contained 10 mg/L Np, 2400 Bq/L ²³⁷Am, 1500 mg/L RE, 300 mg/L Mo, 200 mg/L Fe. In the extraction unit, ~99.9 % of the Np, Am, RE, Mo and Zr were recovered, and ~90% of the Fe. However, the element concentrating during extraction was limited by the content of iron in the solution to be treated, as Fe-containing precipitates formed in the solvent phase at the concentration of iron above 600 mg/L in this phase.

Joint stripping of the components (including ZS HDBP) was carried out by weak-alkaline solution of salt-free complexants. The resulting strip solution was evaporated to reduce its volume by a factor of 11 (Table 1). Two phases formed after cooling the solution. The volume of the lighter phase (ammonium dibutylphosphate) was 4.5 times greater than that of the heavier one.

Table 1. Distribution of elements between two liquid phases during strip solution evaporation

<table>
<thead>
<tr>
<th>Stripping agents</th>
<th>Evapo-</th>
<th>Organic-to-</th>
<th>Distribution coefficients</th>
<th>Phosphorus in aqueous phase, mole/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂CO₃ +</td>
<td>ration</td>
<td>aqueous</td>
<td>²⁴¹Am</td>
<td>Zr</td>
</tr>
<tr>
<td>0.05 mole/L (NH₄)₂EDTA</td>
<td>ratio</td>
<td>volume ratio</td>
<td>0.14</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The lighter (organic) phase liberates HDBP when scrubbed by nitric acid. The HDBP is dissolved in 30% TBP to obtain the regenerated solvent for reuse.

Waste immobilization to obtain solid products fit for long-term storage and disposal

Borosilicate glasses and mineral-like zirconate-based ceramics were tested to immobilize the bottoms of evaporated strips. The conditions for bottom calcinations were optimized in order to ensure complete destruction of EDTA, simultaneously avoiding sublimation of MoO₃.

The charge mixture with borosilicate matrix was melted in an electric resistance furnace at 1150-1300°C. The fabricated glass specimens are characterized with a reasonable content of the target elements (18-23% oxides of Zr, Mo, RE and TPE) and demonstrate high leaching resistance, comparable with the best standards of ceramics and synrock-type materials.

In the zirconate ceramics, the content of oxides of the target elements exceeds 80% and the leaching rates for Zr, RE and TPE are much lower as compared to glass, the leaching rate for Mo also being acceptable in the presence of Pb (Table 2).

Table 2. Leaching resistance of the best ceramics specimen obtained by pressing at room temperature in air and subsequent specimen sintering at 1300°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxide concentration in specimen, % mass</th>
<th>Equilibrium leaching rate at 90°C, g/m²/day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>7 days</td>
</tr>
<tr>
<td>Nd</td>
<td>24.1</td>
<td>1.7 • 10⁻⁴</td>
</tr>
<tr>
<td>Zr</td>
<td>30.7</td>
<td>&lt;10⁻⁵</td>
</tr>
<tr>
<td>Mo</td>
<td>6.8</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe</td>
<td>3.6</td>
<td>&lt;10⁻⁵</td>
</tr>
<tr>
<td>Pb</td>
<td>14.7</td>
<td>7.2 • 10⁻⁴</td>
</tr>
</tbody>
</table>
Elaboration of the basic process flowsheet

The basic flowsheet of the process has been proposed (Fig. 2), which includes: extraction of radionuclides and accompanying elements with 0.2 - 0.6 mole/l. ZS HDBP in 30% TBP (excluding Cs which should be dropped to the raffinate); stripping of all the elements, extracted from the waste (together with HDBP) using ammonium carbonate solution containing ammonium ethylenediaminetetraacetate (NH₄)₂EDTA; 10-12 fold concentration of the stripping product by evaporation; separation of bottoms in two phases in centrifuge; scrubbing of the organic phase with the weak solution of nitric acid, separation of HDBP and regeneration of the solvent; calcination of the concentrated aqueous products of stripping; joint or separate treatment of calcines and fabrication either as glass or ceramics, depending on the composition of the waste to be processed; joint treatment of the calcines includes their mixing with the furnace charge, the mixture being either melted to obtain a borosilicate glass; in the case of separate treatment, the calcine containing radionuclides is vitrified or converted or pressed and heat-treated to obtain a mineral-like ceramics, while the calcine of the nitrate-containing scrubbing solution is directed to cementation. The flowsheet includes also the step of Cs-containing raffinate treatment to immobilize Cs in zeolite and to cement the residual low-active solution.

![Flowsheet Diagram]

Fig.1. Process flowsheet for radwaste treatment finished with fraction immobilization

The research was performed under ISTC Project #1608. The above flowsheet is approved for optimization and testing with the use of real radwaste, containing actinides, rare-earth elements, Cs and other radionuclides within the framework of the next ISTC project # 2762.

References

10. Radioecology and Environmental Sciences
AN INVESTIGATION INTO THE ROLE OF COLLOIDS AT A LOW-LEVEL WASTE REPOSITORY SITE

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To assess the possible effect of colloids on radionuclide transport in and around the BNFL owned low-level radioactive waste site at Drigg near Sellafield in Cumbria, UK, samples of groundwaters were extracted from the near-field, i.e. from the trenches and from the far-field, i.e. outside the trenches to determine the properties of the groundwaters with respect to the physical characterisation of the waters, colloid population, colloid characterisation and radionuclide leading of colloids.

Experimental
Samples of water were taken anaerobically, at low flow-rates (using a micro-purge low-flow procedure [1]), by use of a submersible pump at depths between 8 and 11 metres below ground level. Conductivity, Eh, pH, temperature, dissolved oxygen concentration (DOC) and iron content measurements were monitored throughout the sampling. Radioactivity measurements of the gross activity (by liquid scintillation counting, Packard 2750 TR/LL using Ultima Gold LLT), tritium activity (by distillation then liquid scintillation counting), gamma activity (by gamma spectrometry, EG & G Ortec GEM series high purity Germanium coaxial detector and an ORTEC Maestro II program) and gross alpha/gross non-tritium beta activity (by gas proportional counter, FAG FHT650K1) were made on each groundwater sample. The samples were ultrafiltered sequentially (12 µm, 1 µm, 30 kD and 500 kD) under nitrogen to separate the size fractions of the particles present into “particulate” (> 1 µm), “colloidal” (1 µm – 30 kD), “small colloidal” (30k D – 500 D) and “ionic (< 500 D). The membranes were analysed for colloid content by SEM (Cambridge Stereoscan 360 with Link System Energy Dispersive Analyser or a LEO 1530VP SEM coupled to an EDAX Phoenix Energy Dispersive analyser). EDS enabled the elemental composition of the colloids to be determined. Microwave acid digestion was used to digest the membranes and the resulting liquor used for radioactivity measurements. The radioactive content of the filtrates were measured.

Results and discussion
For brevity, the results for the trench samples only are discussed. The in-situ measurements (conductivity, DOC, Eh, pH and iron content) taking during sampling showed that the groundwaters contained medium to high total dissolved solids (TDS) (220 – 1000 mg dm⁻³) [2] and that they were pH neutral and reducing. The groundwaters were relatively low in DOC. The iron content was < 17 % of the TDS. Measurements using a Zetamaster S (Malvern
Instruments) showed that the average size of particles in the groundwaters is < 1 μm in diameter, i.e. colloids, and that the particles were negatively charged.

Colloid population.
Colloidal population was determined by counting the number of colloids on a number of different sections of the 30 kD membranes observed by SEM. Colloid population was in the order of $10^9 - 10^{11}$ colloids dm$^{-3}$, which is in agreement with values reported in other work [3].

Colloid characterisation.
The most abundant elements found in the colloids were iron and silicon, which were present in almost all of the colloids analysed. Other (minor) elements identified were Na, Mg, Al, S, Cl, K, Ca, Mn, Ti, Ni, Cr, Cu, and Pb. The results also showed that the elemental composition was the same regardless of particle size. The majority of the particles analysed had a Si:Fe ratio of > 0.5 and up to 15.5% of the colloids analysed were 100% silicon. Colloidal aggregates and single colloids were also compared for elemental composition and were found to show no significant difference to aggregate their tendency to aggregate or remain separate is not a function of their elemental composition. The presence of 100% silicon colloids implies that the majority of colloids are silicon based with an iron coating. The anaerobic to aerobic transition of the groundwaters caused the precipitation of an amorphous red-brown solid produced by the oxidation of Fe(II) to Fe(III).

Activity analyses.
The majority of the radioactivity in the trench groundwater samples was due to tritium and was between $10^2 - 10^3$ Bq dm$^{-3}$. Gross alpha activity levels were generally less than 1 Bq dm$^{-3}$. Gross non-tritium beta and $^{137}$Cs activity levels were of the order of $10^2 - 10^3$ and $10^0 - 10^3$ Bq dm$^{-3}$ respectively. $^{40}$K and $^{60}$Co activity levels were generally below the minimum detectable amount. Seasonal variations were noted in the activity measurements but samples taken from different parts of the same trench showed similar activity levels.

For the trench samples, results showed that there was some decrease in alpha activity due to filtration and some retention on the 1 μm (16%) and 30,000 D (9.8%) membranes. In all samples half of the alpha activity was retained on the 500 D membrane and half was present in the 500 D filtrate. This indicated that half of the alpha activity was associated with the colloidal (1 μm - 30,000 D) size fraction and half was associated with the ionic (< 500 D) size fraction. In contrast, there was little decrease in the non-tritium beta activity with filtration suggesting that the majority of the non-tritium beta activity was associated with the ionic size range. Results also showed that there was little decrease in the $^{137}$Cs activity after filtration. Less than 1% of the activity was retained on any of the membranes. This suggested that the majority of the $^{137}$Cs activity was associated with the ionic size fraction (< 500D).

Once the filtrates and total samples were allowed to go aerobic the activity analyses showed that the majority of the $^{137}$Cs activity remained in the supernatant and therefore was not associated with redox-sensitive colloids. The majority of the $^{40}$K activity was below the minimum detectable amount, 3.8 Bq dm$^{-3}$. Other radionuclides identified, but not at quantifiable levels within samples were $^{210}$Pb ($^{238}$U decay chain) and $^{212}$Pb ($^{232}$Th decay chain). Additional radionuclides present in other samples were $^{138}$Ba, $^{155}$Eu, $^{214}$Pb and $^{214}$Bi ($^{238}$U decay chain), $^{228}$Ac ($^{232}$Th decay chain) and possibly $^{222}$Ra and $^{211}$Bi ($^{235}$U decay chain), $^{216}$Pb ($^{238}$U decay chain), $^{234}$Th and $^{239}$Pu.
Consideration of colloids within the Drigg Post Closure Safety case. Disposals at Drigg are carried out under the terms of an authorisation granted by the UK Environment Agency. The authorisation is periodically subject to formal regulatory review. In September 2002 BNFL produced, an updated post-closure safety case (PCSC) [4,5] supported by a post-closure radiological safety assessment (PCRSA) for the Drigg site. The PCRSA considers the radiological consequences through the groundwater and gaseous pathways, and the possible effects of human intrusion and disruptive events.

The PCRSA considers all features events and processes (FEPs) relevant to the release of radionuclides from the Drigg near-field in a systematic manner [4]. These FEPs include biogeochemical processes of LLW degradation, steel corrosion and cement degradation, which control the chemical environment in the Drigg trenches and vaults and which hence influence the release and transport of radionuclides from LLW. Some of these processes could generate colloids.

The experimental and field work which is reported in this paper indicates that colloidal sized particles are present in the Drigg near field environment under present day conditions. The PCRSA has utilised the results of this characterisation work to model the transport of colloidal sized material bearing radionuclides under post closure conditions [5].

Colloids cannot be directly addressed using the software tools and codes utilised within the 2002 Drigg PCSRA. Therefore BNFL undertook what were called “side calculations” to quantitatively address the potential for radionuclide transport on colloidal phases outside of the main PCRSA calculations. These calculations were undertaken through the GRM biogeochemical contaminant transport code [6]. The code allows for the simultaneous transport of three independent types of colloids. For the purposes of the GRM modelling the Drigg near-field colloids were considered to be composed of clay, quartz or iron oxyhydroxide. Using side calculations, the transport of uranium on colloids was modelled.

Figure 1 illustrates the results for U-234 of the runs with a colloid size of 100 nm and of the extreme case where colloid concentration is raised by 3 orders of magnitude [5]. The presence of colloids has no effect on uranium flux for the runs with realistic colloid concentrations. When colloid concentrations are increased to extreme values then the flux of U-234 during the period up to 5,000 y is increased and approaches that of uncertainty runs investigating high solubilities (case 1c). These results indicate that the impact of colloidal transport on uranium fluxes out of the near field is well within the bounds of the uncertainties associated with other processes affecting radionuclide transport.

Conclusions
The groundwaters sampled from the trenches at Drigg in Cumbria were low in DOC, pH neutral and reducing. They contained 220 – 1000 mg dm⁻³ of TDS of which less than 17 % was due to iron. Particles present in the samples were negatively charged and were less than 1 μm in diameter on average. Colloids were present at populations of 10⁹ – 10¹¹ colloids dm⁻³. Elemental analysis showed that the colloids were predominantly iron coated silica at a ratio of < 0.5. Other elements present were Na, Mg, Al, P, S, Cl, K, Ca, Mn, Ti, Ni, Cr, Cu, Zn and Pb. The activities of the samples were dominated by tritium (10⁴ – 10⁶ Bq dm⁻³). The alpha activities in the samples are only significantly (approximately 50% of the gross alpha activities) retained on the 500 D membrane. The alpha activities distribute between the supernatant and the precipitate once the samples have been allowed to go aerobic. The alpha
activities are associated with both positively and negatively charged species. The $^{137}$Cs and non-tritium beta activities are not retained significantly by any of the membranes and are thus classed as ionic. Up to 24% of the non-tritium beta and less than 1% of the $^{137}$Cs activity is associated with redox-sensitive colloids. The non-tritium beta and $^{137}$Cs activities are associated with positively charged species which should not be mobile within the environment. Radionuclides from the $^{238}$U, $^{235}$U, $^{233}$U and $^{229}$Th decay chains were identified.

Modelling of colloidal behaviour within the 2002 Drigg PCSC demonstrated that the uncertainty introduced by colloidal behaviour was of the same order of magnitude as other modelling uncertainties, for instance that of uranium solubility. However certain features of colloids, such as the reversibility of radionuclide sorption, requires investigation to challenge the conceptual model.

**Acknowledgements**
The authors are grateful to BNFL for sponsoring this work.

![Figure 1. Comparison of total U-234 flux for uncertainty runs investigating the effect of colloids.](image)

**References**
RADIOECOLOGY OF IODINE

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Iodine is a biophilic element and plays an important role in thyroid function. Nearly 90% of iodine is concentrated in thyroid gland in human body. Iodine is essential not only for mammals but also for other animals, such as fish and amphibians. From a radioecological viewpoint, radiiodine is one of the most important radionuclides released from nuclear industries into the environment. Therefore, it is necessary to obtain information on the behavior of radiiodine in the environment for safety assessment.

Two radioisotopes of iodine, $^{129}\text{I}$ (half-life: $1.6\times10^7\text{y}$) and $^{131}\text{I}$ (half-life: 8 d), are specifically important in terms of radioecology. Since the amount of $^{131}\text{I}$ produced in a reactor is much higher than that of $^{129}\text{I}$, the former isotope should be taken into account at the time of a reactor accident. However, $^{131}\text{I}$ decays away within several months of contamination. The long radiological half-life of $^{129}\text{I}$, on the other hand, prevents this nuclide from disappearing, causing it to enter the ecological and geochemical cycles of stable iodine. Interest in $^{129}\text{I}$ is increasing, particularly with regard to the operation of nuclear fuel reprocessing plants. In the UNSCEAR-2000 Report [1], $^{129}\text{I}$ was regarded as one of the most important radionuclides which should be assessed from the viewpoint of global circulation. However, radioecological behavior of iodine is not sufficiently known, mainly due to the lack of data on iodine concentration levels and its complex behavior in the environment. Therefore, it is important to study biogeochemical cycling of both stable and radioactive iodine in the environment for a reliable assessment.

In this paper, we summarize some of our relevant investigations [2-9] as well as new data on radioecology of iodine, specifically on the following points:

1. Distribution of stable iodine and $^{129}\text{I}$ in the environment
2. Transfer of iodine from soil to plants
3. Deposition of iodine from the atmosphere to plants
4. Effects of microorganisms on the volatilization of iodine
5. Cycling of iodine in the global environment (Fig.1)
Fig. 1 Cycling of iodine in the global environment

References
COLLOID-BORNE URANIUM IN AN ABANDONED URANIUM MINE IN THE STAGE OF FLOODING

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Introduction
Abandoned uranium mines which underwent or just undergo flooding may represent a severe source of radioactive contaminants against groundwater and surface water. The uranium mines operated until 1990 in Saxony and Thuringia left a total void volume of more than 100 million m³ to be flooded. Prognosis of radionuclide emission via the water path needs detailed knowledge about the hydrological regime of the mine and the speciation of the contaminants. The adsorption of radionuclides on colloidal phases may stimulate or delay their transport and migration. Neglecting the colloidal phases may have the following consequences on environmental hazard prognosis [1]:
a) The radionuclide is fully mobile, i.e. it is not adsorbed onto solid phases: colloidal transport is irrelevant and the model description is correct.
b) The radionuclide is regarded as fully mobile in the model, but it adsorbs on colloids which aggregate and settle ('natural attenuation'): the prognosis is too pessimistic.
c) The radionuclide is regarded as immobile in the model due to adsorption on the host rock, but in part it adsorbs on colloids which are transported: the prognosis is too optimistic.

Based on their chemical and colloidal composition, mine waters usually range between the following water types:

i) Type ‘acid pore water’ (acid rock or mine drainage, sometimes called ‘yellow boy’): Very acidic (pH 1-3) and usually anoxic waters with a high salt loading.

ii) Type ‘bulk water’: Near-neutral, oxic or suboxic waters with a moderate salt loading, typically represented by gallery or adit water.

Mine flooding is accompanied by transition of type (i) into type (ii) water, which is crucial for colloidal-chemical processes changing the partitioning of heavy metals and radionuclides. Due to pH increase and access of oxygen, colloids of Fe(III) and Al compounds are formed known to adsorb trace metals [2-4].

To assess the uranium migration at the stage of flooding and afterwards, we performed neutralization experiments by mixing acid floodwater from a uranium mine with oxic groundwater from an aquifer above the mine and studied the formation and composition of colloids as well as the adsorption of uranium onto these colloids by using spectroscopic methods.

Experimental
We mixed 5-6 L of floodwater with up to 100 L of groundwater by stepwise addition of 10-20 L aliquots within five days. Bubbling of oxygen produced turbulence and supported the oxidation process. Three batches with final pH values of 4.5-5.0, 5.0-5.5 and 5.5-6.0 were applied. The freshly generated colloids were characterized by SEM, EDXS, ICP-MS, AAS, XRD, PCS, and laser Doppler electrophoresis. Tangential flow 30 kD ultrafiltration followed by centrifugation was used to compact the colloids as a ‘wet paste’. X-ray adsorption fine structure (XAFS) spectroscopy on this paste at the Fe-K and U-LIII edges at the Rossendorf Beamline of the ESRF in Grenoble to identify the atomic short-range order is under way.
Results and discussion
The floodwater was acidic (pH 2.85) and rich in sulfate, iron, aluminum and uranium (Table 1). A fraction of 30% of the iron was ferric iron, predicted by the EQ3/6 code to be oversaturated. The proportion of colloidal Fe rose with progressive Fe$^{3+}$ oxidation and pH increase and was thus a function of both mixing ratio and time. At pH $>$4.5 colloidal Al and U emerged, reaching a proportion of about 60% at pH 5 and about 100% at pH 6 (Fig. 1). The colloid particles with a size of 75-100 nm had zero points of charge of pH 6 and pH 6.5 in the two batches referred to in Fig. 1. This explains their tendency of rapid aggregation due to low electrostatic stability at pH $>$6.0 (Fig. 2). The main constituents of the air-dried bulk of colloids were, besides oxygen, Fe (27-35%), Al (2-6%), and U (0.3-2.1%). XRD spectra of these samples resembled those of ‘two-line ferrihydrite’ (cf. [5]).

Though the experiments are still in progress, they already show that colloids may scavenge and immobilize uranium in oxide mine waters according to the above mentioned scenario b). EXAFS studies will show the uranyl adsorption partners, the molecular structures of the adsorbent(s), and the type of binding of the uranyl onto the adsorbents. Thus they will provide information on the long-term stability of this kind of U(VI) immobilization.

Acknowledgments
This study is supported by DFG (ZA 238/2-1). We thank S. Weiß, C. Fröhlich, U. Schaefer, D. Birstein, E. Christalle, A. Scholz and V. Brendler for their technical and analytical help.

References

Table 1. Analysis of the floodwater from an abandoned uranium mine and the groundwater from a local aquifer above the mine (Eh in mV, conductivity in mS cm$^{-1}$ and concentrations in mg L$^{-1}$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Floodwater</th>
<th>Groundwater</th>
<th>Parameter</th>
<th>Floodwater</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.85</td>
<td>6.50</td>
<td>[Fe]</td>
<td>276</td>
<td>3.2</td>
</tr>
<tr>
<td>Eh</td>
<td>480</td>
<td>290</td>
<td>[Fe(III)]</td>
<td>84.0</td>
<td>0.76</td>
</tr>
<tr>
<td>Cond.</td>
<td>2.09</td>
<td>0.255</td>
<td>[K]</td>
<td>3.8</td>
<td>1.6</td>
</tr>
<tr>
<td>[O$_2$]</td>
<td>0.4</td>
<td>6.6</td>
<td>[Mg]</td>
<td>17.2</td>
<td>3.08</td>
</tr>
<tr>
<td>[DIC]</td>
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<td>15.1</td>
<td>[Mn]</td>
<td>12.4</td>
<td>0.012</td>
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<tr>
<td>sulfate</td>
<td>1260</td>
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<td>[Na]</td>
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<tr>
<td>[Al]</td>
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<td>[Ni]</td>
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<tr>
<td>[As]</td>
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<td>[Si]</td>
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<tr>
<td>[Ca]</td>
<td>122</td>
<td>35.5</td>
<td>[U]</td>
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<tr>
<td>[Cd]</td>
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<td>0.00007</td>
<td>[Th]</td>
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<tr>
<td>[Co]</td>
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<td>0.007</td>
<td>[Zn]</td>
<td>13.0</td>
<td>0.116</td>
</tr>
</tbody>
</table>
Fig. 1. Percentages of colloidal U, Al, Fe, and fraction of Fe(II) (left ordinate) and pH (right ordinate) as a function of mixing ratio (lower abscissa) and course of time (upper non-linear abscissa) in two batches of acid floodwater mixed with oxic groundwater up to a final pH of 5.0-5.5 (a) and 5.5-6.0 (b). The colloidal fraction was identified by 3 kD ultrafiltration.

Fig. 2. SEM image (30000 x) of colloidal particles and aggregates in the first batch and pore of a 1 μm filter membrane.
SURFACE COMPLEXATION MODELING OF ACTINIDE BINDING TO COLLOIDS

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Colloidal particles are ubiquitous in natural systems but their role in radionuclide migration is not understood till now for effective transport modeling. It is very likely that colloid-facilitated transport is the primary mechanism of environmental migration of low-soluble radionuclides, for example Pu, Am, etc. Kersting and co-authors [1] showed that Pu and other low-soluble radionuclides were transported with colloids over the distance over 1 km in a saturated system at the Nevada Test Site that is sufficiently higher than values predicted from the formal thermodynamic modeling that utilize Kd-concept. Surface complexation data can appear to offer the foundation for the models that quantify the effect of colloids on radionuclide transport.

Several natural and synthetic colloidal phases were taken to study Pu and Np sorption with subsequent surface complexation modeling including α-FeOOH, α-Fe2O3, γ-Fe2O3, σ-MnO2 (Ca, Mn(II))O3-Mn(IV)O2, bentonite clay and humic acids. Colloidal phases were characterized by powder XRD, potentiometric titrations, SEM, BET surface analysis including porosity measurements.

Actinides were taken initially either in pentavalent or tetravalent form and sorption was studied as a function of time, pH, ionic strength and metal concentration. Redox speciation after the sorption was studied by solvent extraction for tracer levels of radionuclides and X-ray photoelectron spectroscopy for macroconcentrations. The actinide redox form was determined using 4f electron energy. For XPS calibration the number of modeled compounds were used as presented in Table 1.

Table 1. The results of XPS of model compound and Np sorbed to synthesized mineral phases

<table>
<thead>
<tr>
<th>Formal valence</th>
<th>Compound</th>
<th>Energy of Np4f electrons, eV</th>
<th>Np4f7/2</th>
<th>Np4f5/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>NpO2</td>
<td>402.5</td>
<td>414.3</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>RbNp(NO3)2·2H2O</td>
<td>403.6</td>
<td>415.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cs2NpO2(CH3COO)2</td>
<td>403.0</td>
<td>414.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cs,NpO2Cl4</td>
<td>403.4</td>
<td>415.2</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>Cs2NpO2Cl4</td>
<td>404.6</td>
<td>416.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaNpO2·(CH3COO)2</td>
<td>405.2</td>
<td>417.0</td>
<td></td>
</tr>
<tr>
<td>Np sorbed to α-FeOOH</td>
<td></td>
<td>403.5</td>
<td>415.4</td>
<td></td>
</tr>
<tr>
<td>Np sorbed to α-Fe2O3</td>
<td></td>
<td>403.4</td>
<td>415.3</td>
<td></td>
</tr>
<tr>
<td>Np sorbed to γ-Fe2O3</td>
<td></td>
<td>403.4</td>
<td>414.9</td>
<td></td>
</tr>
</tbody>
</table>
The experimental equilibrium sorption data were modeled using FITEQ software and stability constants of surface complexes were determined. Figure 1 demonstrates the dependence of Pu sorption upon pH for \( \sigma \)-MnO\(_2\) and \( \alpha \)-Fe\(_2\)O\(_3\).

fig. 1. The dependence of Pu sorption upon pH by \( \sigma \)-MnO\(_2\) (A) and \( \alpha \)-Fe\(_2\)O\(_3\) (B)

It was found that colloids containing Mn(IV) oxidize actinides to hexavalent state and form surface complexes that are more stable than for Fe(III) oxides. The equilibrium distribution of Pu at the colloidal surface is presented in Table 2.

| Table 1. Equilibrium distribution of Pu sorbed on different colloids |
|-----------------------------|-----------------------------|-----------------------------|
| pH                          | \( \sigma \)-MnO\(_2\) initially Pu(IV) | Oxidation state at equilibrium |
| 2.41 ± 0.05                 | < 5% Pu(V) 19 ± 4%            |
| 4.54 ± 0.05                 | < 5% Pu(V) 37 ± 5%            |
| 7.19 ± 0.05                 | < 5% Pu(V) 18 ± 4%            |
| \( \gamma \)-Fe\(_2\)O\(_3\) initially Pu(V) | < 3% Pu(V) 98.4 ± 4%            |
| 6.01 ± 0.05                 | < 3% Pu(V) 49.4 ± 3.3%        |
| \( \alpha \)-FeOOH, initially Pu(V) | < 3% Pu(V) 50.3 ± 1.1%        |
| 6.40 ± 0.06                 | < 3% Pu(V) 91.6 ± 6%          |
| \( \alpha \)-Fe\(_2\)O\(_3\) initially Pu(V) | < 3% Pu(V) 91.6 ± 6%          |

The strength of complexation of actinides with Fe- oxides and oxyhydroxides increases in the following sequence: \( K_{\text{FeOOH}} > K_{\text{FeF2O3}} > K_{\text{Fe2O3}} \). The stability constants of the surface complexes are presented in Table 2. The iron coordination geometry of the (001) and (012) faces is different – iron in (001) face exhibit tetrahedral geometry, while it is octahedral on the (012) surface. As a result the surface charge and point of zero charge are different for these two geometries. The low temperature preparation gives \( \gamma \)-Fe\(_2\)O\(_3\) with (012) face with higher pH of point of zero charge than in case of \( \alpha \)-Fe\(_2\)O\(_3\) that is synthesized at higher temperatures that favors (001) face. The difference in electostatics result in difference in adsorption isotherms for a given metal cation. It was shown that humic acids reduce Pu(V) to tetravalent state and this reactions is pH dependent.
Table 2. Stability constants of surface complexes

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma \text{-Fe}_2\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe-OH} + \text{NpO}_2^- \rightleftharpoons \text{Fe-ONpO}_2 + \text{H}^+ )</td>
<td>-1.41</td>
</tr>
<tr>
<td>( \alpha \text{-Fe}_2\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe-OH} + \text{PuO}_2^- \rightleftharpoons \text{Fe-OPuO}_2 + \text{H}^+ )</td>
<td>-2.49</td>
</tr>
<tr>
<td>( \alpha \text{-Fe}_2\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe-OH} + \text{NpO}_2^- \rightleftharpoons \text{Fe-ONpO}_2 + \text{H}^+ )</td>
<td>-2.37</td>
</tr>
<tr>
<td>( \alpha \text{-Fe}_2\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe-OH} + \text{PuO}_2^- \rightleftharpoons \text{Fe-OPuO}_2 + \text{H}^+ )</td>
<td>-2.12</td>
</tr>
</tbody>
</table>

The work was performed under special RFP in Russia (grant M6RAS0008, administrated through CRDP, grant RC0-20003-SC14).

Reference
SPECTROSCOPIC STUDY OF THE INTERACTION BETWEEN TRIVALENT AND TETRAVALENT ACTINIDES

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Institut für Radiochemie, Technische Universität München, 85748 Garching, Germany

Tetravalent actinides (Th, U, Np, Pu) have a strong tendency to hydrolysis, polymerization and colloid formation even in acidic solutions. To quantify and characterize the formed actinide species is of utmost interest for the mechanistic understanding of chemical behaviors of actinides in natural waters. Here we present the spectroscopic study on interactions between Cm/Eu and Th in the course of coprecipitation, employing a novel combination of different laser spectroscopic approaches. Speciation is studied by time-resolved laser fluorescence spectroscopy (TRLFS), and the colloid formation by laser-induced breakdown detection (LIBD).

The coprecipitation study is carried out by a titration of $1.5 \times 10^{-7}$ M Cm and $1 \times 10^{-6}$ M Th in 0.03 M HCl solution with 0.03 M NaOH solution in the pH range of 2-9. Some selected emission spectra are shown in the upper part of Fig. 1. The spectroscopic speciation reveals the formation of three different Cm species; the Cm$^{3+}$ aquo ion with the emission peak at 593.8 nm and two different colloid-borne Cm species, indicated as Cm-Th species I and II, at 598.0 nm and 604.8 nm, respectively, as illustrated at the bottom of Fig. 1. The emission spectra recorded at pH 2-9 are deconvoluted, and individual species at each pH are quantified. The red shift of the fluorescence band is attributed to the formation of inner-sphere complexes owing to a change in the ligand field of the Cm$^{3+}$ ion [1]. The evaluated fractions of each Cm species are shown in Fig. 2. The first species Cm-Th(I) appears in minor quantity with a maximum at around pH 5.5 and the second species Cm-Th(II) dominates at pH ≥ 6. The characterization of two colloid-borne Cm species, Cm-Th(I) and Cm-Th(II), is further pursued by the fluorescence life-time measurement at 598.0 nm ($\tau = 136$ µs) and 604.8 nm ($\tau = 331$ µs), respectively. According to Kimura et al. [2], the number of hydrated water molecules of Cm for Cm-Th(I) and Cm-Th(II) is calculated to be 3.9 and 1.1, respectively. The former species Cm-Th(I) is ascribed to the surface complex of Cm. The latter species Cm-
Cm-Th(I) is ascribed to the surface complex of Cm. The latter species Cm-Th(II) undergoes nearly complete dehydration of Cm, concluding that Cm is incorporated into the colloidal bulk structure of Th.

![Fig. 1: Spectroscopic speciation of colloid-borne Cm species by TRLFS at 1.5×10⁻⁷ M Cm and 1×10⁻⁹ M Th in 0.03 M HCl titrated with 0.03 M NaOH in the pH range of 2-9. Some selected emission spectra are shown in the upper part, whereas individual spectra after the peak deconvolution of the composite spectra are shown at the bottom for the Cm³⁺ ion and the colloid-borne species, Cm-Th(I) and Cm-Th(II).](image)

![Fig. 2: Fraction of each Cm species as a function of pH, evaluated by the peak deconvolution of emission spectra, as shown in Fig. 1.](image)

To ascertain how and when a colloidal species is formed, the colloid formation is directly confirmed in the course of the coprecipitation by LIBD. This method is highly sensitive to detect small colloids (<100 nm) at low particle number densities (10⁷-10⁹ ml⁻¹). An increase in the LIBD signal is the most sensitive indication that colloids are formed. Fig. 3 shows the breakdown probability as a function of pH for the acidic solutions of 1×10⁻⁷ M Eu, as a homologue for Cm, and of 6.5×10⁻⁷ M Th as well as a mixture of both solutions. The concentration ratio of Eu to Th is kept constant, and is identical with that of the TRLFS study. In addition, the implication of the blank solution on the present experiment is separately examined. At pH < 6, we found that the presence of aqueous Eu ions enhances significantly the amount of tetravalent Th colloids and their stability, suggesting that the aggregation rate of Th colloids is smaller in the mixed system.
pared to the pure Th solution. Formed Eu-Th particles are around 10 nm in size and remain stable for 120 days. Although high purity chemicals have been used in the present work (NaOH: 99.996%), their purity was not sufficient. In particular at pH > 6, the high background signal from the blank solution (0.03 M HCl titrated by 0.03 M NaOH) due to colloidal impurities leads to difficulties in data interpretation. The development of chemical procedures to suppress particulate impurities is in progress.

![Graph](image)

Fig. 3: Colloid generation observed by LIBD at $1\times10^{-7}$ M Eu and $6.5\times10^{-7}$ M Th in 0.03 M HCl solution titrated by 0.03 M NaOH solution in the pH range of 2-9.

The present work shows that two different colloid-borne Cm species are formed appreciated by the TRLFS speciation: the first species Cm-Th(I) ascribed to the surface complex of Cm and the second species Cm-Th(II) with Cm(III) incorporated into the colloidal bulk structure of Th. Furthermore, Eu ions can significantly affect Th polymerization and precipitation, and thus increase the mobility of tetravalent actinides in natural aquifer systems.

References


GAS PHASE SEPARATION OF LIGHT ACTINOIDES FROM A SOIL SAMPLE IN A TEMPERATURE GRADIENT TUBE

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2Spiez Laboratory, CH-3700 Spiez, Switzerland

Introduction

The long-term objective of this study is the development of a gas phase separation technique for plutonium from soil samples as a preparation step for ICP-MS measurements. Due to mass interference of $^{239}$Pu by $^{238}$UH, a foregoing Pu/U separation is required. The behavior of some actinoides and the main- and trace elements of IAEA Soil-6 has been investigated with chlorinating and brominating reactive gas mixtures in an extended temperature gradient from 1120° to 30°C [1].

Experimental

The experimental setup is shown in Fig. 1. Separations are carried out in filled columns (4) consisting of a quartz glass tube (60 cm * 10 mm * 12 mm) with a filling of quartz glass sand (0.3 – 0.6 mm) fixed between quartz wool plugs. In order to clean and dry all surfaces first, the column is placed into a vertical electric tube furnace (3) and pre-treated for one hour at 950°C in a stream of either chlorine or argon saturated with bromine, depending on the halogenating system to be used in the forthcoming experiment. After cooling down to 50°C in the gas stream, the column is flushed with dry argon.

In these studies, for comparability reasons, always about 1 g of the IAEA Soil-6 reference material is used under varying experimental conditions. The soil sample is spiked with actinoides ($^{237}$Np, $^{242/244}$Pu, $^{243}$Am), treated with 30% H$_2$O$_2$, with either 37% HCl or 47% HBr and evaporated to dryness after each step. The pre-halogenated soil sample powder is loaded into the column and fixed with pre-treated quartz wool (5).

Immediately, the column is placed in a setup of two vertical electric tube furnaces (6, 7) and the separation experiment started. Reactive gas mixtures of Ar/SOCl$_2$, Cl$_2$/SOCl$_2$, Cl$_2$/CCl$_4$, HBr/Br$_2$, Br$_2$/Br$_2$, or Ar/Br$_2$/SOBr$_2$ are passed with 40 ml/min from the bottom to the top while the furnaces are slowly heated up, achieving a stable gradient after two hours. The high
temperature is kept for two additional hours. A filled Liebig condenser (8) cooled by 2-propanol and dry ice can be put at the top of the column to sample very volatile compounds condensing below room temperature.

Afterwards, the column filling with mobilized halogenides is sampled in 1 cm steps by means of a fine glass tube connected with a vacuum cleaner. The obtained quartz glass sand fractions are leached by 3% HNO₃ and the resulting solutions measured by ICP-MS or ICP-OES.

Fig. 1: Experimental setup with (1) molecular sieve 5Å, (2) saturation of the gas with halogenating liquid, (3) furnace for column pre-treatment, (4) filled quartz glass tube, (5) sample, (6) main furnace, (7) gradient furnace, (8) filled Liebig condenser, (9) 5 M NaOH.

Results
Generally, the element distributions along the temperature gradient reveal the formation of binary halogenides as well as of numerous halogeno-complexes. Additionally, evidence for compound formation of AlCl₃ or UCl₅ with sulphur chlorides could be found when SOCl₂ saturated reactive gas mixtures were used.

In chlorinating gas mixtures (e.g. Cl₂/SOCl₂ Fig. 2), AmCl₃ is partially evaporated from the CaCl₂ rich molten sample residue. It always stops on the KCl peak, obviously forming less volatile complexes. NpCl₄ and PuCl₄ (latter in gas phase only), due to earlier evaporation or
with the aid of AlCl₃, pass over the KCl position and stop at the KAICl₄ peak around 400°C. In certain cases parts of neptunium and of plutonium (only with Cl₂/CCL₄) are carried over the KAICl₄ position and form a peak at even lower temperature (not shown). ThCl₄ and UCl₄ are also found at the KAICl₄ peak while the main part of uranium forms more volatile higher chloride compounds which are transported to the cold parts of the column. By using chlorine gas, the UCl₄ fraction can be reduced.

![Graphs showing element distributions](image)

**Fig. 2:** Element distributions in a chlorinating gas, PuCl₄ stops together with UCl₄ on KAICl₄.

**Fig. 3:** Element distributions in a brominating gas, PuBr₃ behaves like AmBr₃ and stops on KBr, being separated from a small uranium peak.

In brominating gas mixtures, PuBr₃ is formed, which behaves like AmBr₃, showing only a single peak. Very little uranium is retained around the KBr peak. When the sample is mixed with charcoal using HBr/Br₂ (Fig. 3), uranium and plutonium are found in different positions within the KBr peak – the separation is complete. But for the total plutonium evaporation from the sample residue a longer duration of the experiment is necessary. With this gas mixture no actinoid-catching KAIBr₄ is formed. Thus, NpBr₄, UBr₄ and ThBr₄ show broad peaks at relatively low temperatures.

**Reference**

PLUTONIUM FROM GLOBAL FALLOUT RECORDED IN AN ICE CORE FROM THE BELUKHA GLACIER, SIBERIAN ALTAI

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Anthropogenic plutonium is present in the environment as a consequence of nuclear weapons testing and via releases from nuclear industry during the second half of the 20th century [1,2]. It is important to know its atmospheric concentration or deposition rates for environmental monitoring, radiological health protection, studying actinide transport mechanisms or for air circulation studies [3]. Although glaciers are especially attractive to study anthropogenic impacts on the environment, only few ice core records of plutonium fallout exist because of the low plutonium concentration found in glacier ice and the associated requirement of large samples. In this study we present the history of mid-latitude atmospheric plutonium fallout reconstructed from an ice core from the Belukha glacier [4] using the highly sensitive accelerator mass spectrometry (AMS) technique.

Ice core samples (2-3 kg) for Pu analysis were melted, spiked with 242Pu yield tracer and acidified to pH 0.3 with 65% HNO3. The samples were then pre-concentrated by means of MnO2 co-precipitation [5]. The MnO2 precipitate was dissolved in 7 ml 65% HNO3, 0.5 ml 30% H2O2 and 160 µl 40% HF. After evaporation to dryness, the salt cake was dissolved in 1 M HNO3 and Pu was forced into oxidation state (IV) by reduction with Fe(NH4)2(SO4)2·6H2O and, after addition of further 65% HNO3 oxidation with NaNO2.

U was separated from Pu by ion exchange chromatography using Dowex® 1x2 resin (100-200 mesh). The 8 M HNO3 Pu(IV) solution was filtered (0.45 µm) and transferred to a pre-conditioned column. After washing with 8 M HNO3 and 37% HCl, the Pu was selectively eluted with a 0.1 M NH4Cl/37% HCl solution. The extract was taken to dryness in turn with 65% HNO3, 37% HCl, and 65% HNO3, respectively.

To prepare the target for the AMS measurement, the residue was dissolved in 1 M HNO3 and 0.37 mg Fe and 4.5 mg Ag were added as nitrate solutions. Pu was again forced into oxidation state (IV) by adding NaNO2 and then was co-precipitated with iron hydroxide and silver oxide.
by raising the pH with NaOH. The precipitate was centrifuged and thoroughly rinsed twice with ultrapure water before being dried and baked in a crucible at 450°C. Finally, the resulting blend of Pu, Ag and Fe oxide was mixed with high purity Ag powder, firmly pressed into an aluminium AMS sample holder, and measured using the 14UD tandem accelerator at the Australian National University, Canberra [6].

The $^{239}$Pu and $^3$H concentration records from the upper 40 m of the Belukha ice core are presented in Figure 1. The Pu deposition peaks in 1963, coinciding with the maximum of the nuclear weapons tests (1960-1965) and in concordance with the $^3$H concentration peak. The difference in the relative extent of the first concentration peak of Pu and $^3$H is probably due to the fact that very little $^3$H was produced by the early fission bomb tests compared to the later fusion detonations [7].

![Graph](image)

**Fig. 1:** $^{239}$Pu (bold line) and $^3$H (dashed line) concentration records. The $^3$H concentration was decay-corrected to the time of deposition as derived from the $^{210}$Pb.

The shapes of the $^3$H and $^{239}$Pu concentration records reflect two main periods of nuclear weapons testing. The first peak is attributed to pre-moratorium testing before 1958 and the major maximum to post-moratorium testing in 1961 and 1962 [1]. Contributions from French and Chinese atmospheric tests after the 1962 Test Ban Treaty are negligible. About 45% of the integrated plutonium inventory in the Belukha ice core is contributed by pre-moratorium tests, in approximate agreement with the estimated atmospheric bomb yield ratio of post to pre-moratorium testing of around 70:30 [1,7]. The small difference may be explained by the fact that plutonium emissions from nuclear testing are not necessarily expected to correlate with total bomb yield since Pu is not a fission product and its release also depends upon the type of weapon detonated [7].

In Table 1 the integrated ice core inventory of $^{239+240}$Pu is compared to values obtained from other archives. The Altai sediment value is derived from a lake sediment core taken from Uzun Kol (50°29′N, 87°36′30″E, 1985 m a.s.l., [8]), about 90 km to the northeast from the Belukha glacier. The Altai soil plutonium inventory is the average value of two samples taken
near Ak-kem, a meteorological station 7 km north of Belukha. Surprisingly, the plutonium inventories derived from the different archives in the Altai region agree very well. Also, the order of magnitude of the $^{239+240}$Pu inventory in the Altai is in good accordance with the average value of soil samples from the corresponding latitude [9].

<table>
<thead>
<tr>
<th></th>
<th>$^{239+240}$Pu</th>
<th>Soil average of the</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altai, Belukha ice core [this work]</td>
<td>4.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Altai, lake sediment core [8 and this work]</td>
<td>4.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Altai, soil samples [this work]</td>
<td>4.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Greenland, 64°N, ice core [7]</td>
<td>1.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Agassiz Ice Cap, 81°N, ice core [3]</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The Belukha glacier is located relatively close to the two nuclear test sites Semipalatinsk (50°N, 78°E) and Lop Nor (40°N, 90°E) as well as to the two USSR’s nuclear facilities of Tomsk (56°N, 85°E) and Krasnoyarsk (56°N, 92°E). Given this proximity, the radionuclides released to the atmosphere may have been deposited with snow onto the glacier. Any tropospheric fallout from tests performed at those test sites or from accidental releases would probably have resulted in a plutonium flux enhancement and/or a deviation of the $^{239}$Pu/$^{238}$Pu isotopic ratio from the global fallout ratio of 0.18 [2]. Surprisingly, all measured samples showed an average $^{239}$Pu/$^{238}$Pu isotopic ratio of 0.18 ± 0.03, indicating that most of the plutonium in the Belukha glacier originated from global stratospheric fallout rather than from direct tropospheric input. In addition, the measured plutonium inventory is approximately equal if not smaller to that expected (Table 1), implying that possible inputs due to emissions from close-by nuclear facilities must be negligible.

**References**

SORPTION OF Cm(III) ONTO SAPPHIRE (α-Al₂O₃) SINGLE CRYSTALS

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Mechanistic insight into radionuclide interaction with mineral surfaces is of great importance for performance assessment of nuclear waste repositories. For a fundamental understanding of sorption/incorporation processes and a reliable thermodynamic description, e.g. by surface complexation models, all relevant processes have to be identified and quantified. A major point in this respect is the detailed knowledge of the properties and constitution of the reactive mineral surface and the nature, distribution and concentration of surface sites which is not available or only in a limited way for most of the selected minerals. An auspicious possibility to get a deeper insight in processes at the mineral surface is the use of single crystal surfaces. The main advantage of using single crystals is the possibility to investigate the metal ion sorption on various well characterized and clear defined crystal plane surfaces. Due to their low roughness, the availability of different crystal planes and dimensions and their suitability for performing TRLFS studies, sapphire (α-Al₂O₃) single crystals were selected for this study. α-Al₂O₃ is taken as a model mineral for trivalent iron oxides and other Al-containing minerals in the nature as clays and gibbsite which are of great importance for metal ion sorption under natural conditions.

In the present study, the Cm(III) sorption onto different crystal planes (018), (104), (012), (110), (001) of sapphire single crystals (area: 1cm²) is investigated at low Cm(III) concentrations and at pH 4.5 and 5.1 by time resolved laser fluorescence spectroscopy (TRLFS), XPS, α-spectrometry and autoradiography. The findings are compared with results from earlier studies on the Cm(III) sorption onto colloidal γ-Al₂O₃ particles [1, 2]. Based on crystallographic considerations, Barrón and Torrent [3] calculated the oxide/hydroxide
density on various hematite surfaces. As hematite is isostructural to sapphire [4] we assume those data being applicable to the sapphire surfaces. Surface oxide and hydroxyl groups differ in type and concentration for the surface planes and thus should have an influence on Cm(III) reactions at the sapphire surface/water interface.

A homogenous Cm(III) distribution on the sapphire surfaces is demonstrated by autoradiography for all samples. Sorbed Cm(III) concentrations are in the range \(2 \times 10^{12} - 7 \times 10^{11}\) mol/cm\(^2\) or 0.02 - 0.4 atoms/nm\(^2\). TRLFS and XPS spectra of sufficient intensity are obtained for all samples proving the sensitivity of these methods and their applicability at very low Cm(III) concentrations. TRLFS spectra of Cm(III) sorbed onto the (001) surface show distinct differences with regard to peak position and fluorescence lifetime compared to those obtained for the four other crystal planes. Similar information is available from XPS. The extent of Cm(III) sorption differs for the individual crystal planes with the highest sorption taking place at the (001) the lowest at the (018) orientation. The very similar TRLFS spectra for Cm(III) sorbed at the (001) plane and onto colloidal \(\gamma\)-Al\(_2\)O\(_3\) suggest the presence of similar surface species. Variations in the TRLFS and XPS spectra for Cm(III) sorbed at the (001) plane after high vacuum treatment and subsequent water contact suggest an important influence of surface relaxation processes on the surface properties. Such an effect is much less pronounced for the other sapphire crystal planes. Further on, Cm(III) sorption onto sapphire single crystals is considerably increased as compared to interaction with \(\gamma\)-Al\(_2\)O\(_3\) colloids probably due to different acid base properties of the respective surface hydroxyl groups.

By combination of different experimental methods a better understanding of the reactions on the water/single crystal surface interface is achieved. The outcome of the study points to the important influence of the surface structure and notably the surface hydration state on the sorption reaction. In order to get a deeper insight into the exact structure of the formed surface species, more experiments in a wider pH range and application of additional spectroscopic techniques as X-Ray spectroscopy are required.
Fig. 1: TRLFS spectra for the Cm(III) sorption onto different sapphire single crystals (001), (110), (012), (104) and (018) at pH 5.1 and 0.1 M NaClO$_4$ normalized to the same peak height. Cm(III) surface concentrations measured by $\alpha$-spectrometry are added in brackets in atoms/nm$^2$. Also the spectra for the unsorbed free Cm$^{3+}$ aquo ion and for the first Cm(III) sorption species onto $\gamma$-Al$_2$O$_3$ colloids derived by peak deconvolution at similar pH [1] are included.

References

INTERACTION OF Cm(III) WITH AQUEOUS MONO- AND POLYSILICATES
STUDIED BY TIME-RESOLVED LASER FLUORESCENCE SPECTROSCOPY (TRLFS)

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Silicates, either dissolved or in colloidal form, are ubiquitous in natural waters as a result of weathering processes of amorphous silica or silicate-bearing minerals [1,2]. The aqueous chemistry of silicates is determined by various coupled processes such as dissolution, precipitation, complexation of cations and anions in solution or at particle-water and mineral-water interfaces, and biological uptake. Because of the omnipresence of Si in natural aquatic systems the interaction of trivalent actinides with both, orthosilicic acid and oligomeric Si species can have a significant influence on the migration behavior of radionuclides.

Our research focuses on the interaction of monomeric and oligomeric silicates ([Si]_tot = 2.7-9.6x10^-3 mol/L) with trace amounts of Cm(III) in the pH region from 1.5 to 9.0. Objectives of this work are to identify and characterize the different Cm-complexes formed with silicates and to determine the stability constant of the Cm(III)-monosilicate complex. We use time-resolved laser fluorescence spectroscopy (TRLFS) to characterize the complexes formed with Cm(III). This method is a versatile tool for speciation of Cm(III) in the nano-molar concentration range without disturbing the equilibrium of the system. In addition, the differentiation between soluble Cm-orthosilicate complexes and Cm-species bound to Si-polymers is performed by ultracentrifugation.

For speciation of Cm(III)-silicates fluorescence spectra are measured as a function of pH using three different Si concentrations (2.7x10^-4 mol/L, 4.9x10^-4 mol/L, and 9.6x10^-4 mol/L). The emission band at low pH with a peak maximum of 593.8 nm corresponds to the Cm^{3+} aquo ion. The intensity of the 593.8 nm peak decreases with increasing pH and a shoulder appears at 598.5 nm. A further increase of the pH causes a further bathochromic shift of the emission band to 603.2 nm. No significant shift of the fluorescence spectrum is observed in the pH range from 6.7 to 8.2. Peak deconvolution provides the spectra of the three Cm species
with peak maxima at 598.5 (Cm-Si(I)) and 603.2 nm (Cm-Si(II)) are formed. The right figure shows the species distribution for [Si]_aq = 4.9x10^{-4} mol/L as a function of pH. Below pH 5.5 the Cm^{3+}aq ion is the dominating species. The formation of Cm-Si(I) starts at pH 4. A maximum fraction of 41 % is reached at pH 5.7. The Cm-Si(II) complex is formed at pH > 5.5 and predominates above pH 6.2. The fluorescence lifetime is determined by the ratio of radiative and non-radiative decay processes. Replacement of water molecules by ligands reduces the non-radiative decay and hence causes an increase of the fluorescence lifetime from 67 ± 3 μs (Cm^{3+}aq) to 85.1 ± 2.5 μs (Cm-Si(I)) and 198.2 ± 7.2 μs (Cm-Si(II)). According to Kimura and Choppin [3], the number of water molecules in the inner coordination sphere can be calculated from the fluorescence lifetime. The lifetime of the Cm-silicate complexes corresponds to 6.8 ± 1 and 2.4 ± 1 water molecules, respectively.

Fluorescence spectra of Cm^{3+}aq and the two Cm-silicate complexes (Cm-Si(I) and Cm-Si(II)) (left) and the species distribution as a function of pH ([Si] = 4.9x10^{-4} mol/L) (right).

The first Cm-silicate species (Cm-Si(I); 598.5 nm) present at pH 4.7-6.7 is attributed to the (1:1)-complex of curium with orthosilicic acid (CmOSi(OH)_{3}^{2+}). The stability constant determined from the three series of measurements at an ionic strength of 0.03 M NaCl is log β = 7.32 ± 0.08 corresponding to log_{10} K = -2.07 ± 0.1 and log β^{0} = 7.74 for I = 0. These values are compared to literature data of Eu(III) [4], Am(III) [5], and Cm(III) [6]. At higher pH (pH >5.5) the second Cm-silicate species (Cm-Si(II)) with a peak maximum at 603.2 nm is formed. Our results show that this Cm-species is not the Cm-disilicate complex

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separated from Cm-monsilicate by ultracentrifugation. We conclude that the affinity of oligomeric Si-species toward Cm is higher than that of monosilicic acid. This leads to a preferential formation of oligomeric Cm-silicate species instead of the Cm-disilicate, even in Si solutions below the saturation concentration with only trace concentrations of Si-oligomers.

Our results have shown that trivalent actinides form strong complexes with orthosilicic acid and oligomeric silicate species. Because of the omnipresence of silicates in natural waters and the magnitude of the stability constant silicates are considered as important inorganic ligands for actinide complexation in mildly acidic to neutral aquatic systems in nature. Therefore, silicate complexes can have a strong influence on the migration behavior of trivalent actinides and has to be taken into account for Cm/Am speciation in natural systems.

References

LONG-LIVED RADIONUCLIDES IN THE ENVIRONMENT: ON THE RADIOECOLOGY OF IODINE-129

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Atmospheric nuclear weapons tests, nuclear accidents, and emissions from reprocessing plants have changed the natural abundances of the long-lived radionuclide \(^{129}\text{I}\) \((T_{1/2} = 15.7\) Ma) in a sustainable manner. Mainly as a consequence of the \(^{129}\text{I}\) releases from the European reprocessing plants stable and radioactive iodine isotopes are in disequilibrium in all the abiotic and biotic environmental compartments in Western Europe. Iodine from precipitation is accumulated in soils, transported by surface water, infiltrating groundwater and makes its way into the biosphere. But still today, the radioecology of \(^{129}\text{I}\) is incompletely known [1]. Here, we present new results of a project aimed at a comprehensive understanding of the abundances of \(^{129}\text{I}\) and \(^{127}\text{I}\) in Lower Saxony, Germany, and of their pathways through the different environmental compartments to man; see [2-6] for references of published results. Accelerator mass spectrometry, radiochemical neutron activation analysis, ion chromatography, and ICP-MS were applied to measure the iodine isotopes in sea-water, air, precipitation, surface and ground waters, soils, plants, animals, foodstuffs, total diet, and human and animal thyroid glands. For air-borne iodine, the speciation as well as the particle size distribution of aerosols was determined. Soil depth profiles were investigated down to depths of 2.5 m in order to study the iodine migration as well as individual surface soil samples to allow for the determination of transfer factors of the iodine isotopes into plants. Transfer factors for soil-plant, feed-milk, and feed-meat transfer were determined both for farm and wild animals.

The pre-nuclear equilibrium \(^{129}\text{I}/^{127}\text{I}\) isotopic ratio in the biosphere was determined to be \(2.0 \times 10^{-13}\) with a geometric standard deviation of 1.4. \(^{129}\text{I}/^{127}\text{I}\) ratios in the atmosphere and in precipitation increased from the pre-nuclear equilibrium value to \(10^{-9}\) between 1940 and 1950 in background regions of the northern hemisphere. In 1950, atmospheric \(^{129}\text{I}/^{127}\text{I}\) ratios exceeded \(10^{-9}\). \(^{129}\text{I}\) deposition in Western Europe does not show a prominent bomb peak as for instance observed for \(^{14}\text{C}, ^{36}\text{Cl}\) and \(^{137}\text{Cs}\) in archives like alpine ice cores from Switzerland. Isotopic ratios and deposition densities continued to increase until the end of the 1980ies. Since then, ratios of nearly \(10^{-9}\) were observed in Germany and Switzerland and remained constant until today. The fall-out of the Chernobyl accident by \(^{129}\text{I}\) deposition was just a short-term episode with a highest measured \(^{129}\text{I}/^{127}\text{I}\) ratio of nearly \(10^{-5}\). The North Sea appears as the dominant
source of air-borne iodine in coastal regions of Northern Germany due to the emissions of European reprocessing plants.

Today, $^{129}$I and $^{127}$I are in disequilibrium in all the investigated environmental compartments. The measured $^{129}I/^{127}I$ isotopic ratios ranged from $2.7 \times 10^{-6}$ in coastal seawater from the North Sea to $1.0 \times 10^{-11}$ in groundwater. Except for samples of thyroid glands, the concentrations of $^{129}I$ were between $10^{-12} \ g \ g^{-1}$ and $10^{-18} \ g \ g^{-1}$, i.e. 6.5 mBq kg$^{-1}$ and 6.5 nBq kg$^{-1}$. The concentrations of $^{127}I$ were found in the range from $10^{-2} \ g \ g^{-1}$ to $10^{-10} \ g \ g^{-1}$. Man-made $^{129}I$ was found at all depths sampled so far: in soils down to a depth of 2.5 m and in groundwater to an infiltration depth of 10 m.

At the North sea, the $^{129}I/^{127}I$ isotopic ratios in air ($3.1 \times 10^{-7}$ (gaseous) to $8.4 \times 10^{-7}$ (particulate)) in the year 2002 and in precipitation (ca. $8 \times 10^{-7}$ during the years 1997 - 2002) are significantly lower than in the coastal North Sea water ($1.0 \times 10^{-6}$ to $2.7 \times 10^{-9}$). In areas of Lower Saxony remote from the North Sea coast the $^{129}I/^{127}I$ isotopic ratios in precipitation are lower with ca. $5 \times 10^{-7}$. The $^{129}I$ deposition rates due to precipitation increased since 1950 from 0.01 mBq m$^{-2}$ a$^{-1}$ by nearly three orders of magnitude and have levelled off after 1987. During the years 1997 - 1999, the annual $^{129}I$ deposition rate had a geometric mean of 6.4 mBq m$^{-2}$ a$^{-1}$ with a geometric standard deviation of 2.1 in Lower Saxony. The integral deposition density was 170 mBq m$^{-2}$ in Lower Saxony in 1999. The present deposition is inhomogeneous with time and place showing even some seasonal dependence.

This deposition density in Lower Saxony is more than three orders of magnitude higher than the pre-nuclear value derived for Lutovinovo, Russia. The integral deposition in Germany is also higher than in Moscow, Russia, or Zhitomir, Ukraine, both regions being not significantly contaminated by fall-out from the Chernobyl accident. Only in areas of Ukraine seriously contaminated by this accident we observed higher integral deposition densities than in Germany. There, $^{129}I$ can be used for estimates of the fall-out of $^{131}I$ from the Chernobyl accident. In the highly contaminated areas of Ukraine the majority of $^{129}I$ deposition occurred instantaneously. In Lower Saxony, Germany, the situation is much more complicated due to the complex fall-out pattern with a continuous, but strongly time-dependent deposition.

The annual deposition rate of $^{127}I$ is 2.4 mg m$^{-2}$ on the average. The stable $^{127}I$ in surface soils is the result of thousands of years of atmospheric input with precipitation. The $^{127}I$ concentrations in soils are strongly influenced by hydrological conditions. In surface soils, $^{127}I$ concentrations ranged from $2 \times 10^{-5} \ g \ g^{-1}$ to $5 \times 10^{-7} \ g \ g^{-1}$, those of $^{129}I$ were between $2.2 \times 10^{-13} \ g \ g^{-1}$ and $3 \times 10^{-14} \ g \ g^{-1}$, i.e. 1.1 mBq kg$^{-1}$ and 0.2 mBq kg$^{-1}$. The $^{129}I/^{127}I$ isotopic ratios in surface waters ($2.2 \times 10^{-6}$ to $1.7 \times 10^{-5}$) and in surface soils ($2.1 \times 10^{-7}$ to $1.7 \times 10^{-5}$) are lower than those in precipitation. In surface waters, a dilution of the fall-out iodine takes place with stable $^{127}I$ which is just weakly adsorbed in the soils and a considerable run-off of iodine must be taken into account. The isotopic ratios in soil profiles and ground waters demonstrate a high mobility and an accumulation of $^{129}I$ in the water unsaturated soil zones, an efficient migration into the water saturated soil layers and an ongoing transfer of man-made $^{129}I$ into the groundwater. In surface soils, the $^{129}I/^{127}I$ ratios are inversely proportional to the $^{127}I$ concentrations. In the soil samples, the highest $^{129}I$ concentrations went up to $6.4 \times 10^{-13} \ g \ g^{-1}$, i.e. 4.2 mBq kg$^{-1}$, and $^{129}I/^{127}I$ ratios up to $4.8 \times 10^{-7}$ in forest soils.
$^{129}$I and $^{127}$I concentrations in vegetation and foodstuff and the transfer factors for $^{129}$I and $^{127}$I show influences of various effects. For grass, cereals and leafy vegetables elevated $^{129}$I/$^{127}$I ratios point to the direct contamination by wet and dry deposition. For other vegetables, milk, meat, and mushrooms the root uptake is clearly seen; for equal $^{129}$I/$^{127}$I ratios their $^{129}$I and $^{127}$I concentrations are in-between those of soils and surface water.

The $^{129}$I/$^{127}$I ratios in human thyroid glands sampled around Hanover and Hamburg during the years 1999- 2002 are not different. With ratios between $3 \times 10^{-8}$ and $3 \times 10^{-4}$ they are similar to earlier measured values [7]. The average $^{129}$I/$^{127}$I isotopic ratios of $1.1 \times 10^{-4}$ in human thyroid glands are equivalent to an annual radiation exposure due to $^{129}$I of about 5 nSv. The $^{129}$I/$^{127}$I ratios in human thyroid glands are lower than other biospherichfs. This can be explained partially that those foodstuffs with the highest $^{127}$I contents show the lowest $^{129}$I/$^{127}$I ratios because of the dilution with stable iodine from the soils. The $^{129}$I/$^{127}$I ratios of the thyroids are not correlated with the $^{127}$I concentrations; with the $^{129}$I concentrations they are correlated, but not proportional to the latter. This correlation points to the importance of other sources of iodine in the diet which are not directly connected to the radioecological conditions in Germany. Our results for total diet support this view. Thyroid glands from cows and sheep exhibit $^{129}$I/$^{127}$I ratios which are higher by an order of magnitude than those of humans and reveal the ongoing influence of wet and dry deposition onto the pastures.

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MICROANALYTICAL $^{14}$C AMS MEASUREMENTS ON CARBONACEOUS PARTICLES


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Carbonaceous particles are increasingly recognized as an important atmospheric constituent. These small atmospheric particles, including black carbon (BC) and organic carbon (OC), are produced by incomplete combustion of fossil fuels, biofuels and outdoor biomass. It has been suggested, that climate forcing by BC contributes substantially to global warming although OC might partly reduce warming effects due to indirect effects such as cloud brightness and cloud cover. Current investigations aim at a partitioning of BC and OC to biogenic and anthropogenic sources to improve our knowledge on the contribution of each fraction to the ambient atmosphere. One approach to solve this problem is a determination of the $^{14}$C concentration. The $^{14}$C activity in ambient, biogenic carbon is 227 Bq/kg C and the corresponding atomic ratio for $^{12}$C/$^{14}$C approx. 10^{12}. OC and mainly BC are also produced in fossil fuel burning. In this fraction $^{14}$C is extinct.

In addition, $^{14}$C measurements in OC separated from carbonaceous particles has been suggested as a dating tool. Scavenging processes by snow or rain deposit atmospheric aerosol particles onto the surface of archives such as glaciers. Ice cores therefore bear the potential to reconstruct past atmospheric composition, a well known approach to reconstruct past climatic variability. Such investigations are not only performed in polar areas but also at high altitude glaciers from mid-and low latitudes worldwide. In the past (pre-industrial era) OC has been mainly emitted from biogenic sources, its $^{14}$C concentration resembles contemporary condition. Therefore, $^{14}$C measurements of OC might enable a dating of ice cores. One shortcoming is the low mass concentration of carbonaceous particles in air and ice archives. Typical values in the lower troposphere range from ng/m$^3$ to µg/m$^3$ in polar and urban sites, respectively. In ice cores typical concentrations are in the 1 to 100 µg/kg range.

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To reach this goal a novel separation procedure for OC and BC from aerosol samples has been developed that bases on a temperature controlled combustion of both fractions at different temperatures [1]. Samples prepared on quartz fibre filters are first heated in an oxygen stream to 340 °C to convert OC into CO₂ and then to 650 °C to also combust BC to CO₂. Both gaseous CO₂ fractions are collected in capsules. Then the CO₂ is reduced to filamentous carbon on a heated (650 °C) Mn/Co catalyst. The final carbon samples are used as target ion source in a 500 kV pelletron accelerator for an AMS determination of the ¹³C/¹²C ratio [2].

In a first series of measurements sub-milligram amounts of the NIST standard SRM1649a (urban dust) was analysed and the fraction of contemporary ¹³C determined for OC and BC [1]. This was the first determination of ¹³C in the OC fraction of an ambient aerosol sample. In two field campaigns conducted in the city of Zürich aerosol samples were collected in summer and in winter [3]. Though the total amount of typically bi-daily samples amounted to only approx 20 µg of total carbon, ¹³C measurements revealed interesting differences in the composition of both fractions with respect to their biogenic and anthropogenic composition, as defined by the contemporary fraction f₀. A value for f₀ of one means that the carbon originated entirely from biogenic sources whereas the sources are anthropogenic (fossil fuel) for the value zero. As an example, it was observed that even down-town Zürich the carbonaceous aerosol is dominated by the vicinity of the rural vicinity (high values of f₀) [4].

As a spin-off of these investigations, currently attempts are made to measure ¹³C from the OC and BC fractions of carbonaceous particles contained in glacier ice cores as a dating tool. Typical values for BC concentrations are 0.1 to 0.5 µg/kg at the South Pole, 1 to 5 µg/kg in Greenland and 5 to 50 µg/kg at mid-latitude sites in the Northern Hemispher [5]. OC concentrations are mostly unknown except for the Alps where they are approx. 100 µg/kg [6].

In the Alps, during the Industrial era OC and BC concentrations increased by roughly a factor of three [7].
$^{14}$C measured in OC fractions from an ice core from Colle Gnifetti (4450 m asl, Swiss Alps) yielded promising first results [8]. Currently, measurements on dated samples from Greenland are performed to calibrate this novel dating tool back to about 7000 y BP (before present). In addition, ice samples from a recently drilled ice core from the Colle Gnifetti that reached bedrock are analysed in a project to search for the oldest ice from the Alps.

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DETERMINATION OF NEPTUNIUM IN SOIL SAMPLES BY ICP-MS

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Introduction

Actinide analysis is important for monitoring their releases from nuclear facilities, nuclear weapon tests, nuclear accidents as well as for research. In nuclear reactors $^{237}$Np is produced by thermal neutron interaction on $^{235}$U and by fast neutron interaction on $^{238}$U. With a half-life of 2.14x10$^9$ years it possesses low specific activity, but due to this longevity and the in-growth from the parent $^{241}$Am and $^{241}$Pu, $^{237}$Np is among the actinides with the greatest concern from radiological hazard point of view [1]. It is difficult to measure $^{237}$Np at environmental levels through the conventional alpha counting methods. In the last few years the progress in mass spectrometric methods has lead to a very low detection limit and made this technique a better choice [2]. Typically the actinides in the environmental samples are present at very low activities and are found in complex multi element matrices. A large number of radiochemical procedures are commonly used for the separation and concentration of the actinide elements. In principle these include precipitation, ion exchange, and liquid-liquid extraction, each of which demonstrates different advantages and disadvantages [3]. The aim of our study was to develop fast and reliable method for separation and concentration of neptunium in soil and sediment samples and its determination by ICP-MS.

Experimental

Sample treatment: A big amount of soil material (200 – 400 g) with high silicate content and known $^{238}$U and $^{232}$Th content was ashed and milled. $^{237}$Np spike was added and the sample homogenised. Analysis of environmental levels of actinides in soils and sediments is often hampered by sample depending problems. Sample digestion is a critical step for actinides determination. In order to obtain total sample digestion two grams of the soil were fused with LiBO$_2$-Li$_2$B$_4$O$_7$ in a Pt-Au crucible. The sample melt was directly poured into 4
From the resulting solution the silicates were precipitated with PEG (polyethylene glycol). The solution was filtered and diluted to 3M HNO₃. 0.1 M Fe(OH)₃ was added to the solution in order to reduce Np(V) to Np(IV). The solution was processed on a TEVA extraction chromatography column (Eichrom Technologies Inc.). Np(IV) was retained on the column while U was washed out with 3 M HNO₃/0.1 M Fe(II). Th(IV) was washed out with 9 M HCl and Np(IV) was eluted with 0.02 M HNO₃/0.02 M HF. Any organics stripped from the column were digested with concentrated HNO₃. The analytical fractions were solved in 2.5 % HNO₃ and filtered through 0.45 μm filters. Bismuth was added as internal standard for the ICP-MS measurement. Figure 1 shows the separation scheme.

**Mass spectrometry:** Mass spectrometric measurements were performed on a Finnigan Element2 HR-ICP-MS. A self-aspirating PFA nebulizer was used with a spray chamber cooled to 1 °C. The instrument sensitivity was daily optimised to 10⁶ cps for 1 ppb²³⁸U.

**Alpha spectrometry:** Alpha spectrometry was applied for Np determination. Eight channels Alpha Analyst, Canberra Inc equipped with 600 mm² PIPS detectors were used. The sources for alpha spectrometry were electroplated onto stainless steel disks using a modified Talvitie method [4].

**Results**

**Chemical recovery and limits of detection:** The yield of Np determined by ICP-MS and alpha spectrometry are presented on Table 1.
Table 1. Chemical yield of Np measured by ICP-MS and \( \alpha \)-spectrometry.

<table>
<thead>
<tr>
<th></th>
<th>ICP-MS</th>
<th>( \alpha )-spectrometry(^a)</th>
</tr>
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<tbody>
<tr>
<td>With Fe(I) reduction of Np</td>
<td>80±5</td>
<td>69±9</td>
</tr>
<tr>
<td>Without Fe(II) reduction of Np</td>
<td>40±5</td>
<td>31±12</td>
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</tbody>
</table>

The Neptunium yield is high and reproducible. It was observed that if no ferrous ions were used for the reduction of Np(V) to Np(IV), the yield is still high. A possible reason could be the total sample digestion method. After the borate fusion the melt was dissolved in concentrated acid which stabilizes the fourth oxidation state of Np. The proposed extraction chromatography procedure separates neptunium from large amounts of \(^{238}\)U and \(^{232}\)Th and thus eliminates spectral overlaps with \(^{237}\)Np for ICP-MS analysis. The detection limit for \(^{237}\)Np with ICP-MS is 3 orders of magnitude lower compared to the detection with alpha spectrometry (Table 2.).

Table 2. Limits of detection.

<table>
<thead>
<tr>
<th></th>
<th>Limits of detection for 2 grams of sample material, Bq/kg, (ppq)</th>
<th>( \alpha )-spectrometry(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-MS</td>
<td></td>
<td>2x10(^4)</td>
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<tr>
<td></td>
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<td>0.7</td>
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<td>(7.1)</td>
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<td></td>
<td>(24844)</td>
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</table>

\(^a\)obtained for measuring time 30000 sec.

Conclusions
Borate fusion is a fast and an effective method for sample pre-treatment. Within 20 min the samples are totally digested. Neptunium can be separated from soil samples with high chemical recovery by using extraction chromatography. Compared to alpha spectrometry, HR-ICP-MS is faster and more sensitive. In conjunction with extraction chromatography it is the preferred method for the determination of the long-lived actinides.

References
DETERMINATION OF FALLOUT $^{238}$Pu, $^{239}$Pu, $^{240}$Pu AND $^{241}$Am IN SOIL SAMPLES FROM SWITZERLAND USING HIGH-RESOLUTION $\alpha$-SPECTROMETRY AND MC-ICP-MS

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Introduction. Monitoring of nuclear weapon testing fallout or accidental released neutron fission or activation products around nuclear facilities is of major concern by environmental immission investigations. Of particular interest are activity determinations of highly toxic radioisotopes such as $\alpha$-emitters of anthropogenic Pu Am and Cm due to their long residence time in the biosphere, bio-availability for certain dietary products and high dose conversion factors. In order to obtain the levels of the present-day radionuclide inventory of the anthropogenic fallout actinides in Switzerland, about 50 samples were taken and analysed initially by $\alpha$-spectrometry to precisely determine the $^{238}$Pu/$^{239-241}$Pu activity ratio (levels of $^{238}$Pu were too low to allow mass spectrometric detection, details in Table 1). The samples were then analyzed by MC-ICP-MS to obtain the $^{239}$Pu/$^{240}$Pu atomic ratio because both isotopes are characterized by almost identical $\alpha$-particle emission energies at 5.1 MeV (i.e. cannot be distinguished by counting even with high resolution surface barrier detectors).

Results and discussion: Typical long-lived products from nuclear fallout debris are isotopes of Pu ($^{239}$Pu, $^{240}$Pu), Am, Cm and fissiongenic $^{137}$Cs and $^{90}$Sr. In more contaminated samples also trace amounts of short-lived $^{134}$Cs from the Chernobyl event may still be detected using extreme low level counting techniques. If the isotopic signature from the different atmospheric emission sources (bomb testing, reactor explosions, ignited satellites, etc.) shows a different pattern, the fine structure of the isotopic composition can be applied to allow distinguishing between such sources.

Table 1: Typical environmental levels as well as detection limits for $^{238}$Pu and $^{239}$Pu in soil samples in Switzerland: comparison between $\alpha$- and mass spectrometry

<table>
<thead>
<tr>
<th>isotope</th>
<th>typical activity levels (this study)</th>
<th>lower limit of detection</th>
<th>$\alpha$-spectrometry</th>
<th>Mass spectrometry</th>
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</thead>
<tbody>
<tr>
<td>$^{239}$Pu</td>
<td>$3 \times 10^{-3} - 1 \times 10^{-1}$</td>
<td>$3 \times 10^{-3}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>$6 \times 10^{-4} - 2 \times 10^{0}$</td>
<td>$3 \times 10^{-3}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>$4 \times 10^{-3} - 1 \times 10^{0}$</td>
<td>$3 \times 10^{-3}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

1 values valid for a 30 g sample aliquot
Typical activity concentrations of $^{239,240}\text{Pu}$, $^{239,240}\text{Pu}$ and $^{241}\text{Am}$ from various sites in Switzerland are shown in Fig. 1. The data for $^{239,240}\text{Pu}$ scatter typically between 0.1 and 3 Bq/kg with an average of 0.5 Bq/kg, while the activity concentration of $^{238}\text{Pu}$ (that was released into the atmosphere by ignition and disintegration of the satellite SNAP-9A in 1964) is considerably lower. Although the contribution of $^{238}\text{Pu}$ on total Pu is insignificant in the soil samples presented in Fig. 1, a good correlation between the isotopes of Pu is indicated and the $^{239,240}\text{Pu}/^{238}\text{Pu}$ ratio of 0.03 ± 0.01 calculated via regression analysis agrees well with that obtained from other sites in the northern hemisphere [1, 2]. Fig. 1 displays also the $^{241}\text{Am}$ vs. $^{239,240}\text{Pu}$ data of the same samples, which also strongly correlate and the regression line through the data yields a result for $^{241}\text{Am}/^{239,240}\text{Pu}$ of 0.38 ± 0.04 (reference date: 01.01.2003). This result is within uncertainty identical to the year 2003 $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio of 0.36 calculated via $^{241}\text{Pu}/^{241}\text{Am}$ progenitor/progeny relationship assuming (i) meaningless initial $^{241}\text{Am}$ during the atomic weapon tests (Fig. 2) and additionally considering (ii) that the initial $^{241}\text{Pu}(t)/^{239,240}\text{Pu}(0)$ ratio resulting from nuclear weapon testing in the 60ies was about 13 [3]. The $^{241}\text{Pu}/^{241}\text{Am}$ progenitor/progeny relationship is illustrated in Fig. 2 with the relative activity development as a function of time. The figure shows clearly that the activity of $^{241}\text{Am}$ produced via decay of $^{241}\text{Pu}$ is about at maximum at begin of this millenium (i.e. $^{241}\text{Am}(t)/^{241}\text{Pu}(0) = 0.028$ about 40 years after the maximum of the surface nuclear tests). With additionally $^{240}\text{Pu}(0)/^{239,240}\text{Pu}(0) = 13$ it follows that $^{241}\text{Am}(t)/^{239,240}\text{Pu}(0) = 0.36$ (decay of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ after 40 years is negligible). This result is in good agreement with data from [4] and shows clearly that $^{241}\text{Am}$ measured in soil samples in Western Europe can be well explained via support from decaying $^{241}\text{Pu}$ initially released during the surface A-bomb testing period. It can be concluded consequently that the contributions of heavy particles from the Chernobyl accident 1986 are not significant in Western Europe.

For distinguishing between two components also normalized three isotope plots such as Fig. 3 are useful. This figure indicates that the reactor Chernobyl component is characterized by considerably higher levels of $^{239}\text{Pu}$ and $^{241}\text{Am}$ compared to $^{239,240}\text{Pu}$ [5]. As clearly shown in Fig. 3 the $^{239,240}\text{Pu}/^{238}\text{Pu}$ and $^{241}\text{Am}/^{239,240}\text{Pu}$ isotope ratios measured here and other locations in Western Europe [1, 2, 4] are within uncertainty identical with the average actinide isotope ratios resulting from the surface atomic bomb tests. The MC-ICP-MS derived concentration values for $^{239}\text{Pu}$ and $^{240}\text{Pu}$ are shown in Fig. 4 that indicates a strong correlation between both isotopes. The regression fit yields a value of 1.48 ± 0.05 which matches closely to the literature bomb fallout activity ratio of 1.5 [6].
Figure 1: Correlation diagram with $^{239,240}$Pu vs. $^{239,240}$Pu and $^{241}$Am vs. $^{239,240}$Pu obtained on Swiss soil samples from various locations.

Figure 2: Progeny/progenitor relationship for the $^{241}$Pu-$^{238}$Am couple with time.

Figure 3: $^{241}$Am-$^{239,240}$Pu vs. $^{238}$Pu-$^{239,240}$Pu three isotope normalization diagram to distinguish between two components with different isotope patterns.

Figure 4: Concentrations for $^{239}$Pu and $^{240}$Pu obtained via ICP-MS.

REFERENCES


EVALUATION OF PRIMORDIAL RADIONUCLIDES IN BUILDING MATERIALS USED IN THE RAWALPINDI/ISLAMABAD AND KARACHI AREAS BY $\gamma$-RAY SPECTROMETRY AND INAA

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Indoor pollution in residences, offices, schools and other buildings is widely recognized as a serious environmental risk to human health. The concern about indoor exposures stems from the fact that most of the people spend around 90% of their time indoors. The presence of primordial radionuclides in building materials is a source of indoor radioactive pollution. Continuous exposure to even low level radiation may adversely affect human health. Environmental protection agencies world-wide are working on the legislation to set upper limits for the natural radiation exposure in new constructions. It is, therefore, mandatory to determine the concentration of naturally occurring radionuclides in building materials. Most of the countries are working to assess the amount of natural radioactivity in building materials in order to evaluate possible radiological hazards and to set safety limits [1-4].

The estimated average indoor-absorbed dose rate in air from terrestrial sources of radioactivity is 70 nGy h$^{-1}$ [5]. The elevated external dose rates are suspected to arise from high activities of radionuclides in building materials. Extensive survey of the concentrations of radionuclides in construction materials has been summarized in the reports of the United Nations [5,6].

In literature the specific activity of natural building materials and those produced from industrial waste and by-products have been reported for many countries [Refs. 1, 4, 7-9]. In Pakistan some studies have been made on the measurement of radon in houses [10]. However the first systematic study was undertaken by our group to measure the levels of natural radioactivities in building materials [11]. This study was undertaken to measure the concentration of $^{238}$U, $^{232}$Th and $^{40}$K in different building materials.
collected from Rawalpindi/Islamabad and Karachi areas using γ-ray spectrometry. Uranium and thorium were also determined by instrumental neutron activation analysis (INAA). The specific activities of primordial radionuclides in these samples were compared with the world averages for soil. The results are presented and discussed on the basis of a criterion formula for acceptable radiation dose rates attributable to building materials suggested for use in the Federal Republic of Germany [12]. The specific activities in these materials, having a radium equivalent activity less than 370 Bq kg⁻¹, when evaluated for radiological effects show that all materials meet the external γ-ray dose limitation of 1.5 mSv y⁻¹. The γ-ray spectrometric and INAA techniques complemented each other well in this study. A summary of most relevant data is given in Tables 1 and 2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample</th>
<th>²³⁵U</th>
<th>²³²Th</th>
<th>⁴⁰K</th>
<th>²²⁶Ra</th>
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<tr>
<td>1</td>
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<td>14±2</td>
<td>225±12</td>
<td>44±5</td>
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<tr>
<td>2</td>
<td>Non-sieved sand</td>
<td>9±1</td>
<td>15±2</td>
<td>290±15</td>
<td>53±6</td>
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<td>Block 1</td>
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<td>9±1</td>
<td>306±17</td>
<td>50±5</td>
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<td>Block 2</td>
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<td>13±2</td>
<td>622±36</td>
<td>79±9</td>
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<td>12±2</td>
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<td>7</td>
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<td>Stone</td>
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<td>9</td>
<td>Roof tile</td>
<td>14±2</td>
<td>10±4</td>
<td>282±14</td>
<td>50±6</td>
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Table 2. Comparison of U and Th concentrations (in µg/g) determined by two techniques

<table>
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<tr>
<th>Material</th>
<th>INAA</th>
<th>Uranium spectrometry</th>
<th>INAA</th>
<th>Thorium spectrometry</th>
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<td>Sieved sand</td>
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<td>0.54±0.06</td>
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<tr>
<td>Non-sieved sand</td>
<td>0.68±0.06</td>
<td>0.64±0.08</td>
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<td>1.06±0.09</td>
<td>1.01±0.11</td>
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<td>Block 2</td>
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<td>0.95±0.10</td>
<td>3.4±0.3</td>
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<td>Block 3</td>
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<td>0.81±0.09</td>
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<td>0.41±0.05</td>
<td>2.4±0.2</td>
<td>1.9±0.2</td>
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<td>ZP cement</td>
<td>3.0±0.3</td>
<td>2.6±0.3</td>
<td>7.5±0.7</td>
<td>6.8±0.8</td>
</tr>
<tr>
<td>Stone</td>
<td>0.55±0.04</td>
<td>0.49±0.05</td>
<td>4.0±0.3</td>
<td>3.5±0.4</td>
</tr>
<tr>
<td>Roof tile</td>
<td>1.07±0.06</td>
<td>1.0±0.1</td>
<td>2.6±0.2</td>
<td>2.2±0.2</td>
</tr>
</tbody>
</table>
References


PRECONCENTRATION OF $^{198}$Au BY MIMUSOPS ELENGI SEED PROTEINS

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¹Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata-700 064, INDIA, dnayak@hotmail.com

²Natural Product Laboratory, Department of Chemistry, The University of Burdwan, Burdwan 713 104, INDIA

Introduction

Several analytical techniques are available for preconcentration of scantly distributed metals. These include precipitation, co-precipitation, electrolysis, liquid-liquid extraction and solid-liquid extraction. Recently, because of their ability to absorb ions from solutions, attention has been devoted to the use of biological organisms for accumulation or preconcentration process for different metal ions. Proteins derived from various natural sources may also act as potential agents for metal separation as well as preconcentration, through their selective metal binding affinity. Plenty of abundance of these materials and their selectivity towards particular metals, have made them powerful reagents in analytical measurements. The sorption of element species by biological substrates offers interesting technological applications in the recovery of precious metals. Bio-sorption of gold has been reported in fungi and algae, but not in seed protein [1-3]. In all of these cases stable gold was used for studying the accumulation process and was detected by atomic absorption spectrometry.

The present study was performed to study the preconcentration of trace amount of $^{198}$Au by proteins extracted from Mimusops elengi seed. Bakul (Mimusops elengi Linn.) belonging to the family Sapotaceae, grows wildly and is also cultivated for its ornamental appearance and fragrant flowers throughout India. The wood from Bakul tree is used for building purposes, bridges, boats, cars and also as folk medicines [4, 5]. Although the plant is widely cultivated under Indian natural forestry program, a large amount of seed is thrown away, even though it contains appreciable amount of nitrogen and protein. We have studied the analytical use of this seed protein for preconcentration of trace amount of gold using $^{199}$Au as precursor. The use of spiked radionuclides to understand the efficacy of protein in metal binding process is an efficient method as it estimates the accurate amount of metal binding at very low concentration and also the detection of metal becomes much easier than the conventional methods. Thus in the present study $^{198}$Au has been spiked with macro amount gold of specified concentrations to study the gold binding.

Materials and methods

Collection, isolation of M. elengi seed protein

M. elengi seeds were collected from the Forest Department, Burdwan, W. Bengal, India, in the middle of January 2003. Finely powered bakul (M. elengi) seeds were deoiled and protein content was estimated. Protein extracted from the deoiled seed at room temperature for 30 min using distilled water at pH 8, dialyzed against 0.01 M phosphate buffer (pH 7.0) for 48 h
at 4°C and freeze dried. Molecular weight of the protein was determined by gel filtration technique [6].

Adsortion of radioactive gold to the protein solution

The $^{199}\text{Au}$ was obtained from Board of Radiation and Isotope Technology (BRIT), Mumbai, India in the form of chlorauric acid solution. The amount of gold adsorbed was measured by γ-ray spectroscopic study with the help of an HPGe detector coupled with a PC based multi channel analyzer and having a detector resolution of 2.53 KeV at 1.33 MeV.

Protein solution of concentration $4\times10^{-5}\text{M}$ was prepared in distilled water, the pH of the solution was 7.3. Measured amount of protein solution was incubated with a measured amount of $^{199}\text{Au}$ solution of concentration 43.5 ng/mL for 40 min at room temperature ($20\degree\text{C}$). The pH dependence of $^{199}\text{Au}$ binding with protein was studied separately with 10 mM tri-sodium citrate and 10 mM phosphate buffer at four different pH levels such as 7.1, 7.2, 7.4 and 7.7 by mixing equal volume of protein and buffer solution. After incubation, 0.1 g of Amberlite IRA 400 an anionic exchanger, was added to each solution, shaken for 10 m, then centrifuged and settled. A fraction of supernatant was removed and assayed for radionuclides by means of HPGe detector and was compared to those of the standard $^{199}\text{Au}$ solution. Appropriate decay corrections have been made in each set of data. Only the free gold ions will bind to Amberlite and the gold bound to protein will remain in the solution.

To study the effect of concentration of gold on its binding with protein the other three sets of experiments were carried out without addition of buffer. Protein solution of same concentration was incubated with 1ppm, 10ppm and 50 ppm gold solutions spiked with $^{199}\text{Au}$ at room temperature ($20\degree\text{C}$). Adsorption of gold was measured by similar process, shaking with the anionic exchanger Amberlite IRA 400 followed by centrifugation. The results are expressed as adsorption (A) in the protein (in percentage):

$$A = \frac{[1 - c_t]}{c_0} \times 100\%$$

where, $c_0$ = count/mL of radionuclide of the standard solution after time t.

$c_t$ = count/mL of radionuclide of the standard solution after time t (with appropriate decay correction).

Results and discussion

The interaction of gold with M. elengi seed protein was analyzed from the present data. The anion exchanger Amberlite IRA 400 adsorbs ~100% of AuCl$_4^-$ ions. Thus it was added to the protein solution after incubation with $^{199}\text{Au}$. Amberlite leaving gold bound with protein in the supernatant should adsorb the free AuCl$_4^-$ ions present in the solution. From figure 1 it is evident that the gold adsorption is almost pH independent and it is neither dependent on the addition of buffer nor the composition (phosphate/citrate) of buffer.

Three different concentrations of gold solutions (1ppm, 10ppm and 50ppm) were used in absence of buffer to understand the role of substrate concentration on the adsorption process. Figure 2 depicts the fact that the adsorption of gold is maximum (93%) in 1 ppm and decreases with increasing concentration from 10 to 50ppm due to finite binding sites.
Figure 1. Adsorption percentage of $^{198}$Au in protein with tri-sodium citrate and phosphate buffer of varying pH.

Figure 2. Adsorption percentage of $^{198}$Au in protein with varying concentration of gold solutions in absence of buffer.

From the present experiment it can be concluded that the protein derived from the *Mimusops elengi* seed efficiently accumulates gold and may be useful bio-reagent for preconcentration of gold from natural solution. However, further investigation is required to identify the exact binding sites to which gold is attached.

References

Po-210 DATING OF YENISEI SEDIMENTS

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In the years 1999 and 2001 sediment samples were taken from the river Yenisei, Sibiria, downstream of three weapon grade plutonium producing reactors near Krasnoyarsk. In order to reconstruct the historical radioactive discharges into the river and to learn about the migration behavior of artificial radionuclides in the river system it is very important to have an independent scale for the age of the activity. In the case of advection of pore water this scale is not identical to the scale for the age of the individual sediment layers.

$^{210}$Pb has a half-life of 22.3 a and falls out of the atmosphere with a constant rate. It is especially well suited to establish an independent time scale for the last 50 years. To determine the activity concentration of unsupported $^{210}$Pb the difference of the total $^{210}$Pb and the supported $^{210}$Pb (i.e. produced within the sediment) has to be determined (see Fig. 1). In principle, the measurements are the following: The total $^{210}$Pb can be measured $\gamma$-ray spectrometrically by its 46.5 keV line [1] and the supported $^{210}$Pb, e.g. by the 295.2 keV and 351.9 keV lines of $^{214}$Pb which is - while hindering the $^{222}$Rn to diffuse out of the samples - after several weeks in radioactive equilibrium with the supported $^{210}$Pb.

Atmosphere:Unsupported $^{210}$Pb

$^{222}$Rn $\rightarrow$ $^{218}$Po $\rightarrow$ $^{214}$Pb $\rightarrow$ $^{214}$Bi $\rightarrow$ $^{214}$Po $\rightarrow$ $^{210}$Pb

Fallout, precipitation

Sediment:Supported $^{210}$Pb

$^{226}$Ra $\rightarrow$ $^{222}$Rn $\rightarrow$ $^{218}$Po $\rightarrow$ $^{214}$Pb $\rightarrow$ $^{214}$Bi $\rightarrow$ $^{214}$Po $\rightarrow$ $^{210}$Pb $\rightarrow$ $^{210}$Bi $\rightarrow$ $^{210}$Po $\rightarrow$ ...  

$T_{1/2} = 1600$ a  3.8 d  3.1 min  27 min  20 min  160 $\mu$s  22.3 a  5.0 d  138 d

$\alpha$: 5.3 MeV

Fig. 1: Ra-226 decay chain in sediment and atmosphere including the respective half-lives.

In the Yenisei sediments analyzed by us the $^{152}$Eu activity concentration is in the order of 100 Bq/kg to 1000 Bq/kg. As $^{152}$Eu emits in its decay 46.6 keV X-rays with an emission probability of about 2 % it is not possible to discriminate between $^{210}$Pb and $^{152}$Eu reliably. Therefore, we decided to determine the $^{210}$Po concentration $\alpha$-spectrometrically [2]. In order not to introduce larger systematic uncertainties by taking the difference of $\alpha$- and $\gamma$-
measurements and in order to keep the amount of laboratory work low, our main idea is to determine not the “total” but the “unsupported” $^{210}$Po directly by a suited extraction.

The unsupported $^{210}$Po is present in all fractions of the sediment produced on a time scale of < 22.3 a before deposition. We tried to extract it with hot nitric acid. In this way the organic components, carbonates and probably other fractions of the sediment are destroyed. The remaining fractions are quartz, feldspars, clay minerals etc. (Sequential extraction experiments are going to be made in spring 2004 to show that the extraction with hot nitric acid only destroys the freshly produced fractions.) In the next step Po is transformed into a chloride. The chloric ions help to extrude the nitric ions; adding distilled water - which is then evaporated - removes the excess of chloric ions.

To determine the efficiency of the measurement a $^{208}$Po tracer was added in the beginning of the process. In order to prevent precipitations, ascorbic acid is added to reduce Fe(III) to Fe(II). In order to keep the Po-ions in solution TeCl$_4$ is added. An excess of Te$^{4+}$ ions acts as competing ion for the binding places on the remaining fractions of the sediment which offer large surfaces. Finally the supernatant liquid is used to deposit the Po thermally onto a polished silver disk.

Fig. 2 shows a typical $\alpha$-spectrum produced in this way. The broadening of the peaks is due to a thin dark blue film which was deposited on the silver disk during the process and which is due to the interaction of Te$^{4+}$ ions and the ascorbic acid. In this way we arrived at a compromise between large efficiency (about 5 % efficiency including chemical processing, deposition and detection) and energy resolution.

![Image of a spectrum showing peaks at 5.304 MeV and 5.115 MeV]

Fig. 2: Sediment $\alpha$-spectrum with the 5.0304 MeV line of the “unsupported” $^{210}$Po and the 5.115 MeV line of the $^{208}$Po tracer.
In Fig. 3 the vertical distribution of “unsupported” $^{210}$Po in the Yenisei sediment about 220 km downstream the nuclear reactors is shown. Fitting an exponential function to the $^{210}$Po activity concentration (constant input concentration, CIC [3]) leads to a “sedimentation rate” of $(1.46 \pm 0.36)$ cm/a. In a depth between 10 cm and 30 cm the $^{210}$Po activity concentration seems to be rather constant. This feature which can be seen also in the distribution of other short living artificial radionuclides like e. g. $^{60}$Co is probably due to mixing of the sediments.

Determining the $^{154}$Eu/$^{152}$Eu ratio (the half-lives are 8.8 a and 13.3 a, respectively) and assuming a discharge with a constant initial ratio leads to a “sedimentation rate” of $(1.8 \pm 0.2)$ cm/a which already agrees quite well with the Po measurement.

Fig. 3: Vertical distribution of “unsupported” $^{210}$Po in the Yenisei sediment about 220 km downstream the nuclear reactors.

At the conference more vertical $^{210}$Po-distributions will be presented, especially from positions where the vertical distribution of artificial radionuclides could be modeled so that the sedimentation rate is already approximately known.

The authors gratefully acknowledge the support by the Spiez Laboratory (Bundesamt für Bevölkerungsschutz, Schweiz).

FORMATION OF HYDROXY-ALUMINOSILICATE COLLOIDS:
THE PROCESS OF ACTINIDE INCORPORATION


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The formation of hydroxy-aluminosilicate (HAS) colloids, as kernels of aquatic colloids may incorporate a number of different trace elements of higher oxidation state in their oxo-bridge structure. In this reaction aquatic trace actinide ions can take part and become colloid-borne species, which may then undergo migration in natural aquifer systems with little geochemical hindrance [1]. The present work is intended to elucidate the fundamental aspects of the provenance of aquatic colloids and how actinides can be incorporated in them to become colloid-borne species.

HAS colloids are synthesized through heterogeneous nucleation of Si and Al under normal conditions of temperature and pressure in the pH region from 4 to 9 as described in our previous work [2]. The Si concentration is maintained at an over-saturation state (10^{-2} mol/l) mixed with 10^{-4} mol/l Al and also at an under-saturation state (10^{-5} mol/l) mixed with 10^{-5} mol/l Al. In the former solution Si appears to be oligo-silanol and in the latter mono-silanol. Tri- and tetravalent actinides, e.g. ^{241}Am and ^{234}Th, are allowed to participate in the colloid formation process or added to aged colloids in order to simulate the actinide interaction with colloids of different origin, either from dissolved groundwater components through nucleation at supersaturation, or from the solid geomatrix through dispersion of nanoparticles at weathering. Incorporation of actinides in the colloidal phase is measured by radiometry with the aid of ultrafiltration as a function of the different experimental parameters. The stability of incorporation is analyzed either spectroscopically or by means of desorption experiments.

An overview for the formation of colloid-borne Am- and Th-species from HAS colloids in statu nascendi under the above mentioned conditions is shown in Fig.1. Incorporation of Am in colloids is observed in two pH regions: one around pH 5 and another at pH 8-9. When the Si concentration is oversaturated, the contour patterns of the colloidal
formation become different from the undersaturated Si concentration. Using the optically sensitive element Cm, the chemical nature of colloid-borne trivalent actinides is characterized by TRLFS (time-resolved laser fluorescence spectroscopy). The formation of two colloid-borne Cm species is shown in Fig.2 (upper part) as a function of pH. The first species (Cm-HAS(I)) appears in a small amount in the whole pH range with a maximum of 20% fraction at pH 6 and the second species (Cm-HAS(II)) is beginning to form at pH ≥ 5, then predominates at pH ≥ 7. The number of hydration water molecules bound to colloid-borne Cm, as derived

![Diagram of Th(IV) and Am(III)](image)

**Fig.1:** Contour diagrams of the colloid-borne Th (left side) and Am (right side) fraction (z-axis) normalized to the initial Th and Am activities, respectively, after 35 of conditioning as a function of pH. Concentrations for Si and Al (including blanks) are indicated in the central part and on the right y-axis, respectively.

from the fluorescence life-time of each Cm-HAS species, is found to be 7 for Cm-HAS(I) and 6 for Cm-HAS(II), which suggest bidentate and tridentate binding of Cm in the aluminosilicate structure, respectively. Either aging or tempering of Cm-HAS colloids leads to a nearly complete dehydration of colloid-borne Cm, forming the third species: Cm-HAS(III). The same species is readily produced, when the initial species appears to be
Fig. 2: Distribution of the Cm species as a function of pH in a sample with 1E-3 mol/l Si, 1E-5 mol/l Al and 5E-8 mol/l Cm (upper part) and in a sample with 1E-2 mol/l Si, 1E-4 mol/l Al and 5E-8 mol/l Cm (lower part). The speciation is made by TRILFS.

Oligosilanol, e.g. at conditions of supersaturated Si (1E-2 mol/l) in the pH range from 6.5 to 9 (Fig.2, lower part). The present experimental results infer that Am(III) takes part as a contestant of Al(III) in the nucleation process of aluminosilicate colloids and becomes incorporated into their molecular structure. Aged aluminosilicate colloids are not tied up to bind Am but the affinity for Th is unchanged or even higher, suggesting another incorporation mechanism by displacement of Si in HAS colloids.

References
**137Cs LOW-LEVEL DETERMINATION IN DRINKING WATER USING A SILICA GEL IMPREGNATED WITH MOLYBDOPHOSPHATE (ASG ADSORBENT)**

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**Introduction**

137Cs released to the biosphere has to be determined in water samples to study subsequent pathways of this element to man. This radioisotope is usually only present in drinking water at extremely low concentrations and complex radiochemical procedures are necessary before the 137Cs concentration can be determined by gamma ray spectrometry.

In this paper, an improved method has been developed in order to reduce the cost of analysis and the required time. In this procedure 137Cs is removed from water by using adsorption on silica gel impregnated with molybdophosphate (ASG adsorbent).

The analytical procedure has been validated according to the quality requirements of the ISO 17025 Standard [1] by evaluating the following parameters [2]: selectivity, minimum detected activity (MDA), precision, accuracy and expanded uncertainty.

The method has been applied to different samples taken from the Barcelona (Spain) water supply.

**Materials**

Silica gel impregnated with molybdophosphate (ASG adsorbent) was prepared in the laboratory as described by Terada et al. [3].

In order to prepare the adsorption column, 30 g of dried ASG adsorbent was transferred to a methacrylate tube (30 cm long and 1.9 cm inner diameter) using acidified distilled water (pH 1-2) and two pieces of fiberglass were placed at the bottom and top of the column.

Tapped water samples were collected from a single water source in the city of Barcelona (Spain).

137Cs standard water samples were prepared by adding a 137Cs standard solution, certified by Darmi, to the tap water.

Gamma standard water samples were prepared by adding a mixed gamma standard solution, certified by Amersham, to the tap water.

**Radiochemical procedure**

A 600-L polyethylene container was filled with tap water. The water was then acidified up to pH 1-2 by adding nitric acid concentrate (65%) and stirred for about 30 minutes.

The 137Cs was removed from the water sample by passing the water through the adsorption column at a flow rate of about 6 L/h. At the end of the process the ASG adsorbent was dried and measured with a germanium detector, with 40% of efficiency, for a 3-day counting period.

Blanks were prepared with 30 g of ASG adsorbent and measured with a germanium detector for a 3-day counting period.

**Results and discussion**

- **Selectivity of the method**

The selectivity of the method was tested by passing 100 L of gamma standard water through 30 g of ASG adsorbent and measuring the gamma ray activity both in the ASG adsorbent and outflows.
Table 1 shows the activity in the ASG adsorbent. Only $^{113}$Sn and $^{137}$Cs are adsorbed, nevertheless, the $^{113}$Sn peak at 392 keV does not interfere with the $^{137}$Cs peak at 661.6 keV. For $^{137}$Cs the ASG adsorbent is selective with 99 ± 3 % of retention. No $^{137}$Cs activity above the MDA of 0.6 Bq/L was detected in the outflows. The other gamma ray emitting isotopes were detected in the outflows according to the initial activity in the gamma standard water.

<table>
<thead>
<tr>
<th>ARTIFICIAL ISOTOPE (Photoneak energy, keV)</th>
<th>INITIAL ACTIVITY (Bq)</th>
<th>ACTIVITY IN ASG ADSORBENT (Bq)</th>
<th>% ADSORBED</th>
</tr>
</thead>
<tbody>
<tr>
<td>An-241 (59.54)</td>
<td>660 ± 20</td>
<td>8.8 ± 0.4</td>
<td>1.33 ± 0.07</td>
</tr>
<tr>
<td>Cd-109 (88.03)</td>
<td>1730 ± 110</td>
<td>&lt;1.7</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Co-57 (122.1)</td>
<td>39.8 ± 0.6</td>
<td>&lt;0.09</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ce-139 (165.9)</td>
<td>14.5 ± 0.2</td>
<td>0.18 ± 0.07</td>
<td>1.2 ± 0.5</td>
</tr>
<tr>
<td>Sn-113 (391.7)</td>
<td>33 ± 1</td>
<td>29 ± 1</td>
<td>88 ± 4</td>
</tr>
<tr>
<td>Sr-85 (514.0)</td>
<td>4.0 ± 0.1</td>
<td>&lt;0.24</td>
<td>&lt;6</td>
</tr>
<tr>
<td>Cs-137 (661.6)</td>
<td>595 ± 10</td>
<td>592 ± 16</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>Y-88 (898.0)</td>
<td>53.6 ± 0.8</td>
<td>0.44 ± 0.04</td>
<td>0.81 ± 0.08</td>
</tr>
<tr>
<td>Co-60 (1173)</td>
<td>591 ± 8</td>
<td>0.25 ± 0.03</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>

- **Efficiency of the process**

The efficiency of the process was studied by passing $^{137}$Cs standard water through the ASG adsorbent and collecting outflows for each 50 L.

The $^{137}$Cs non-adsorption factor was calculated as the ratio of the $^{137}$Cs outflow activity and the initial $^{137}$Cs activity.

In Fig. 1 the graph shows the $^{137}$Cs non-adsorption factors plotted against the volume of $^{137}$Cs standard water passing through different columns containing 10, 20 or 30 g of ASG adsorbent. The points show the values of MDA and the points with bars represent the detected values and their uncertainty (k=2).

With 30 g of ASG adsorbent and a volume of 600 L the non-adsorption factor is lower than 5%.

- **Repeatability**

This parameter was determined by measuring the relative repeatability standard deviation [2]. The obtained value was 4 % (k=2).

- **Accuracy of the process**

The accuracy of the procedure was tested by using 5 columns with 30 g of ASG adsorbent in each, and passing $^{137}$Cs standard water volumes ranging between 100 L and 600 L through the columns. The calculated mean value of the accuracy is + 3.6 %.

- **Minimum Detected Activity (MDA)**

The MDA [4] for 600 L of drinking water in a 3-day of counting period was 20 mBq/m².

- **Combined Uncertainty [5]**

The combined uncertainty (k=2) was estimated by taking into account all the known components that affect the final result [5].

The contribution of different factors in the combined uncertainty was studied in $^{137}$Cs standard water and tap water. In standard water the gamma detection smooth efficiency
and the repeatability uncertainty are the greatest factors that affect the combined uncertainty, whereas in tap water the photo-peak area is the main factor.

**137Cs concentration in drinking water**

The method was applied to different samples taken from the Barcelona (Spain) water supply. In year 2002 the monthly 137Cs concentrations was close to the MDA (0.02 Bq/m³).

![Graph](image)

**Figure 1:** 137Cs non-adsorption factor as a function of the volume of 137Cs standard water and quantity of ASG adsorbent

**Conclusions**

A procedure for 137Cs low-level determination in drinking water has been developed and validated. The proposed procedure allows both selective and quantitative adsorption of 137Cs without addition of a caesium carrier. The amount of caesium in the water sample (ranging between 2·10⁻⁵ and 14·10⁻⁵ mg/L) should be sufficient to enable full retention of this metal.

The efficiency of the process is close to 100% using 30 g of ASG adsorbent and a volume of 600 L.

**References**


RADIOTRACER STUDY OF DIALYSIS, ELECTROPHORESIS, ION EXCHANGE AND ULTRAFILTRATION AS METHODS FOR ANALYSIS OF METAL-HUMATE COMPLEXATION

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Interaction with humic substances in natural waters and soils represents an important process affecting toxicity and behaviour of toxic metals and radionuclides in the environment. Therefore the formation of aquatic metal humate complexes and other forms of the interaction have been rather extensively studied. Existing data on metal ion humate interaction frequently contradict each other due to lack in critical assessment of experimental methods applied. This is especially true at low metal ion concentrations and leads to lack in confidence in experimental data, process understanding and thus predictive geochemical modelling. Such a modelling is particularly important for performance assessment of nuclear waste disposal. Recently the role of humic substances in nuclear waste disposal became a target in a project of EC EURATOM Programme entitled "Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field (HUPA)". One of its objectives was to provide the necessary knowledge to improve confidence in own and published experimental results on radionuclide-humate interaction [1]. The approach chosen was the comparison and evaluation of results obtained with several experimental methods applied to the analysis of complexation of europium with Aldrich humic acid (HA) under similar experimental conditions. Europium was used as an analogue of trivalent actinides representing important components of spent nuclear fuel.

In this work, applicability of four experimental methods was tested: dialysis, electrophoresis, ion exchange and ultrafiltration. Radiotracer arrangement of the methods using $^{152,154}$Eu facilitated examination of fulfillment of basic assumptions of the methods and of the effects of sorption losses of the metal on apparatus and vessel walls. In order to work with a standardized HA, lyophilized sample of solid HA purified by a standard procedure was prepared and characterized by "baryta" method and acidobasic titration (for determination of total proton exchange capacity and proton dissociation characteristics, respectively), thermogravimetry and FTIR [2].

Standard conditions for complexation experiments were selected in order to enable comparability of the results: room temperature (18-25°C), pre-equilibration of europium with HA for 1 and 7 d, pH 4 and 6, ionic strength I (adjusted with NaClO4) = 0.1 and 0.01 mol/L, HA concentration 10 mg/L, total europium amount in the system to obtain the following loading of HA with europium: 1%, 10% and 50% of total proton exchange capacity of HA present in the system divided by three (PEC/3). The degrees of europium complexation with HA (%EuHL) determined by individual methods were compared.

Basic assumption in equilibrium dialysis is the establishment of equilibrium, when uncomplexed metal (Eu$^{3+}$) is distributed evenly between two reservoirs A and B separated by a semipermeable membrane, whereas metal humate complex is retained in reservoir A containing all HA. The dialysis was successfully tested at the volume ratio of reservoirs A/B
when shift of equilibrium due to diffusion of Eu\(^{3+}\) was suppressed. Reservoir B was represented by a bag made of Spectra/Por Biotech CE tubing (MWCO 500 Da) clamped on both sides. Only small penetration of HA into the bag was observed, a near-to-constant concentration of Eu in the bags was achieved after 6-12 days. Very significant sorption losses of Eu were found which, however, did not prevent obtaining correct values of %EuHA, if the losses were neglected and the starting concentration of Eu in reservoir A was used for calculation of %EuHA. This was probably due to predominant sorption of Eu\(^{3+}\) complexes that remained in equilibrium with Eu\(^{3+}\) even after the sorption. Due to possible disequilibrium in distribution of Eu\(^{3+}\) between the reservoirs and due to possible sorption losses of Eu\(^{3+}\), the value of %EuHA calculated from equilibrium dialysis data must be considered as the maximum possible value.

Examination of data presented in Table 1 shows that the results of dialysis are the same as or lower than those obtained by two other methods. This indicates achievement of equilibrium and negligible effect of Eu\(^{3+}\) sorption. Thus equilibrium dialysis can yield correct data on the complexation. Its main disadvantage is the long time needed for establishment of equilibrium.

Table 1 - Comparison of %EuHA values obtained by dialysis (DIA), electrophoresis (EP) and ion exchange (IE) with retention of Eu (in %) in ultrafiltration through 1 kDa ultrafilter (UF, in brackets).

<table>
<thead>
<tr>
<th>Loading (%)</th>
<th>pH</th>
<th>I</th>
<th>DIA</th>
<th>EP</th>
<th>IE</th>
<th>UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>0.01</td>
<td>98.7±0.2</td>
<td>99.3±0.6</td>
<td>99.1</td>
<td>(80.0)</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0.1</td>
<td>94.6±0.7</td>
<td>97.2±0.7</td>
<td>99.7</td>
<td>(79.7)</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0.01</td>
<td>99.6±0.2</td>
<td>99.6±0.3</td>
<td>99.7</td>
<td>(90.9)</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0.1</td>
<td>99.6±0.2</td>
<td>98.7±0.3</td>
<td>100.0</td>
<td>(94.1)</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.01</td>
<td>96.0±0.2</td>
<td>98.8±0.9</td>
<td>91.9</td>
<td>(64.9)</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.1</td>
<td>81.8±1.8</td>
<td>88.3±2.7</td>
<td>82.6</td>
<td>(27.9)</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>0.01</td>
<td>99.9±0.1</td>
<td>99.4±0.4</td>
<td>99.5</td>
<td>(73.1)</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>0.1</td>
<td>99.3±0.2</td>
<td>97.6±1.7</td>
<td>99.5</td>
<td>(71.4)</td>
</tr>
<tr>
<td>50</td>
<td>4</td>
<td>0.01</td>
<td>62.5±2.0</td>
<td>78.9±3.9</td>
<td>64.6</td>
<td>(62.1)</td>
</tr>
<tr>
<td>50</td>
<td>4</td>
<td>0.1</td>
<td>35.9±5.0</td>
<td>35.1±2.0</td>
<td>34.7</td>
<td>(26.5)</td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>0.01</td>
<td>98.2±0.2</td>
<td>95.1±2.2</td>
<td>95.7</td>
<td>(43.0)</td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>0.1</td>
<td>84.9±1.0</td>
<td>94.5±2.5</td>
<td>84.0</td>
<td>(41.8)</td>
</tr>
</tbody>
</table>

In free liquid electrophoresis, electrophoretic mobilities of \(^{152,154}\)Eu in 10 mg/L HA solutions were measured in a broad range of Eu total concentration (10\(^{-8}\)-10\(^{-2}\) M). The mobilities towards cathode were used to calculate %EuHA. The dependence of %EuHA on the total Eu concentration was curve-fitted and values corresponding to 1%, 10%, and 50% metal loading were interpolated for comparison with other experimental methods (Table 1).

The method can be affected by sorption losses of uncomplexed metal on electrophoretic cell and by retardation of electrophoretic mobility of radiotracer by isotope exchange with unlabelled species [2]. Both the effects can lead to apparent increase in calculated %EuHA and therefore the values of %MHA determined by electrophoresis represent a maximum possible degree of complexation in the system. Comparison of data in Table 1 suggests that the effects caused increase in %MHA determined by electrophoresis only at the highest metal loading. Otherwise the data from electrophoresis agree well with data from dialysis and ion exchange. Thus the method was found well suited for determination of %EuHA.
Ion exchange method was used in batch arrangement with cation exchanger Amberlite IR-120(Na). Basic condition of the method is that complexed metal is not adsorbed in the system and distribution of uncomplexed metal between solution and ion exchanger is well known. Therefore non-linear equilibrium sorption isotherms of Eu$^{3+}$ on Amberlite IR-120(Na) were first measured in the absence of HA. Then equilibrium concentrations of complexed and uncomplexed metal ($EuHA$, $Eu_{free}$) and the actual metal loadings of HA were determined with $10^{-3}$ M Eu and 1-80 mg/L HA or with 10 mg/L HA and $1 \times 10^{-5}$-$5 \times 10^{-4}$ M Eu. Using the data obtained the stability constants of EuHA complex were calculated for each set of experimental conditions using the charge neutralization model [3] and plotted as a function of equilibrium concentration of Eu in solution ($EuHA + Eu_{free}$). Constants corresponding to required values of metal loading, pH and I were used for calculation of %EuHA. The results shown in Table 1 agree well with %EuHA values determined by equilibrium dialysis and by electrophoresis. It can be concluded that the ion exchange method yields reliable complexation data if the isotherm for distribution of uncomplexed metal ions between solution and ion exchanger is adequately investigated and a suitable model is used for evaluation of results. Sorption losses need not play a significant role.

Ultrafiltration was tested with two types of ultrafilters: Amicon YC50 (MWCO 500 Da) and Millipore PLAC (MWCO 1 kDa). The effect of sorption on the results and the efficiency of separation of Eu forms were studied using a newly designed arrangement and two methods of evaluation. Large sorption losses of Eu on ultrafiltration cell were found during ultrafiltration. Such losses significantly complicated evaluation of ultrafiltration results from the activity retained in the cell and to less extent also from the activity of ultrafiltrate. Efficient corrections for the losses are difficult to apply and require detailed analysis of the sorption. The sorption need not result in a significant shift of complexing equilibria in the system, which can also be avoided by limitation of the part of solution filtered. However, the ultrafiltration used were unable to well separate EuHA complex from uncomplexed Eu, since they partially retained Eu$^{3+}$. This, together with incomplete retention of EuHA, led to values of Eu retention, which differed from %EuHA obtained by the other methods (see Table 1). Thus fulfillment of the basic condition of the method was not confirmed. It can be concluded that unless good separation of complexed and uncomplexed metal forms and efficient correction for metal sorption on cell and ultrafilter are ensured, ultrafiltration based humate complexation data need to be interpreted with great caution.

Acknowledgement

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References


RELEASE AND SORPTION OF URANIUM IN THE SYSTEM WASTE ROCK FROM URANIUM MINING – NATURAL WATER

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The release and migration of uranium from uranium mining waste rock piles can represent a considerable environmental hazard, as the piles are often situated, like in Germany and Czech Republic, in densely populated areas. The piles can partly serve also as a geological analogue of other nuclear waste repositories. Modelling of the release and migration of pollutants on the field scale, necessary for prediction of their environmental effects, requires understanding of interaction processes at the basic level, which can be achieved in a laboratory study. An extensive environmental study was performed in the waste rock piles region at Schlema-Alberoda (Saxony, Germany) mainly in 1990-2000 but, as reported in [1], necessary observations and data for performance assessment modelling are still missing. Therefore laboratory work was undertaken with a sample of waste rock from uranium mining to improve understanding of uranium release/uptake processes and to obtain input data for modelling of uranium migration in the rock.

Waste material from rock pile No. 66 at Schlema-Alberoda was selected for the study. Sampling of the rock and its characterization (elemental composition, mineralogy, total carbon, inorganic carbon and specific surface area) was organized by Research Center Rossendorf [2], granulometric analysis, determination of exchangeable uranium and sorption/desorption studies by batch and column experiments were performed in our laboratory. Most of the experiments were carried out by radiotracer method using $^{238}$U as the tracer. Distribution of $^{238}$U was measured with liquid scintillation counting. The rest of evaluations were based on determination of $^{234}$U and $^{235}$U by means of ICP-MS.

First experiments aimed at determination of uranium in the rock sample accessible to leaching with natural water and exchangeable with ions in the water. This so called exchangeable uranium ($U_{ex}$) was determined by isotope exchange with $^{238}$U in two aqueous media with different initial composition: (i) $10^{-3}$ M HNO$_3$ and (ii) simulated seepage water from the pile No. 66 (0.0175 M MgSO$_4$, 0.0091 M CaSO$_4$, 0.00258 M NaHCO$_3$). The experiments, with contact time of 14 days, resulted in similar mean values of $U_{ex}$ ($\approx 20 \mu$g/g) for both the media, which represented approx. 34 % of total uranium in the sample. This result was in good agreement with evaluation of kinetics of desorption of natural uranium by simulated seepage water (see below).

Further batch experiments carried out with synthetic seepage water examined effects of concentration of added uranium and humic acid on uranium distribution and kinetics of uranium sorption and desorption. The near-to-equilibrium distribution data corresponded to approximately linear sorption isotherm ($K_d \approx 20$ mL/g), with no significant dependence on the volume to mass ratio ($V/m = 10-100$ mL/g). The effect of added Aldrich humic acid (HA, 10 and 50 mg/l) was almost negligible with exception of experiments at higher concentration of added uranium, when the addition of HA caused an increase of $K_d$ to 25-30 mL/g. The small effect of HA could be explained by saturation of HA added by Ca and Mg present in the simulated water.
Slow kinetics of $^{233}\text{U}$ uptake was found with about two weeks required to obtain a steady-state distribution at $V/m = 10-100$ mL/g. Rather complicated effects of experimental conditions (total uranium added, $V/m$, concentration of HA, the pre-equilibration of phases preceding addition of the spike) on the kinetics were observed. Most of these effects can be explained if the distribution of uranium initially present in the rock material and of uranium added are considered separately. E.g., when very small concentration of labelled uranium is initially present in the solution, uptake of $^{233}\text{U}$ is measured but the actual flow of uranium in the system can be dominated by the release of exchangeable uranium from the rock. In this case the uptake of $^{233}\text{U}$ should be interpreted as isotopic exchange with the exchangeable uranium rather than as the uptake of uranium added. This seems to be obvious but has often been overlooked in environmental studies. Additional experiments to elucidate methodical aspects of the radiotracer study and its results are underway. It is clear that the study of the sorption/desorption kinetics by this method can give relevant results only if the kinetics of the isotope exchange is known.

![Fig. 1. Kinetics of uranium release from the rock material with simulated natural water at room temperature and $V/m = 20$ mL/g - concentration of uranium in water measured by ICP MS or calculated from $^{233}\text{U}$ activity.](image)

Kinetics of uranium release from the rock material was studied both by radiotracer method and by direct (ICP-MS) measurement of released uranium. In the first case, the material was pre-equilibrated with $^{233}\text{U}$. In order to avoid premature release of uranium, the pre-equilibration was made with $6.6 \times 10^{-6}$ M solution of uranium labelled with $^{233}\text{U}$. This concentration is near to that in equilibrium with $U_{eq}$. Two different times of pre-equilibration were used to check possible effect of time caused by slow isotope exchange or by a leaching of the rock material. The direct measurement of released uranium was made without pre-equilibration of the rock with the simulated natural water. Results of the experiments at $V/m = 20$ mL/g are presented in Fig. 1. As can be seen, the longer time of pre-equilibration led to apparently smaller release of uranium, probably due to the isotope exchange of $^{233}\text{U}$ with less
leachable forms of uranium. Good agreement between the results of the direct U measurement and of the radiotracer method was obtained if the activities of released \(^{233}\text{U}\) were transformed into dissolved concentrations of U assuming \(K_{d} = 16.8 \text{ mL/g}\) and \(U_{0} = 22.5 \mu\text{g/g}\). This suggests that the radiotracer method used is suitable for determination of input data for modelling of uranium release from the pile.

Column experiments aimed at simple modelling of dynamic conditions of uranium leaching and migration in waste rock pile as well as at testing applicability of batch data for the modelling. They were carried out with small columns (inner diameter 0.9 cm, height of rock layer 3 and 5 cm) and linear flow-through velocities 2.8 and 6.3 cm/h. The flow-interruption technique showed that non-equilibrium conditions existed during the experiments. The elution experiments using \(^{233}\text{U}\)-spiking were preceded by a sufficient equilibration of the rock sample with spiked uranium solution directly in the assembled circuit (column and tubings). Parallel experiments were run with the non-spiked and non-equilibrated rock. Considerable disagreement was found between elution curves of \(^{233}\text{U}\) and of natural uranium in these two systems, respectively, the reasons of which are not yet clear. Solution of this problem is related to the analysis of the role of isotope exchange in the kinetics of the uptake of \(^{233}\text{U}\).

Because of the small amount of the waste rock material in the column, used for technical reasons (e.g. to limit duration of the experiment to 7-10 days for both equilibration and elution steps), sorption of uranium on the walls of column and tubings should also be taken into account. For instance about 10-20 \% of \(^{233}\text{U}\) retained during the equilibration in the assembled system was found sorbed on the walls after the elution step.

In contrast to batch experiments, significant influence of humic acid on U release was observed; presence of HA (about 10 mg/L) in the elution solution caused about 30\% increase in elution rate compared with the rate in the absence of HA under the same conditions. This result well corresponds with findings about the role of complexation with humic substances in the environmental migration of contaminants. Large retention of humic acid in the waste rock layer was observed, probably aided by the high content of small particles in the sample (33 wt. \% of particles with size under 0.1 mm). The studies of uranium leaching and sorption under dynamic conditions will continue.

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References


RADIOCAESIUM IN WATER AND SEDIMENTS OF LAGO MAGGIORE: MEASUREMENTS AND MODELING

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Lago Maggiore with a surface area of 212 km² and a maximum depth of 370 m is one of the largest drinking water reservoirs at the southern rim of the Alps. Originally, Lago Maggiore was an oligotrophic lake but during the 1960s it was rapidly eutrophied to a mesotrophic state. Meanwhile it became oligotrophic again [1]. After the fallout of the Chernobyl accident in 1986 roughly 20 kBq/m² of 137Cs were deposited onto the lake surface, about the same amount as on the neighboring Lake Lugano. But in contrast to Lake Lugano which has a different limnological character the fate of 137Cs in Lago Maggiore is practically still non-investigated. Therefore, in order to examine the 137Cs balance in Lago Maggiore and, in particular, its migration behaviour into and within the sediment, water samples and sediment cores were taken in 2003 from two positions in the northern basin of Lago Maggiore. Position 1 with a depth of 96 m is in front of the mouths of Ticino, Versasca and Maggia; position 2 with a depth of 285 m is in the middle of the basin between Cannobio and Brisago.

The following measurements and investigations have been done:

- Measurement of 137Cs activity concentration and other relevant parameters in the water column and in suspended matter,
- determination of the vertical 137Cs distribution in the sediment,
- sequential extractions to determine the association of 137Cs to the different geochemical fractions,
- modeling of the input of activity into the sediment and its migration within the sediment.

The activity concentration in the water increases only slightly with depth and is about 1 mBq/l. The concentrations of the competing ions [K⁺] and [NH₄⁺] within the water column are 2 and 0.01 mg/l, respectively. In the pore water of the sediment these values increase to 5 mg/l for K⁺ and more than 9 mg/l for NH₄⁺. Here, both competing ions have an influence on the 137Cs migration by increasing the retarded diffusion in the sediment. Other water parameters such as pH (almost 7) and oxygen (about 6.5 mg/l) also stay rather constant over the whole water column.

Fig. 1. shows as an example the profile (left) and vertical 137Cs distribution (right) of a sediment core taken in May 2003 at the position 2. Two maxima are recognizable which can be assigned to the fallouts after the Chernobyl accident and atmospheric nuclear weapon tests in the 1960s. The lamination of the annually registered layers can be well recognized. Between 13 and 33 cm depth there is one layer with uniform colour. The activity concentration of 137Cs and 210Pb as well as the density within this layer are constant. From that we can conclude that this layer corresponds to one single event. It is marked as “turbidite”. At position 1 within the washing area of Ticino, Versasca and Maggia, the sediment deposition rate is much higher than here at position 2.
Fig. 1: Vertical distribution of $^{137}$Cs in the sediment of Lago Maggiore (0-47 cm) at Position 2 with a depth of 295 m. Decay-corrected to 1.05.1986.

Since the activity concentration of $^{137}$Cs at position 2 was determined both in water and in the suspended matter the distribution coefficient $K_D$ can be calculated. In the surface water it corresponds to the value of $(33 000 \pm 5 000)$ l/kg while the weighted average over the rest of the column is $(92 000 \pm 18 000)$ l/kg. Calculating a $K_D$ as the ratio of the activity concentrations in the top layer of the sediment and in the deep lake water, one receives the value of $(72 000 \pm 7 000)$ l/kg. These values have to be compared with the outcome of the model.

Table 1: 5-step extraction procedure and portion of extracted $^{137}$Cs at position 1 of Lago Maggiore (9.5-24.0 cm, Chernobyl-Cesium).

<table>
<thead>
<tr>
<th>Chemical Reagent</th>
<th>Phases with Target Ions</th>
<th>Portion of extracted $^{137}$Cs in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH$_3$COONH$_4$ (1 mol/l)</td>
<td>“Exchangeable Ions”</td>
<td>0.45</td>
</tr>
<tr>
<td>2. CH$_3$COONH$_4$ (1 mol/l) + HNO$_3$ (1mol/l), pH $\geq 5$</td>
<td>“Carbonates”</td>
<td>0.2</td>
</tr>
<tr>
<td>3. NH$_3$OH-HCl (0.2 mol/l) in CH$_3$COOH (25 %)</td>
<td>“Oxides and Hydroxides of Iron and Manganese”</td>
<td>0.15</td>
</tr>
<tr>
<td>4. H$_2$O$_2$ (35 %) + HNO$_3$ (1 mol/l) up to 0.05 mol/l</td>
<td>“Organic Matter”</td>
<td>2.2</td>
</tr>
<tr>
<td>5. NaOH (0.2 mol/l) (40 min Stirring at 80 °C)</td>
<td>“Amorphous Silicates”</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The binding of the $^{137}$Cs to different geochemical fractions of the sediment has been examined by sequential extraction experiments on samples from different depths and positions. The procedure and some results for position 1 are shown in Tab. 1. Compared to similar positions at Lake Lugano the activity is rather strongly fixed [2]. 91.5 % is associated to the residue which mainly consists of clay minerals, feldspars and quartz. Only the amount of $^{137}$Cs associated to “organic matter” and to the “amorphous silicates” is in the order of some
percent. Regarding our model we decided to use the exchangeable activity as it is measured in the first step as one fraction; all the rest is put into fraction of the “fixed” activity.

The concentration of radionuclides in the sediment changes with depth due to the time dependent input of activity as well as due to different transport mechanisms. Our model which is a system of two coupled partial differential equations takes into account the input of $^{137}$Cs into the sediment via suspended matter which is assumed to be in equilibrium with the lake water, fixation and redissolution processes, retarded diffusion of the exchangeable $^{137}$Cs, bio- or physical turbation in the top layer of the sediment, and radioactive decay. This model has already been used to analyze other pre-alpine lakes [3]. In this work we use a finite-element-programme (FEMLAB 2.3) which enables us to model the Chernobyl-$^{137}$Cs as well as the $^{137}$Cs from the fallout of the atmospheric nuclear weapons testing.

The activity concentration in the lake water is used as boundary condition for the partial differential equations. As it has not been measured throughout the time span considered it is calculated by MOIRA [4] which works quite reliably with some general information on the lake and its watershed (information on relevant equations used in MOIRA can be found in [5]). The output of MOIRA is then calibrated by our data measured in 2003.

Further improvements of our model are a varying sedimentation speed within the sediment due to compaction which is inversely proportional to the density and two different distribution coefficients $K_s$: One is responsible for the uptake of $^{137}$Cs into the top layer of the sediment, whilst the other one regulates the retarded diffusion within the sediment. The ratio of both $K_{sb}$ is given by the inverse ratio of the concentration of competing ions in water and sediment, respectively. Also, an extra term to handle large turbidites is included.

Main free parameters are only the distribution coefficient $K_0$ and the sedimentation speed. Results of modelling will be presented and compared to other lakes at NRC 6.

We gratefully acknowledge the support of Labor Spiez, Bundesamt für Bevölkerungsschutz, Schweiz. We want to thank Dr. Piero Giulizzoni and Stefano Vanetti of „CNR-Instituto per lo Studio degli Ecosistemi” (I.S.E) in Verbania Pallanza, Italy, for enabling sampling with their boat on Lago Maggiore.

REFERENCES

DETERMINATION OF HEAVY METALS IN AEROSOL FRACTIONS OF DIFFERENT PARTICLE SIZES FROM THE HEALING GALLERY OF BADGASTEIN (AUSTRIA)

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Introduction

In the healing gallery of Badgastein, a famous radon spa in the Austrian Alps, aerosol samples were collected with an 8-stage cascade impactor device. The grain size fractions were 62-125 nm, 125-250 nm, and so on, up to 8-16 μm. In the gallery, where the temperature is about 40°C and the air humidity is near to 100%, the radon activity concentration was measured, as well as ²¹⁰Pb and its daughter products were determined; the found ²¹⁰Po/²¹⁰Pb and ²¹⁰Bi/²¹⁰Pb ratios, which showed extremely elevated ²¹⁰Po values compared to ²¹⁰Bi as well as compared to ²¹⁰Pb, were already published (1).

The therapeutic section, where the cascade impactor was situated, is separated from the entrance gallery by a door, which reduces the natural ventilation in the mine system. Fresh air can be supplied by artificial ventilation. During therapy periods on weekdays between 7:30 a.m. and 6:00 p.m. the door is closed, resulting an air exchange rate of η=0.035 h⁻¹; overnight the fresh air supply is shut off completely (full ventilation with the door open gives η=6.35 h⁻¹ or a full air exchange within 3 hours). Sampling started on May 27, 1999, at 10:30 during a therapy period, went on overnight and ended the next day at 14:10, again during a therapy session. A sampling time of 27.3 hours corresponds to the collection of aerosols contained within 50.46 m³ of air.

Weighing the aerosol samples, we found very high aerosol masses compared to samples taken outdoors (157 μg/m³ and 5.6 μg/m³, respectively); moreover, the samples showed a very distinct brown colour, which might be caused by iron, stemming from the tracks of the Diesel-driven gallery train or from old wirings. To get information of the grain size
distribution of the Fe and other metals in the aerosols we used instrumental neutron activation analysis.

Experimental

Irradiations of the samples adherent to the foils were performed in the research reactor at Budapest, Hungary (thermal neutron flux $8 \times 10^{13} \text{ s}^{-1} \text{cm}^{-2}$) and the prominent $\gamma$-lines of the respective nuclides representing the elements Fe, Cr, Zn, Co and Sc were measured after sufficient cooling time with a high purity Ge detector. The latter was used as a "tracer" for Ca, which could not be measured due to the short half-lives of its activation products. Fe powder samples were used as standards. As the sampling foils in the impactor were aluminum foils, corrections had to be made for the metallic impurities of the foils. The samples from the impactor stages 7 and 8 (aerosol sizes 4-8 and 8-16 $\mu$m) could not be investigated due to too low aerosol mass spread over a too large foil area. The lower limits of detection (LLD) for the different elements were given by the amount of the respective foil impurities; they were calculated as the $3 \sigma$-errors of the impurities in the foil carrying the aerosols. The range of the LLDs is given in table 1. In addition, also a rock sample from the healing gallery and wipe test samples from the train tracks and the gallery floor were irradiated.

Table 1. The range of the LLDs (in $\mu$g) for the determined elements.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Zn</th>
<th>Co</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>1.6-3.2</td>
<td>0.004-0.009</td>
<td>0.021-0.052</td>
<td>0.001-0.0025</td>
<td>5$\times 10^{-4}$-1$\times 10^{-4}$</td>
</tr>
</tbody>
</table>

Results

Results of the element analysis as well as the aerosol mass distribution are summarized in table 2. The $1\sigma$-error of the element masses is smaller than 7% for Fe, Cr and Zn; it is up to 40% for Co in the three larger impactor stages and up to 30% for all Sc measurements. The Zn and Sc contents in the 2-4 $\mu$m sample were below detection limits.
For all investigated elements we found a peak in the grain size distribution at the 0.25-0.5 μm fraction; at the next grain size fraction (0.5-1.0 μm) there was a minimum (the same pattern was also found for the activity of $^{210}$Pb). However, Fe was the only element which showed even higher levels in the 1-2 and 2-4 μm fractions (about two times the peak level). In the fraction containing particles with a size of 1-2 μm, which is thought to be the smallest grain size produced by mechanical grinding, the Fe$_2$O$_3$ (rust) fraction is 19% of the aerosol mass. However, also in the samples representing smaller grain sizes we found Fe$_2$O$_3$ contents between 1.6 and 5%. From calculated metal ratios in the aerosols as well as in the rock sample (Fe/Cr, Fe/Zn and Fe/Co) we concluded that the metals in the aerosols do not stem from weathered rock: besides, the Fe concentration in all aerosol fractions was larger than 1%, while in the rock sample it was only 0.6%. The ratios of the largest measured aerosol fraction (4-8 μm) resembled the ratios found for the track wipe test, indicating mechanical grinding. For the metal contents of the smaller aerosol fractions, however, other processes like chemical weathering or fractionation effects during aerosol formation might be important.

Table 2. Mass of aerosol fractions and element contents; the air volume is 50.46 m$^3$.

<table>
<thead>
<tr>
<th>grain size</th>
<th>mass</th>
<th>Fe</th>
<th>Cr</th>
<th>Zn</th>
<th>Co</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>μm</td>
<td>μg</td>
<td>μg</td>
<td>μg</td>
<td>μg</td>
<td>Mg</td>
<td>Mg</td>
</tr>
<tr>
<td>0.062-0.25</td>
<td>697</td>
<td>18.6</td>
<td>0.076</td>
<td>0.43</td>
<td>0.019</td>
<td>1.3*10$^{-4}$</td>
</tr>
<tr>
<td>0.125-0.250</td>
<td>1930</td>
<td>36.0</td>
<td>0.069</td>
<td>2.10</td>
<td>0.006</td>
<td>4.4*10$^{-4}$</td>
</tr>
<tr>
<td>0.25-0.50</td>
<td>3362</td>
<td>40.4</td>
<td>0.100</td>
<td>3.13</td>
<td>0.017</td>
<td>4.7*10$^{-4}$</td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>755</td>
<td>27.2</td>
<td>0.063</td>
<td>0.73</td>
<td>0.003</td>
<td>2.0*10$^{-4}$</td>
</tr>
<tr>
<td>1.0-2.0</td>
<td>623</td>
<td>80.8</td>
<td>0.113</td>
<td>0.28</td>
<td>0.004</td>
<td>1.7*10$^{-4}$</td>
</tr>
<tr>
<td>2.0-4.0</td>
<td>235</td>
<td>83.2</td>
<td>0.146</td>
<td>&lt;LLD</td>
<td>0.006</td>
<td>&lt;LLD</td>
</tr>
</tbody>
</table>

Reference

ADSORPTION BEHAVIOR OF STRONTIUM ON KAOLINITE AND MONTMORILLONITE AND THEIR MIXTURES

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89Sr, with a long half-life of 28.5 years, is the most dangerous strontium isotope. The adsorption behavior of radionuclides in the environment are closely related to the safe disposal of radioactive wastes[1-3]. Since various types of minerals may exist in and around the repositories used for ultimate disposal of nuclear waste, the adsorption behavior of certain radionuclides onto and from these minerals and similar adsorbents should be studied in order to estimate the rates of transport of the nuclides in the event of water penetration into and through the repository. Information on the adsorption properties of the purified individual clay minerals may not be sufficient to predict the adsorption properties of a corresponding mixture, because these clay minerals may interact with each other and lead to modification of the adsorption properties of the mixture as compared to the pure minerals.

The adsorption behavior of strontium on kaolinite and montmorillonite minerals and their mixtures was studied by means of a batch method and a tracer technique. Kaolinite and montmorillonite type clay minerals used as adsorbent were supplied from two regions of Turkey (Balıkesir and Edirne). The concentrations of strontium ions in the solution was between $10^{-6}$ and $1.10^{-7}$ M. The solutions were spiked with $^{89}$Sr. All experiments were carried out in pure water as well as in the presence of a supporting electrolyte (0.01 M NaCl).

The distribution coefficients, $K_d$, both of kaolinite and montmorillonite decreased with the increasing concentration of SrCl$_2$ both in pure water and in the presence of a supporting electrolyte. The effect of Sr loading in solid phase on distribution coefficient is shown in
Fig. 1. Distribution coefficients ($K_d$) are higher than in montmorillonite. $K_d$ values are almost the same at low Sr loading regions until about $1 \times 10^3$ mol.g$^{-1}$ while they decrease after this value.

Fig. 1 Change of the distribution coefficients depending on Sr loading in pure water and in supporting electrolyte.

Fig. 2 Comparison between the observed and calculated distribution coefficients for Sr adsorption.
The adsorbed amount of radionuclides by mineral mixtures was always characterised by the quantity, $X_{\text{ads}}$ [4]. A comparison between observed and calculated values of $K_{\text{d,meq}}$ which can be predicted from the $K_w$-values of the pure materials is shown in Fig 2. The observed values showed an excellent agreement with the calculated values in aqueous solutions (solid line) whereas the calculated $K_w$-values (dashed line) were slightly smaller than observed values in 0.01 M NaCl solutions.

Freundlich and D-R isotherms were applied to the adsorption data of kaolinite and montmorillonite. The values of adsorption capacity of adsorbents and mean adsorption energy decreased from montmorillonite to kaolinite and increased with increasing temperature from 298 K to 333 K. Similar trends were observed in the presence of supporting electrolyte but the values of adsorption capacity and energy were lower than those found in pure water.

The mean adsorption energy values were found to be $8.0-9.5 \text{ kJ.mol}^{-1}$. Magnitude of $E$ can be correlated with reaction mechanism. When $E$ is in the range of $8-16 \text{ kJ.mol}^{-1}$, ion exchange affects adsorption mechanisms. The Freundlich parameters could be used in the calculation of site distribution functions on kaolinite and montmorillonite for a binary exchange between Sr and Na[5]. These functions indicate that most of the adsorption sites have higher affinity for Na than for Sr.

References

DETECTION OF ENVIRONMENTAL RADIOACTIVE MICRO-PARTICLES BEARING FISSILE MATERIAL

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Dispersion of actinides and/or fission products in the environment is mainly due to radioactive micro-particles. The determination of the isotopic composition of the major constituents and fissile material in environmental micro-particles is a fundamental fingerprint for the detection of their source term. Secondary ion mass spectrometry (SIMS) has been widely applied for this purpose [1-4, 6]. Specifically, SIMS is used to distinguish U-bearing particles from Pu-bearing particles (as a backup to electron probe and energy dispersive X-ray analyses) and to measure, accordingly, the U and Pu isotopic compositions [2, 3]. From these results, the enrichment of the material produced, the process used for the enrichment, as well as the starting material employed (natural or reprocessed uranium) can be identified.

The capabilities of this methodology have been exploited in safeguards for verification of adherence to international treaties [5], and research efforts have been intensified in nuclear forensic science in order to develop and improve methods for the identification of seized nuclear materials. The particles to be analyzed are obtained from the environment (e.g. soil, vegetation) or from “swipes” taken at nuclear installations as well as from packing materials in the case of smuggled nuclear samples. Environmental samples are collected in a suspected region or in the vicinity of the nuclear facilities where clandestine nuclear activities are anticipated.

In order to facilitate the localisation of interesting particles on samples with low density of actinide containing particle and their successive isotopic composition analysis, complementary techniques based on the fission track method and thermal ionisation mass spectrometry (FT-TIMS) are being developed. The main purpose is to use the solid state nuclear track detection (SSNTD) method for the localisation of interesting particles as well as a first estimation of their activity and content of fissile material. In the present work a procedure of rapid recognition of $^{235}$U-enriched particles using this technique is presented as a first step of an analytical procedure for environmental particle survey. For U-containing particles of a given size, there is a correlation between the number of tracks and the enrichment level. The qualitative test performed with four SSNTD allowed discarding two of them that were not suitable for the experimental procedure. No tracks could be observed neither on CR39, which seemed to be insufficiently etched for track development, nor on LR115, which was more or less partially digested during chemical etching. The results on Lexan and Makrofol showed that a 1min irradiation time allowed to distinguish 3, 10 and 50% $^{235}$U enriched particles, that 3min permitted at least qualitative distinction of particles from 1 to 50%, and that 5min were so long that 10 and 50% particles gave saturation figures, i.e. overlapping of tracks hindering precise track counting. This made to use 30s, 1min and 3min irradiation times for the further quantitative test. In the latter, the counting was easier with Makrofol than with Lexan.
when particles induced more than about 15 tracks, because of a better optical resolution, as the tracks appeared a bit thinner and more easy to be distinguished. Table 1 shows result of the Lexan experiment (Lexan as particle support and SSNTD). In this table, $^{235}\text{U}_\text{enrich.}$ is the $^{235}\text{U}$ enrichment of the particles in percent, \textit{diam.} the diameter of the main population in \textmu m, \textit{t} the irradiation time in s, \textit{N}_\text{T} and \textit{N}_{T,m} the theoretical (see below) and measured number of tracks per particle. When a second population was detected, the corresponding data are given as $N'_T$ and $N'_{T,m}$. The $2\sigma$ deviation (95% confidence) is that of the Gaussian fitting curves and, thus, reflects the dispersion of the data when the number of available particles allowed an easy statistical treatment, which was mostly the case. The most difficult cases generally yielded the given extreme $2\sigma$ values. High deviations then reflect the lack of clear model value (many counts of similar frequency yielding a flat frequency curve), while low values can sign the fact that the fitting curve is centred on a single count of predominant frequency among few counts. The * symbol indicates that mostly single tracks were observed, and ** that the overlapping of tracks hindered the precise counting of tracks.

The successive aim of this analysis is to correlate the interesting particles with their corresponding fission tracks after irradiation. The topical step is to micromanipulate the particles with a needle and then to deposit them on a filament for analysis by TIMS to measure the isotopic composition of fissile material containing particles. In Fig. 1 uranium reference particles deposited on a policarbonate support analysed under inverted optical microscope are shown (left side). On the right, some fission tracks left by the same particles on a thin film detector after irradiation of the samples are evidenced.

Techniques for manipulating micrometer-sized particles in a scanning electron microscope are also important for research related to safeguards and forensic purposes. It has been demonstrated that uranium oxide microparticles ranging from sub-\textmu m to several 10 \textmu m can be freely manipulated by adhering them to the tip of a probe. In Fig. 2 the ability for precision positioning and picking up of individual particles by means of using microtips (down to 100 nms) is shown.

Table 1. Result of the Lexan experiment (Lexan as particle support and SSNTD).

<table>
<thead>
<tr>
<th>238U enrich. %</th>
<th>t s</th>
<th>N_T</th>
<th>N_T,m</th>
<th>2s</th>
<th>N'_T</th>
<th>N'_T,m</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>2.1</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>4.1</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>180</td>
<td>12.4</td>
<td>3.7</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>5.9</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>11.7</td>
<td>2.2</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>36.1</td>
<td>7.6</td>
<td>3.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>1.8</td>
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<td>76.1</td>
<td>10.4</td>
<td>1.9</td>
</tr>
<tr>
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<td>114.1</td>
<td>10.0</td>
<td>5.5</td>
<td>228.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>74.0</td>
<td>9.7</td>
<td>1.3</td>
<td>148.1</td>
<td>12.9</td>
<td>1.6</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>148.1</td>
<td>17.7</td>
<td>1.3</td>
<td>296.1</td>
<td>23.1</td>
<td>0.7</td>
</tr>
<tr>
<td>50</td>
<td>180</td>
<td>448.2</td>
<td>**</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 1 The picture on the left shows 2 uranium reference particles deposited on a polycarbonate support analysed under inverted optical microscope. On the right, some fission tracks left by the same particles on a thin film detector after irradiation of the sample.

Fig. 2 Example of micromanipulation of μm-size particles with a W tip (2 μm diameter point tip) under UHV on a scanning electron microscope.
POSITRON EMISSION TOMOGRAPHY FOR MODELLING OF GEOCHEMICAL TRANSPORT PROCESSES IN CLAY

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Introduction
Geological clay formations are investigated for use as final underground deposit for heat producing nuclear waste. Special kinds of clay (e.g. bentonite) can also be used for the construction of geotechnical barriers. For the long time safety prognosis of the nuclear waste repositories the development of geochemical transport models is indispensable.

The transport of aqueous solutions in clay is a complex process. The three-layer-minerals bentonite and illite swell by the adsorption of water, if the volume is restricted a high swelling pressure develops. The excellent barrier effect of natural clay formations and geotechnical clay barriers is based on the high swelling pressure and the high adsorption capacity for radionuclides and other pollutants. The two-layer-mineral kaolinite has no swelling capacity. In contrast to sandy layers a special geochemical transport potential exists in clay besides the well known matrix potential which influences essentially the transport process. Therefore important information for the models of the transport process can be obtained if the progress of the solution front in an unsaturated clay layer can be observed. With PET studies it is possible to measure nondestructively the solution transport and to determine quantitative parameters of the spatial flow profiles which are the basis for the modelling of the transport processes.

Experimental
The transport of simulated salt solutions (0.01 M, 0.5 M, 3.5 M) was studied in unsaturated clay and clay stone. Two kinds of clay bentonite (>50 % montmorillonite, 10-15 % illite, quartz, feldspar, mica) and kaolin (60 % kaolinite, 20 % quartz, 20 % feldspar) were investigated. Bentonite of such composition is tested as material for geotechnical barriers in the underground research laboratory Åspö/Sweden [1]. Bentonite was used in form of Na-bentonite, which has the best properties for the use as geotechnical barrier. The Ca2+-ions were exchanged by addition of Na2CO3 and water and calcite CaCO3 precipitated [2]. Bentonite and kaolin were examined in dried, 20 % H2O-saturated and re-dried state to determine modified structures like swelling, shrinking and cracking. Cylindrical drill cores of clay rock of the deposit Münchhagen (Ø 100 mm with central hole Ø 10 mm) consist of 55 % illite, 10-20 % kaolinite and chlorite and were investigated in the same way.

For the realisation of the PET investigations of the transport processes in clay layers a special cylindrical measuring cell was developed. The milled clay powder was filled into the cell and compressed. In the middle of the cell a filter tube (ceramics 99.8 % Al2O3) with a negligible hydraulic resistance is arranged in which the tracer solution was filled without pressure. At certain times the tracer solution was removed from the filter tube and the PET measurements of the local tracer concentration distribution in the clay layer were carried out at the commercial PET camera ECAT EXACT HR +/CTI Siemens at the University of
Leipzig. Fluoride ions are used as conservative hydrodynamic tracer because their interaction with the negatively charged clay surface is negligible. The tracer \( ^{32}\text{P}\)KF was produced at the cyclotron of the Clinic and Polyclinic of Nuclear Medicine of the University of Leipzig.

The tracer concentration distributions for a stack of 64 different cross sections of the sample are calculated by the image reconstruction algorithm of the PET device. A range of cross sections with tracer concentration distributions can be found which is not disturbed by the boundary conditions of the measuring cell. A mean tracer concentration value was calculated for each pixel of the cross section using the pixel values of three selected cross sections. The tracer concentration profiles were determined for 16 different radii. An average profile was calculated for each stack of PET images with these 16 profiles. These average concentration profiles represent the data set for the model validation and parameter estimation.

**Results and discussion**

The direct observation of the progress of the water front in the clay layers provides very important information for the development of the transport models. Figure 1a shows an example of the homogeneous transport in dry or partly saturated clay samples. Re-dried clay samples show a heterogeneous distribution by shrinking and cracking (Figure 1b). The crack structures caused significantly higher transport velocities of the solution.

![Figure 1](image1.png)

**Figure 1.** 3-D-top view of the tracer concentration distribution in the measuring cell, 0.5 M salt solution, pH 6, left 1a: dry Na-bentonite, right 1b: re-dried Na-bentonite

The tracer concentration distributions in the drill cores of clay rock show a heterogeneous and accelerated transport which is caused by the different swelling of the heterogeneous structures and inclusions and the resulting cracks (Figure 2).

![Figure 2](image2.png)

**Figure 2.** Tracer concentration distributions of water in the cross sections at a distance of 5mm each after 320 min in a drill core of clay rock

Figure 3 shows some examples of the radial concentration profiles in the swelling three-layer-clay bentonite. Two characteristics of the curves are important for the modelling: the flow
713

Figure 3. Radial profiles of the water and solution transport in dry Na-bentonite profiles are s-shaped and the concentration on the input increases slowly up to a maximum value corresponding to the tracer input concentration. This points to a model formulation on basis of the advection-dispersion-equation to describe the solution transport in clay. The simple diffusion equation used frequently to model the transport processes in clay is unsuitable for transport processes under unsaturated conditions. For radial symmetric conditions the advection-dispersion-model has the form:

\[
\frac{\partial}{\partial r} \left( D \cdot r \frac{\partial c}{\partial r} \right) - \frac{\partial}{\partial r} \left( u \cdot r \cdot \frac{\partial c}{\partial r} \right) = r \frac{\partial c}{\partial t}
\]

with the initial and boundary conditions:

\[ c(t, 0) = c_0, \quad c(t, 0) = 0, \quad c(t, l) = 0 \]

The model parameters \( D \) and \( u \) could be determined for the different experimental conditions. The solution transport in clay rock is a heterogeneous process. However a range of homogeneous transport exists nearby the input interface for which an exponential concentration profile could be determined which points to a simple dispersion transport. A dispersion coefficient of \( D = 3.83 \times 10^{-4} \text{mm}^2/\text{s} \) was evaluated.

The results show that in unsaturated clay besides the dispersion process in the pores an advective transport takes place. This is caused by the matrix potential and an additional chemical transport potential. The dispersion in the pores is influenced besides the molecular diffusion by hydrodynamic effects. The structure of clay rock is much more compact. No advective transport is possible in homogeneous ranges but the structure heterogeneities give rise to produce separate flow channels with high transport velocities.

Acknowledgement

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References

TRITIUM ENRICHMENT IN THE HYDRATION SPHERE OF
INORGANIC SALTS

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Introduction
Tritium (3H) is generally considered a not very radiotoxic nuclide which is reflected by its
relatively high exemption limits in radiation protection legislation. Nevertheless, large 3H
activities are produced in nuclear power reactors through ternary fission processes (5.5 -
7.4·10^{14} Bq/1000 MW/year). Essentially all of the 3H is currently released to the
environment, i.e. the reprocessing plant of La Hague monthly emits about 10^{12} Bq 3H to the
sea and 3·10^{12} Bq 3H to the atmosphere, mostly in the form of HTO [1]. Pressurized water
power plants create 3H in their coolant, their moderator, and their control rods by activation
of deuterium, lithium, and boron. Large 3H activities are also produced in heavy water
moderated reactors, i.e. the new research reactor FRM-II in Munich will contain after one
year of operation a 3H inventory of about 10^{16} Bq. The currently known procedures to
selectively accumulate tritium are very time- and energy consuming and not able to condition
large waste streams. However, also the storage of tritiated aqueous solutions poses problems,
since through evaporation of tritiated water and isotope exchange reactions between
hydrogen isotopes, tritium can relatively easily reach the environment.

Earlier studies in our institute showed that 3H is accumulated near and inside DNA [2].
Obviously, 3H was accumulated in exchangeable hydrogen bonds [3]. The strong effect can
be understood as a direct consequence of the much shorter de Broglie wavelength of 3H,
which favors 3H to occupy positions that are most closely confined by barriers, i.e. weak
hydrogen bonds. If this hypothesis is valid, also inorganic substances that form weak
hydrogen bonds with their hydration shields should accumulate 3H. Correspondingly,
inorganic salts, forming hydrogen bonds of different strength with their hydration shields
were investigated.

Experimental set-up
To accurately determine the accumulation of 3H in exchangeable hydrogen bonds, a
procedure must be established that allows separation of bulk water from the substance of
interest. This procedure needs to be as free as possible of isotope effects. Otherwise, the
isotope effect associated with the separation process may contribute a possible source of
error in the assessment of the accumulation effect. A separation procedure approaching this
objective is freeze-drying under non-equilibrium conditions. The employed apparatus is
shown in Figure 1.

A mixture of the substance to be investigated and the H_2O/HTO solution are stored in a
double walled flask (1) connected to a cryo trapping cylinder (2). The mixture in the flask is
cooled to -20 ± 0.1 °C. The sublimation process is started by evacuating the system up to
valve A to a pressure of 10^{-3} mbar. Then the trapping cylinder is cooled with liquid N_2 to
collect the small volume of the condensate (between 10 μl and 1 ml). Then the trap is
ventilated with dried air up to valve A and the trapping cylinder is removed. The condensate
is weighed with a precision balance. The $^3$H activity is determined by liquid scintillation counting.

Figure 1: Schematic drawing of the vacuum cryo sublimation apparatus used to remove bulk phase water (1: double walled flask, 2: cryo trapping cylinder, A-D: vacuum valves)

In order to achieve high evaporation yields freeze-drying near the vapor pressure of ice is used. The evaporation isotope effect at -20 °C, however, is about 1.2; at -50 °C it is larger than 1.3. But Baumgärtner et al. [4] showed, that as soon as sublimation of a H$_2$O/HTO mixture occurs at pressures below the equilibrium vapor pressure at a given temperature, the fractionation of HTO and H$_2$O disappears. Correspondingly, in all experiments the successive removal of bulk phase water occurred at a temperature of -20 °C and a pressure of 10$^{-5}$ mbar, well below the equilibrium phase vapor pressure (~1 mbar). One can therefore safely assume that the ratio of H$_2$O/HTO in the sublimate resembles the H$_2$O/HTO ratio of the original frozen state. Since the successive removal of bulk phase water by cryosublimation is a very time consuming and laborious process which lasts up to several weeks, the apparatus is equipped with an uninterruptible power supply.

**Results and discussion**

First, the pure system H$_2$O/HTO was investigated without the addition of any compound to obtain a reference value for comparison with all other results. An enrichment factor of 1.14 was obtained for this system.

In the following series of experiments NaF, NaI, CsF, and CsI were added to the tritiated water to investigate all possible combinations of anions and cations with large/small ionic diameter. Enrichment factors found are given in table 1. Comparison with the factor obtained for HTO/H$_2$O suggests a possible influence of the ionic diameter of the anion rather than of the cation, see figure 2. The hydrogen position concerned is $^3$O$^-$---H$^{+}$--X$^-$. These results confirm the hypothesis of tritium bridges weaker than those existing between water molecules.

**Table 1: Enrichment factors obtained by cryosublimation of several inorganic salts; the system HTO/H$_2$O is added for comparison**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enrichment factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>1.43</td>
</tr>
<tr>
<td>NaI</td>
<td>1.27</td>
</tr>
</tbody>
</table>
Table 1: Enrichment factors obtained by cryosublimation of several inorganic salts; the system HTO/H$_2$O is added for comparison

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enrichment factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF</td>
<td>1.93</td>
</tr>
<tr>
<td>CsI</td>
<td>1.14</td>
</tr>
<tr>
<td>Al(OH)$_3$</td>
<td>2.47</td>
</tr>
<tr>
<td>AlF$_3$</td>
<td>1.24</td>
</tr>
<tr>
<td>FeO(OH)</td>
<td>1.13</td>
</tr>
<tr>
<td>HTO/H$_2$O</td>
<td>1.14</td>
</tr>
</tbody>
</table>

![Graphical representation of the influence of the anion on enrichment factors of fluoride compounds compared to iodide compounds and pure H$_2$O/HTO](image)

Figure 2: Graphical representation of the influence of the anion on enrichment factors of fluoride compounds compared to iodide compounds and pure H$_2$O/HTO.

Next, aluminum fluoride was studied and subsequently the fluoride anion was replaced by hydroxy groups. The enrichment factors obtained were 1.24 and 2.47, respectively (table 1). The remarkable increase of the accumulation factor shows a significant weakening of the concerned hydrogen bond strength in Al(OH)$_3$. But also the structure of the hydrogen in bridge position is quite different from the anionic H-bond in AlF$_3$ namely cationic: Al—O—H—OH$_2$. Obviously, the electrostatic repulsion effect of the bridging H-nucleus by the +3 charged cation is much larger than the electrostatic attraction of the -1 charged fluoride. Finally aluminum was replaced by iron as the cationic center, which resulted in an enrichment factor of only 1.13. This value corresponds with the enrichment factor of CsI and suggests a structure approaching FeO$_4^{5-}$ resulting in H-bridges like FeO—H—O—H.

References
GEOCHEMICAL CAESIUS FRACTIONATION IN BOTTOM SEDIMENTS

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Introduction

Caesium is one of the most important anthropogenic radionuclides, which was introduced into the environment through nuclear weapons testing and nuclear accidents in Chernobyl; its inventories in radioactive waste are significant as well. Caesium harmful effects on animate nature are evident taking into account its properties: unlimited solubility, potential mobility and high bioavailability. The numerous publications concerning the binding of Cs by clays reflect the importance of this radionuclide relevant to safety assessment, and on the other hand, the search for low-cost barriers for isolation of radioactive wastes [1]. These studies are mostly dealing with a description of the caesium sorption on homogenous particles of clay minerals. In natural environment the complex mixtures of minerals are present and for this reason there are difficulties in extrapolation of data obtained in the laboratory sorption experiments to the far-field conditions. In addition, a variety of factors including the water pH, ionic strength, competitive sorption, complexation with inorganic and organic ligands can influence the sorption process and thereby mobility of radionuclides. However, it is now generally recognised that the sorption of ¹³⁷Cs by soil and sediments is mainly determined by specific sorption onto illite clay minerals, but such parameters as pH and organic matter were found to play less important role in the adsorption of Cs. Three types of ¹³⁷Cs binding sites to sediment clay components have been identified experimentally. The selective adsorption of Cs by clay minerals has been attributed to the large ionic radius, uncomplexing nature and especially to its low hydration energy. Although cations with similar charge and ionic radii are expected to compete with caesium, the sequence of sorption ability of alkali elements Na⁺ < K⁺ < Rb⁺ < Cs⁺ is in good agreement with the sequence of effective ionic radii of alkali elements and the sequence of single ion hydration enthalpies of alkali elements. In the clay mineral muscovite, a negative fixed charge arises primarily from isomorphic substitution of Al³⁺ for Si⁴⁺ in the tetrahedral sheet comprising the siloxane site. In illite mineral whose composition is very close to that of muscovite, isomorphic substitution of Al³⁺ for Si⁴⁺ and partly of Fe²⁺ and Mg²⁺ for Al³⁺ enhances the stability of the Cs⁺-siloxane surface complex, presumably by promoting the dehydration of the sorbed Cs cation.

The layer-type silicates bind Cs either through weak electrostatic interactions or through stronger bonds formed by partial sharing of electrons between Cs and the ligand sites of the clay mineral. Electrostatic associations of hydrated Cs with anionic surfaces within the basal plane or interlayer and dissociated edge hydroxyl groups act as outer-sphere complexes [2-3]. Electronic bonding at the frayed edge sites, external basal sites, or within the interlayer leads to inner-sphere complexes, which usually are much more stable than outer-sphere complexes. Caesium sorbed to outer-sphere complexes can be easily desorbed and more mobile in the environment, while inner-sphere complexes can limit the Cs mobility and bioavailability. These inner-sphere sorption complexes are probably the dominant ones at low concentrations typical of radioactive Cs contamination, and a great amount Cs from contaminated environments is expected to be strongly adsorbed. The complicated behaviour of caesium can be a result of peculiarities of its sorption at various sorption sites of different clay minerals and their mixtures.
In natural environment with complex mixtures of minerals, radionuclides can be retarded through a number physical and chemical processes. Recently, one of the issues under consideration is the coating effect on radionuclide sorption on mineral. The objective of this study is to focus on the sorption and desorption behavior of Cs in the complex heterogeneous system of bottom sediments in order to better understand the cesium behavior during the Baltic Sea water flooding events to the Curonian Lagoon and transfer of suspended particles from the Curonian Lagoon to the Baltic Sea.

**Methods**

A sample of bottom sediments collected in the Curonian Lagoon was used for sorption experiments. Total carbon (TC) and total organic carbon (TOC) were determined using a LECO CS-125 analyser. The stable Cs concentration was determined using ICP–MS, and clay minerals were identified by X-ray diffraction. Filtered sea water of 7.0 salinity labelled with $^{137}$Cs was used for the sorption experiment. The total concentration of Cs in solution was 0.04ppb. The solids were separated by centrifugation at 4000 rpm after different contact time between solution and sediments. Details of the experiment are described in publication [4].

The modified Tessier sequential extraction method was used to study association of Cs in sediments. $^{137}$Cs and $^{134}$Cs activities were measured using an intrinsic germanium detector (resolution 1.9keV/1.33MeV and efficiency - 42%). The precision of $^{134}$Cs measurements by gamma spectrometry was $<3\%$ at $\pm 1\sigma$.

**Results and discussion**

Results of sorption of $^{134}$Cs in sediments after different contact time indicated that more than 70% of $^{134}$Cs tracer was sorbed during the first three days (Fig. 1). Similar results were obtained during the second experiment. The decrease in the caesium amount in the exchangeable fraction desorbed by NH₄⁺ possibly corresponds to the decrease in the number of frayed edge sites available for Cs sorption. The decrease in the sorption rate accompanied by an increase in association of $^{134}$Cs with carbonate fraction can be attributed to the effect of coatings that are usually present in natural heterogeneous sediments. In the sediment sample used for the sorption experiment, a high content of carbonate was determined. The carbonate coatings can inhibit the caesium uptake by

![Fig. 1. $^{134}$Cs fraction distribution (F1 - contact solution, F2 - exchangeable (MgCl₂), F3- exchangeable (NH₄Cl), F4 - carbonates, F5 - organic, F6 - oxides, F7-residue).](image-url)
The comparative analyses of $^{134}$Cs fraction distribution after 241 and 375 days of the sorption experiment with that of the $^{137}$Cs distribution, determined in the same sediment sample before the sorption experiment, indicated that after 375 days of sorption the equilibrium was not fully reached, but distribution was found to be close to equilibrium. The short-term desorption experiments indicated an insignificant release of Cs from the regular exchange complex. The remobilization of "fixed" caesium was not observed, on the contrary, the redistribution of caesium towards its fixation in clay minerals was observed, and on a time scale its fixation kinetics was comparable with the sorption experiment. Experiments have shown the double effect of coatings on sorption of Cs on bottom sediments: at primary stage of sorption coatings inhibit sorption of Cs, however, later they can inhibit the release of Cs to the surrounding solution. Data obtained from these experiments were used to calculate the $K_d$ coefficients both for total bottom sediments and different geochemical sediments phases (Fig 2). It can be seen that residual fraction, which reflects the Cs sorption on clay minerals, is the most important in Cs incorporating to bottom sediments while the role of other geochemical phases is relevant only during two months of the sorption experiment.

This study indicated that flooding events of sea water contaminated with caesium can cause a significant accumulation of caesium in the bottom sediments of the Curonian Lagoon and result in the redistribution of $^{137}$Cs activity concentration in the bottom sediments from one area to another.

Acknowledgment
This work was partly performed under the auspices of IAEA under project LIT/7/002 and the Lithuanian State Science and Studies Foundation project No C-19/2003.

References
PECULIARITIES OF $^{137}$Cs BEHAVIOUR IN MARINE ENVIRONMENT

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Introduction
At present it is generally recognized that a realistic assessment of the long-term consequences of radioactive contamination is possible through the better understanding of physical and chemical processes of radionuclide migration in the environment. To assess the transfer and fate of radioactive contaminants in the marine environment the information on physical and chemical parameters of radionuclide carriers is required. The release of radionuclides associated with particles of different sizes and mineralogical composition to the marine ecosystems can considerably affect their transport and bioavailability. Radionuclides firmly bound with released particles display extremely slow dissolution kinetics and they can be quickly removed from water columns and migrate into sediments. On the contrary, the radionuclide released in water-soluble state or exchangeable state exhibits more rapid distribution in the marine environment. The associations of radionuclides with suspended particles may change dramatically in the zone of interaction between fresh and saline waters due to sorption-desorption processes. Thus, determination of size distribution of particles carrying the radionuclides, their partition between particulate, colloidal and truly dissolved phases is especially important. Activity concentrations and associations of $^{137}$Cs with suspended matter and bottom sediments in the Baltic Sea and the Curonian Lagoon were studied.

Experimental
Water and bottom sediment samples were collected during the expeditions in the Lithuanian economical zone of the Baltic Sea, the Curonian Lagoon and at the seashore of the Baltic Sea and the Curonian Lagoon in 1999–2001. The separation of the suspended matter was achieved using 0.22 μm membrane filtration. In addition, the suspended particle samples were collected in situ by filtering a large volume of water (~400-600 L) through two consecutive 1 μm polypropylene Sediment Filter Cartridges (US Filter Plymouth Products, 1 micron nominal). The specific activity of $^{137}$Cs in suspended matter in water samples of 50–100 l was measured using proportional Emberline FHT 770 T MULTI–LOW–LEVEL–COUNTER after digestion (H2HNO3, HCl) and radiochemical separation in the form of Cs2SbI5. From filtered water $^{137}$Cs was precipitated using the Fe ferrocyanide method and measured with the HPGe detector.

Bottom sediment samples were collected during different sampling companies in the Baltic Sea and in the Curonian Lagoon in 1999-2001. Bottom sediments were sectioned on board ship and the upper layer 0-2 cm of sediments was used for radionuclide speciation analyses. $^{137}$Cs activities were measured with an intrinsic germanium detector (resolution 1.9 keV/1.33 Mev and efficiency 42%).

The fractions of > 50 μm, 50 – 4 μm and < 4 μm were separated using wet sieving and column settling techniques and characterized as sand, silt and clay particles. The separation of 1 – 0.2 μm fraction was achieved using membrane filtration. The modified Tessier sequential extraction method was used for determination of Cs geochemical fractionation [1]. Total car-
bon (TC) and total organic carbon (TOC) were determined using a LECO CS–125. The grain size distribution was determined by the gravimetric pipette method. Cs concentration in sea water was determined using ICP-MS, and clay minerals were identified by X-ray diffraction.

Result and discussion
An increase in the specific activities of $^{137}$Cs (up to 1000 Bq/kg) associated with the fine fraction of < 4 μm and 0.2–1 μm is attributed to the large specific surface area and/or to the variation in the mineralogical composition of bottom sediment particles participating in sorption processes. The correlation of specific activities of $^{137}$Cs in both the Curonian Lagoon and the Baltic Sea sediments with the content of clay (R = 0.95) and total organic carbon (R = 0.75) was determined. Despite the strong correlation with the total organic carbon, studies performed on $^{137}$Cs geochemical fractionation indicated its strong association with the acid-soluble and residual fractions (about 70%), whereas the organic fraction comprised a small part of total activity of $^{137}$Cs in bottom sediments.

Fig. 1. Physicochemical characteristics of $^{137}$Cs in bottom sediment of the Baltic Sea samples F1 – exchangeable, F2 – carbonates, F3 – oxides, F5 – organic, F6 – acid soluble, F7 – residue to be associated with the particles of < 4μm size. It is obvious that partitioning of $^{137}$Cs determined in the fine < 4μm size fraction can be attributed to the binding pattern of $^{137}$Cs by clay minerals. The explanation of a comparatively high content of $^{137}$Cs in the acid-soluble and especially in the residual fraction of coarse fractions can be attributed to sticking of fine clay particles to the coarse sand and silt ones. Specific activities of $^{137}$Cs in suspended particle samples collected in the Curonian Lagoon and separated using the 0.22μm membrane ranged from 16 to 254 Bq/kg. Insignificantly higher activities of $^{137}$Cs (from 15 to 372 Bq/kg) were found in the near shore zone of the Baltic Sea waters. The specific activities of $^{137}$Cs in the surface and bottom waters of the Baltic Sea differ from 84 to 632 Bq/kg and from 89 to 965 Bq/kg, respectively. At all sampling stations the specific activities of particu-

Fig. 2. Excess of $^{137}$Cs specific activity on near bottom suspended matter compared to that of surface suspended particles versus sampling depth.
late $^{137}$Cs in surface samples were lower as compared to the samples collected near bottom. Moreover, a strong relation of specific activities of particulate $^{137}$Cs with depth was found with the exception of the sample collected at the station 6b. It should be noted that the mentioned station is located at the crease of the Nemunas River and water circulation in this area could provide transport of particles from the coastal region. For samples collected at other sampling stations the strong correlation of caesium activities exceed on the suspended particles with the sampling depth was observed (Fig.2). It is obvious that depending on activity concentration of soluble $^{137}$Cs and the particles residence time in water column the different enrichment towards the radiocaesium could be achieved. In samples collected using the sediment filter cartridges with the nominal pore size of 1 μm, the comparatively lower specific activities of $^{137}$Cs (from 20 to 61 Bq/kg) were determined (Table 1). It seems that suspended particles of the 0.22 – 1 μm size, which were lost during this sampling, considerably contribute to the total particulate activity of $^{137}$Cs. Possibly, the fine fraction of suspended particles collected in May 1999 consists mainly of clay minerals which could selectively adsorb Cs even from brackish seawater containing high concentrations of potassium. The increase in the specific activity with salinity and sampling depth is a result of sorption process during particles transport and settling in the seawater. In sampling performed in October 2001 due to different cut off filters the collected suspended matter exhibited rather different sorption ability. The decrease in the specific activity with an increase in water salinity observed in the mentioned samples can be interpreted as the desorption of caesium from suspended particles due to exchange reactions with the highly abundant potassium in sea waters. It seems that stable caesium had no effect on the behaviour of $^{137}$Cs because its concentrations were lower by 7 orders of magnitude as compared to that of potassium.

Our study indicated complicated sorption-desorption behaviour of $^{137}$Cs in the Baltic Sea water as a result of which it can be mobilised by suspended particles or released to the sea water. Thereby the fate of $^{137}$Cs can be considerably affected by mineralogical composition of suspended and bottom sediments, by characteristic geochemistry of sea water and the presence of other pollutants.

**Acknowledgment**

This work was performed under the auspices of IAEA under project LIT/7/002.

**Reference**

EXPRESS DETERMINATION OF SR-90 CONTENT IN DIFFERENT OBJECTS WITH DICYCLOHEXYL-18-CROWN-6 (DCH18C6)

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The present method is worked out for Sr determination in objects of different origin, especially in agricultural production, cattle production, and food. The method may be applied to determine the Sr contamination of objects and territories, which were exposed to accidents at nuclear energy objects, buffer areas of NPP, and possible use of so called “dirty” bombs. The principle of the method is based on chromatographic extraction of strontium from nitrate solutions followed by radiometric determination of Sr activity. A highly porous matrix of styrene-divinyl benzene in the form of beads ~1 mm in diameter is used as a substrate to support the extractant, dicyclohexyl-18-crown-6 (DCH18C6) in tetrachloroethane, which is in the liquid state deep in the pores of the matrix. Dicyclohexyl-18-crown-6 belongs to synthetic macrocyclic polyethers (so-called crown ethers) and has the ability to bind Sr with high selectivity so that Sr is extracted with 90 – 95 % efficiency.

Fig. 1 depicts the structural formula of dicyclohexyl-18-crown-6. The first number in names of crown ethers indicates the size of a ring, and the second number defines the quantity of oxygen atoms in a ring. The properties of crown ethers are described in detail in [1].

Fig. 1. Dicyclohexyl-18-crown-6

The scientific base of the most exact and express method of definition of the Sr-90 contents in the environmental objects of environment was developed in GEOHI of the Russian Academy of Sciences (Moscow) under the direction of academicians B.F. Mjasoedov soon after the accident at the Chernobyl NPP [2]. This method was later adapted at the Institute of Physics of NAS of Belarus. It is meant for Sr determination in soil, water, and milk. It is described in detail in [3].

Now at the Institute of Physics of NAS of Belarus the method of determination of Sr in objects of organic origin (cereals, leguminous plants, meat and milk production, food, etc.) has been developed.

The main stages of the modernized version are:
1. Sample preparation. The method of wet combustion of the samples by aquafortis, filtering, evaporation, and final correction of the nitric acid concentration to 1.5 M of obtained solutions are used. Method «wet combustion» is based on combustion of dry sample by
concentrated nitric acid in the presence of perchloric or sulfuric acid. Reacting with organic substance, nitric acid decays to water, nitrogen dioxide and oxygen. Oxygen in free state has huge reactivity and oxidizes hydrogen of organic substance up to water. The presence of sulfuric or perchloric acid considerably accelerates combustion.

2. Preparation of selective sorbent, extract elution through a chromatographic column. To prepare the selective sorbent, solid extragent (solex) balls are placed in the chromatographic column and a 5% or 10 % solution of the sorbent dicyclohexyl-18 – crown – 6 (DCH18C6) in tetrachlorethane is poured. The nitrate extract of the sample is passed through the chromatographic column (the time of completion of the sample passage is taken for the moment of separation of 90Y and 90Sr). Then the chromatographic column is washed with 1.5 M nitric acid. Next the column is heated to 80 °C by a thermostat, hot water is poured, and strontium desorption from the chromatographic column is carried out. The efficiency of strontium-90 desorption from the chromatographic column depends on the temperature of water and the crown ether concentration. Results of experiment are represented in Table1.

Table1. Desorption of strontium from the chromatographic column

<table>
<thead>
<tr>
<th>Desorption temperature °C</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crown ether conc. %</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Yield %</td>
<td>75</td>
<td>80</td>
<td>91</td>
<td>90</td>
<td>80</td>
<td>90</td>
<td>92</td>
<td>90</td>
</tr>
</tbody>
</table>

Consistent recovery of 92 % can be obtained at a water temperature of 80 °C. The process of elution is shown in Fig.2.

![Fig. 2. Elution curve](chart.png)
With one cycle strontium is almost completely washed from the chromatographic column.

3. Radiometric measurement is performed in the liquid phase by beta-radiometer “Beta-2” using liquid scintillators. The $^{90}$Sr activity is determined with allowance for the scintillating cell background, the conversion factor depending on the $^{90}$Y accumulation time and the $^{90}$Sr and $^{90}$Y detection efficiency. For registration Sr-90 in the given methods scintillator cocktail Ready Safe was used.

The basic technical parameters of the method are represented in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Lower-range value, Bq</td>
<td>1</td>
</tr>
<tr>
<td>Upper-range value, Bq</td>
<td>1000</td>
</tr>
<tr>
<td>Time of realization of one analysis, h</td>
<td>4-5</td>
</tr>
<tr>
<td>Measurement error, %</td>
<td></td>
</tr>
<tr>
<td>1-3 Bq</td>
<td>30</td>
</tr>
<tr>
<td>3-10 Bq</td>
<td>20</td>
</tr>
<tr>
<td>10-1000 Bq</td>
<td>15</td>
</tr>
</tbody>
</table>

The present method provides considerable reduction of time needed for measurement of a sample (4-5 hours) in comparison to traditional radiochemical method (up to 2 weeks). Use of ultrasonic radiation and microwave radiation allows to reduce time of sample preparation.

Now the method is being tested in the Institute of Environmental Physics, University of Bremen. During this work optimum parameters for the given method will be determined. Also the procedure will be tested for low activities (less than 1 Bq).


EUROPIUM SORPTION FROM AQUEOUS SOLUTIONS BY AI\(^{3+}\) - AND Fe\(^{3+}\) - DOPED AMORPHOUS ZIRCONIUM AND TITANIUM PHOSPHATES

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Europium is considered as a chemical analogue of the trivalent americium and as fission product (\(^{156}\)Eu and \(^{155}\)Eu). During this study the sorption of europium from aqueous solutions (Eu-concentration: 10 to 250 mg/L) by amorphous Fe- and Al-doped Zr- and Ti-phosphates was investigated using a batch-type technique and \(^{152}\)Eu tracer. The \(^{152}\)Eu tracer was prepared by thermal neutron irradiation of EuO\(_2\) powder at the 5 MW nuclear reactor of the NRCPs Demokritos (Athens/GR). The initial pH of the solutions was adjusted in the range between 3 and 5. All sorption experiments took place in the presence of 0.15M NaCl.

The investigated Al\(^{3+}\) - and Fe\(^{3+}\)-doped Zr- and Ti-phosphates in H-form (characterized as: ZrFePH, ZrAlPH, TiFePH and TiAlPH) were prepared at the Institute for Sorption and Endoecology Problems of the N.A.S.U. (Kiev, Ukraine) using a previously described sol-gel technique [1, 2]. The Al\(^{3+}\) - and Fe\(^{3+}\)-doping of the starting materials utilized for the synthesis of the phosphates had as aim the increase of their porosity and consequently of their surface area and sorption capacity.

For the experiments 30 mg of the individual sorbents were shaken for 48 hours in polypropylene centrifuge tubes with 10 mL of europium solutions at ambient temperature. After centrifugation, the europium concentration was determined in 2 mL of the clear supernatant solution by means of high resolution gamma-ray spectrometry. For the determination the 122 and 344 keV gamma-lines of \(^{152}\)Eu were utilized. The uptake (mg/g) and sorption coefficient (mL/g) values were determined using the gamma-ray spectroscopic data.

Speciation calculations performed using the computer code MINEQL+ [3], using the corresponding constants obtained from the MINTEQA database, indicated that the main europium species present in the solutions in the pH region of interest (pH 3-5) were Eu\(^{2+}\) (ca. 92%) and EuCl\(^{3+}\) (ca. 8%). Europium starts to precipitate as solid Eu(OH)\(_2\) at pH just below 7. It could be noted that, these calculations are for bulk solutions and, when a solid interface is present, it is possible that the surface excess of europium species may lower the precipitation pH by 1 to 1.5 pH units.

The europium uptake values of the different sorbents for solutions of pH\(_{ini}\) value 3 and 5 are given in Fig. 1; the conditions are referred inside the diagrams. The modeling of the data with Langmuir-type adsorption isotherms is also shown in the same diagrams; the dashed lines represent the 95% confidence intervals. It can be seen that all the experimental data
(symbols) are in good agreement with the calculated values (solid lines). The maximum capacity values and the correlation coefficients of the theoretical curves are given in Table 1.

Fig. 1: Eu-uptake from aqueous solutions of pH 3 and 5 by the studied Al$^{3+}$- and Fe$^{3+}$-doped Zr- and Ti-phosphates in the presence of 0.15 M NaCl.
Table 1. Maximum capacities and correlation coefficients of theoretical curves

<table>
<thead>
<tr>
<th>Material</th>
<th>pH$_{int}$</th>
<th>$Q_{max}$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrFePH</td>
<td>3</td>
<td>26.2</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>29.9</td>
<td>0.966</td>
</tr>
<tr>
<td>ZrAlPH</td>
<td>3</td>
<td>31.1</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>30.5</td>
<td>0.960</td>
</tr>
<tr>
<td>TiFePH</td>
<td>3</td>
<td>19.1</td>
<td>0.950</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>35.9</td>
<td>0.968</td>
</tr>
<tr>
<td>TiAlPH</td>
<td>3</td>
<td>19.8</td>
<td>0.949</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>35.9</td>
<td>0.968</td>
</tr>
</tbody>
</table>

From the above data the following conclusions can be drawn:
- All investigated materials follow the Langmuir-type adsorption model, indicating a monolayer sorption. Correlation coefficients of 0.95 or higher indicate the good agreement of the calculated values with the experimental ones.
- The Zr-phosphates are generally more effective sorbents for europium than the Ti-phosphates as their maximum capacities are higher.
- The Ti-phosphates seem to be very little affected by the used doping cation (Al$^{3+}$ or Fe$^{3+}$). Both sorbents show an almost similar behavior and are more effective at pH 5 than at pH 3.
- The sorption behavior of Zr-phosphates is practically not affected by the doping cation. Both sorbents are similarly effective at pH 3 and 5. The europium removal efficiency of the Zr-phosphates at pH 3 can be considered as quite good since it is well-known that the most sorbents are less effective in removing cations from solutions of low pH values due to the high competition from the side of H$^+$-cations.

Further sorption experiments using europium solutions of pH$_{int}$ 4 indicated a similar behavior with that observed at pH$_{int}$ 3 and 5 for both investigated sorbents. Preliminary experiments at pH$_{int}$ 6 have shown a totally different behavior. The sorption curves were quite steep and the maximum removal capacity was not achieved in the studied concentration range. It is believed that this is a clear indication of surface precipitation. The Eu concentration in the solid/liquid interface is much higher than in the solution and the solubility product of solid Eu(OH)$_3$ is reached in lower pH values (around 6) than the theoretically expected value of pH 7.0. So, all further additions of europium resulted in the precipitation as insoluble hydroxide.

As a general conclusion, the investigated Zr- and Ti-phosphate sorbents seem to be quite efficient in removing europium from aqueous solutions.

References

HUMATE COMPLEXATION OF NEPTUNIUM(V)

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The interaction between the actinide inventory of a nuclear waste disposal and humic substances is of particular interest for a predictive modelling of the transport in natural aquifers. Since more than ten years the complexation of Np(V) with humic acids has been investigated [1-8]. From previous works on the humic acid complexation of Np(V) several facts result: with the charge neutralisation model, deduced by Kim for the calculation of complexation constants log β_c [9], consistent constants were obtained for experiments with the following conditions: ionic strength I = 0.001 - 1 M perchlorate media, pH 5 - 9, humic acid concentrations [HA] = 10 - 1000 mg/L (independent of source), Np concentration [NpO(_4)²⁻] = 6*10⁻⁷ M - 7*10⁻⁵ M. Constants up to two orders of magnitude higher were reported by several authors for similar experimental conditions, but with neptunium concentrations < 10⁻⁶ M [1-4]. As NIR-absorption spectroscopy requires 10⁻⁷ M neptunium or higher, these low neptunium concentrations necessitate the investigation by indirect methods, that are based on the separation of the kinetically stable Np-humates from the free neptunyl ions in the solution. No significant difference is observed in the log β_c values for the Np(V) interaction with humic acid, when direct (NIR-spectroscopy) or indirect speciation methods (anion exchange AIX, ultrafiltration UF, electrophoresis ELF) were used [1]. Also in experiments with other indirect methods like dialysis [5] and liquid-liquid extraction [6] this increase in log β_c with decreasing Np(V) concentration is obtained, whereas some polyelectrolytes like polyacrylic acid do not show a comparable behaviour [6]. In Fig. 1 the data from the literature are added to our data for different humic acids (the LC corrected log β values were recalculated from log K or log β values; in some cases an estimation of LC was necessary). The conclusion, that this behaviour might be ascribed to another process than complexation with humate, namely the adsorption of the metal ion on inorganic impurities that remain in the humic acids even during the purification process seems plausible. So experiments with model humic acids (M1 and M42) synthesised at the "Institut für

Figure 1: log β_c at different pH values for several humic acids from the literature and our work. Data regions correspond to Aldrich HA (grey), Gorleben HA/FA (dotted) [5,6], M1 (solid) and M42 (dash). Other symbols correspond to the following literature: hexagons [3], stars [4], pentagon [2], triangle [7], diamond [8].

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Radiochemie" of the Forschungszentrum Rossendorf by the Mailard reaction [10] were performed to verify the influence of mineralised inorganic impurities in the humic acids. With the four speciation methods (AIX, EIP, UF and NIR-spectroscopy), different metal concentration regions were investigated using Aldrich humic acid and the synthetic humic acids M1 and M42. Especially the M42 synthetic humic acid is very pure and contains very few inorganic impurities. As this substance also follows the increase in log β_H_L with decreasing metal ion concentration, it is concluded, that this is not an effect of mineralised inorganic impurities, that may be present in the purified natural humic acids. There is a good match between all the data.

Looking at the absorption spectra of the NpO_2^2- ion and the complexed species, the humate complexed Np(V) appears as a new, bathochromically shifted absorption band with a maximum about 990 nm. For the curve fits, the peak parameters for the NpO_2^2- ion were fixed to parameters deduced from spectra of the pure NpO_2^2-aquo ion in different buffer solutions (peak maximum at 980.4 ± 0.2 nm and 6.2 ± 0.2 nm FWHM). For the spectra of the humate complexed Np-fraction, some problems arise in the deconvolution of the peaks. Using only one peak with free parameters for the humate peak the deconvolution results in a blue shift and broadening of the deconvoluted peak with increasing metal loading of HA. Furthermore, with this procedure, no satisfying reproduction of the spectra is obtained. Therefore we decided to use the fewest number of peaks with only slightly variable parameters to get satisfactory fits for the spectra. Absorption bands of Np(V)-complexes with simple organic substances (see [11] for complete citations) show bathochromic shifts (Δλ) of the absorbance maximum of the NpO_2^2- ion, which follow roughly the complexation strength of the ligands (Fig. 2). Coordination of a second ligand leads to a further shift to a higher wavelength. By plotting the red shift for the Neptunyl humate peak (fitted peaks, respectively) against the complexation constants log β_H_L (Fig. 2), the values are very close to the diketone compounds and dicarboxylic ethers for a 1:1 coordination (and 1:2, respectively), and they are located between values of the 1:1 and 1:2 coordination of dicarboxylic-, α-hydroxycarboxylic and α/β-amino-carboxylic acids. Values for the red shift and the log β for 1:1 complexation with simple monocarboxylic acids are too low, suggesting that these simple structures play a less important role in the humate complexation.

Linear-free-energy relationship - expressed as logarithm of complexation constants relationships - can be useful for understanding the ionic bonding between hard Lewis acids and bases like f-element cations and carboxylic acids [12]. Fig. 3 depicts the relationship
between the logarithmic complexation constants of NpO$_2^-$ and UO$_2^{2+}$ complexes with a variety of organic and inorganic ligands. The uranyl ion was selected for comparison because the hard Lewis character and the steric constraints are similar for both cations. The line obtained by linear regression stands for very similar complexation behaviour of the neptunyl and uranyl ion. Deviations from this line may come from different structures of the NpO$_2$L$_{1-2}$ and UO$_2$L$_{2-0}$ complexes, e.g., a different number of donor atoms per ligand bound to the metal ions. The complexation constants log $\beta_{EC}$ for NpO$_2$HA and UO$_2$HA for Aldrich, M1, M42 and GoHy-573 HA obtained at higher metal concentrations fit very well into the linear relationship, corresponding to a very similar complexation of both. By plotting the log $\beta_{EC}$ for NpO$_2$HA and UO$_2$HA for total neptunium concentrations $\leq 2 \cdot 10^{-4}$ M into the free energy plot of Fig. 3, it is obvious, that the complexes of NpO$_2^-$ become stronger with decreasing metal-ion concentration whereas the UO$_2^{2+}$ complexes are more or less constant.

It seems, that neptunium shows an extraordinary complexation behaviour. In the future, more attention is devoted to the humic acid molecules to elucidate the complexation mechanism. A recent publication [13] mentioned that the general understanding of humic substances as large molecules might be wrong. New studies reveal more and more that humic substances are agglomerates of various smaller molecules with masses $< 2000$ Dalton and that the agglomeration process might be enhanced by metal ions. The impact of these findings on metal complexation reactions has to be considered in future studies.

References

DETERMINATION OF STABILITY CONSTANT OF PLUTONIUM COMPLEXES WITH HUMIC ACID

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Humic substances are naturally occurring organic compounds of high molecular weight. They are capable of interacting with metals by complexation or redox process. Therefore the behavior of trace elements, especially anthropogenic radionuclides, in soils or sediments is greatly influenced by humic substances[1,2]. We have studied complexation of plutonium by Aldrich humic acid in solution at different values of ionic strength.

Purification of humic acid

The commercial sodium salt was purified in order to eliminate mineral impurities and non-humic substances. The method used was adapted from Vermeer et al.[3]. Humic acid is treated with HF-HCl to dissolve mineral impurities. The residue is dissolved in NaOH solution and precipitated in acidic conditions (HCl) to eliminate fulvic acids and humines. Then the humic acid is dialysed against distilled water until chloride free and shaken with a cationic resin in H+ form to remove metallic impurities. After freeze-drying we obtained purified humic acid in protoned form.

Potentiometric titration of humic acid

Acid-base properties of humic acid (AH) were investigated by potentiometric titration in the pH range 4-9 for three different ionic strength. Experiments were carried at 25±1°C under argon atmosphere. The charging of the molecule was calculated for each point of the titration curve according to the charge balance of the solution[4]:

\[
Q = \frac{C_{\text{NaOH}} - C_{\text{HNO}_3} + 10^{p\text{H} + 10^{pK_e}}}{C_{\text{AH}}}
\]
Fig 1: Potentiometric titration of humic acid. $C_{\text{AH}}$ = 400 mg/L, $C_{\text{NaOH}}$ = 4 x 10^{-3} mol/L, Titrant: $\text{HNO}_3$ 0.01 mol/L, Temperature: 25±1°C

**Interactions with plutonium**

Complexing abilities of humic acid were studied at trace plutonium concentration (below $10^{-10}$ mol/L). To evaluate the concentration of free and complexed forms of plutonium in solution, the equilibrium dialysis method[5] and the ion exchange resin method[6] were used. The performances of the two methods were compared.

Plutonium was quantified by alpha spectrometric measurement after electrodeposition on a stainless steel disc[7].

**References**


DEVELOPMENT OF METHODOLOGY FOR CALCULATION OF CONTROL LEVELS (CL) FOR DISCHARGES AND BLOWOUTS IN RAW HANDLING

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Accepted in the world is the non-threshold concept of ionizing radiation effect. This does not allow ruling out the possibility of emergence of certain somatic stochastic effects due to any exposure, no matter how small it is. In practice, provision of the radiation safety of the personnel and population is guided with the principles stipulated in the ICRP recommendations, which are approved in Russia in the normative documents (ND) “Radiation Safety Standards” (NRE-99) and “Basic Sanitary Rules for Provision of Radiation Safety” [1 – 3].

Employing these documents for development of the control levels of radionuclide abundance in the environment, in discharges and blowouts of technological processes at all stages of RAW handling proves to be impractical, as the former ones do not account for the actually existing levels of environmental pollution.

The purpose of the present study is the development of the methodology for calculation of Control Levels (CLs).

These ND stipulate the basic hygienic norms regarding exposure limits.

The principles of establishment of control levels

In establishing the CLs, the following guidelines are applied:
1. The concept of non-threshold effect of radiation factors on the health condition.
2. Radiation effect of small exposures has somatic stochastic (probabilistic) nature.
3. The maximum exposure for the critical population group shall not exceed 0.1 mSv per annum.
4. The limit of acquired lifetime risk for the population is assumed to be 5*10^-5.
5. The negligible risk level is 5*10^-6.
6. In case of effect of a combination of chemical and radiation factors, the possibility of synergism is supposed.

There are three methods suggested for CL calculation:
1. Express method: CL is determined based on Minimum Significant Specific Activity (MSSA)
2. Conservative method: CL is calculated based on radionuclide abundance in potable water
3. Reality method: CL is calculated based on radionuclide concentration in the water of open reservoirs.

The express method

CL calculation is carried out for radionuclides $^{90}$Sr and $^{137}$Cs based on minimum significant specific activity (MSSA) [1], which constitutes $10^5$ Bq/kg for $^{90}$Sr and $10^6$ Bq/kg for $^{137}$Cs.

The limiting exposure for population is 20 times lower than that for the personnel [1]. This serves the justification for establishing the CL 20 times lower that MSSA. Based on the extent of radiation hazard for open irradiation sources, all radionuclides are divided into radio-toxicity groups, $A$, $B$, $C$, $D$ [1]. Therefrom, CL for B group is adopted to be 200 times lower than MSSA, and for $^{90}$Sr, the CL is 500 Bq/l for group C, the respective factor is 20 and for $^{137}$Cs it is 50 Bq/l.
According to the conservative approach, the concentration of radionuclides in the facility discharged waters is assumed to be equal to the allowable radionuclide concentration in potable water and constitutes 5 Bq/l for $^{90}\text{Sr}$ and 11 Bq/l for $^{137}\text{Cs}$ [2], the adopted maximum exposure for the critical population group being 0.1 mSv per annum. At this concentration of the radionuclides in the discharged water, the exposure will constitute 1 mSv per annum. CL calculations for $^{90}\text{Sr}$ and $^{137}\text{Cs}$ yields 0.5 Bq/l and 1.1 Bq/l, respectively, which is an order of magnitude lower than that for the potable water. The conservative method is hardly applicable, as it requires huge expenses related to purification of waste waters down to the unjustifiably low concentrations of radionuclides.

The reality method

It is suggested to perform CL calculations depending on radionuclides accumulation in the environmental objects along the migration chain foodstuffs – humans. Accumulation of a radionuclide in foodstuffs occurs according to the chain water reservoir - fish, water reservoir - soil - animals. The entry of radionuclides into the organism of a human occurs at the following conditions:
1. Accidental swallowing of water (while swimming);
2. Inhalation effect of water;
3. Effect on the skin;
4. Consuming foodstuffs.

The exposure due to inhalation inflow and on-skin effects is negligible [4] and is not taken into consideration. The main contribution in the exposure is due to water entry into the organism of a human. CL is calculated based on radionuclide concentration in the water of open reservoirs. According to recommended practice [5], radionuclide inflow with the water from open reservoirs can be assessed with the equation:

$$NL = \frac{D}{JR \times ET \times RF \times E},$$

where:
- $D$ is the exposure for the critical population group, 0.1 mSv per annum;
- $JR$ is the concentration of the radionuclide in the discharged water, Bq/l;
- $ET$ is the rate of water inflow into an organism, l/hr;
- $RF$ is the duration of possible bathing of a person per annum, days;
- $E$ is the exposure factor, mSv/Bq.

Let us consider the example of the calculation. The values for the factors are taken from the literature [4]: $JR$=0.05 l/hr, $ET$=1 hr, $RF$= 45 days, $E$=8*10$^5$ mSv/Bq for $^{90}\text{Sr}$. The calculation yields CL for $^{90}\text{Sr}$ = 550 Bq/l; for $^{137}\text{Cs}$, the figure is 1700 Bq/l.

Accumulation of radionuclides in foodstuffs is estimated primarily for freshwater fish. For this purpose, the equation derived in [6, 7] is used:

$$D = \frac{CL \times F_{au} \times U_{k} \times E}{n},$$

where:
- $F_{au}$ is the of accumulation factor of radionuclides in the fish (for $^{90}\text{Sr}$ it is 60, for $^{137}\text{Cs}$, 2000);
- $U_{k}$ is the of the individual consumption factor of fish per annum for Moscow and Moscow region equal to 14 kg per annum [3];
- $n$ is the dilution ratio of the waste water discharged in the open reservoir.

$$n = \frac{V_1}{V_2},$$

where:
- $V_1$ is the volume of the reservoir, m$^3$;
- $V_2$ is the volume of the discharged water (per month, year), m$^3$.

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Substituting the numerical values of the factors in the equation, we get the CL value for $^{90}$Sr as $1.5 \times n$, Bq/l; for $^{137}$Cs as $0.3 \times n$, Bq/l.

The values for the risk of emergence of stochastic effects at these CL values is $1 \times 10^{-6}$, which corresponds to the negligible risk for the population \([4 - 7]\). Table 1 shows the values for the risk of emergence of stochastic effects for the population of Russia for the cases of irradiation from various radiation sources and the values for CLs.

Table 1. Risk of stochastic effect emergence for irradiation from various radiation source types \([4]\)

<table>
<thead>
<tr>
<th>Radiation source</th>
<th>Individual risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population exposure due to accidents:</td>
<td></td>
</tr>
<tr>
<td>Bryansk oblast</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>Kaluga oblast</td>
<td>$4.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Oryol oblast</td>
<td>$3.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Tula oblast</td>
<td>$4.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Medical sources</td>
<td>$6.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Natural sources: (1.1 - 1.6) $\times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Discharged water CL</td>
<td>$1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Conclusions

1. We suggest calculating the CLs for waste waters basing on the reality method, accounting for accumulation of the radionuclides in fish and dilution of the discharged water in the open reservoir water.

2. For the express assessment of the CL for discharged water, it is possible to use $1/20$ of MSSA.

3. The conservative method based on calculation of radionuclide CLs for discharged waste waters according to potable water criteria leads to unjustified strictness of the requirements, which entails excessive costs.

References


[3] ICRP publication No. 60, Pt. 1, Pt. 2


ENVIRONMENTAL ISOTOPES FOR DETERMINING THE RESIDENCE TIME AND A QUALITATIVE STUDY OF RECHARGE OF SHALLOW AQUIFER OF GUELMIME, SOUTH MOROCCO

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The study area, of approximately 1000 km², is part of the Assaka basin located in the south-west of Morocco. The climate is arid with 120 mm as an average amount of annual precipitation [1]. The Plio-Quaternary aquifer, in the area, constitutes the main reservoir of water. Increases in population and agricultural activities generate a continuous growth in demand for water and result in a multiplication of pollution sources. As this shallow aquifer is the principal source of fresh water in the region, information on residence time and recharge of the aquifer are of crucial importance for the long-term sustainability of the resource. Environmental isotopes study on the aquifers of the Guelmime provides new information: (1) the Oumlaachar aquifer is characterised by recent water. Its recharge corresponds to infiltration of precipitation along a valley; (2) the Seyyad aquifer recharge proceeds from two different origins: a high recharge at upgradient of the sub-basin and low recharge at the downgradient, and this study already confirms a feeding zone which was not suspected before, at Bani, south of the Seyyad sub-basin. The analysis of isotope, Bouhlassa and Aiachi [2], and chloride data combined with tritium content within a conceptual model based on the hydrogeology of the study area allows us to calculate mean residence time and to evaluate recharge rate of the shallow aquifer of Guelmime plain. Mean residence time in Oumlaachar sub-basin is (500 ± 170) years and (230 ± 70) years in Seyyad sub-basin (Table I) and the average recharge rate values of the two sub-basins would be (2.4 ± 0.28) mm/yr and (5.22 ± 2.58) mm/yr, respectively. This finding points to higher recharge rate and/or lower storage capacity of the phreatic aquifer in the Seyyad sub-basin.

Table I: Results of calculations of mean residence times of water (years) from tritium.

<table>
<thead>
<tr>
<th>Wells points</th>
<th>Oumlaachar sub-basin</th>
<th>Seyyad sub-basin</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Mean residence time (EM)</td>
<td>Mean residence time (EM)</td>
</tr>
<tr>
<td></td>
<td>(years)</td>
<td>(years)</td>
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<tr>
<td>Oumlaachar sub-basin</td>
<td>46</td>
<td>(400 ± 180)</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>(450 ± 140)</td>
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<td></td>
<td>1241</td>
<td>(720 ± 160)</td>
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<td>Seyyad sub-basin</td>
<td>1191</td>
<td>(128 ± 15)</td>
</tr>
<tr>
<td></td>
<td>1192</td>
<td>(162 ± 15)</td>
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<td></td>
<td>900</td>
<td>(350 ± 25)</td>
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<td></td>
<td>899</td>
<td>(350 ± 25)</td>
</tr>
</tbody>
</table>
References


AMS ANALYSIS OF $^{36}$Cl INDUCED IN SHIELDING CONCRETE OF VARIOUS ACCELERATOR FACILITIES

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At the accelerator facilities, shielding concrete of beam lines are exposed to secondary particles during machine operation, and various long-lived radionuclides are accumulated in shielding concrete of beam lines. Quantitative evaluation of radionuclides induced in the shielding concrete is important for radioactive waste management in reconstruction or decommissioning of accelerator facilities. The $\gamma$-ray emitting radionuclides, such as $^{22}$Na, $^{54}$Mn, $^{60}$Co, $^{155}$Eu and $^{154}$Eu, can be easily measured by Ge detectors, and $^3$H can be measured by liquid scintillation counters [1]. On the other hand, low concentration of $^{36}$Cl in concrete samples can be measured only by accelerator mass spectrometry (AMS).

The AMS system constructed in the 12UD tandem accelerator at the University of Tsukuba [2] has been applied for determination of $^{36}$Cl in soil and concrete samples related to Hiroshima atomic bomb, JCO critical accident, and other environmental samples [3]. Chemical procedure for preparing AgCl target for $^{36}$Cl AMS has been established [2]. However, the $^{36}$Cl / $^{35}$Cl ratios in shielding concrete of various accelerators are considered to be in the range $10^{-7} - 10^{-14}$, while the $^{36}$Cl AMS system at the University of Tsukuba is appropriate for the $^{36}$Cl / $^{35}$Cl ratios in the range $10^{-10} - 10^{-13}$. Therefore, dilution of isotope ratios is necessary for $^{36}$Cl analysis in shielding concrete samples by the Tsukuba AMS system. Figure 1 shows the sample preparation scheme developed for $^{36}$Cl AMS measurement of shielding concrete of accelerators. A part of Cl contained in concrete samples was extracted into dilute nitric acid by heating in pressurized decomposition vessel, and the concentration of Cl in the solution was determined by ion chromatography. The $^{36}$Cl / $^{35}$Cl ratios in the extracted solutions were diluted by addition of NaCl ( $^{36}$Cl / $^{35}$Cl below 5x$10^{-14}$ ) solutions. Precipitation of AgCl was formed by addition of AgNO$_3$ solution and purified according to the method developed [2]. In the present procedure, amount of concrete samples sufficient for sample preparation is 1 - 5 g.
Table 1 shows examples of the $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios determined by AMS measurement and the calculated original ratios in concrete samples. The results of Table 1 prove reproducibility and independence of determined $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios (before dilution) on diluting isotope factors.

For four kinds of accelerator facilities, SF cyclotron (Center for Nuclear Study, the University of Tokyo), 300 MeV electron LINAC (Laboratory of Nuclear Science, Tohoku University), 1.3 GeV electron synchrotron (Tanashi Branch, High Energy Accelerator Research Organization), and 12 GeV proton synchrotron (High Energy Accelerator Research Organization), the depth profiles of $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios in shielding concrete of beam lines were analyzed. Figure 2 shows the depth profiles of $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios together with the specific radioactivities of $^{152}\text{Eu}$ and $^{60}\text{Co}$ in the shielding concrete of SF cyclotron. The depth profiles of $^{36}\text{Cl} / ^{35}\text{Cl}$ are in good agreement with those of $^{152}\text{Eu}$ and $^{60}\text{Co}$, which are formed by thermal neutron capture reaction. The maximum $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios were observed at about 10 cm in depth from the inside surface, and similar profiles were observed for other accelerator facilities. These results imply that $^{36}\text{Cl}$ formed in shielding concrete of these accelerators is mainly formed by thermal neutron capture of $^{35}\text{Cl}$. Specific radioactivities for $^{36}\text{Cl}$, which can be determined by the $^{36}\text{Cl} / ^{35}\text{Cl}$ ratios, are much lower than those of other radionuclides, such as $^3\text{H}$, $^{152}\text{Eu}$ and $^{60}\text{Co}$.

References
Table 1  Examples of the $^{36}\text{Cl} / {^{35}\text{Cl}}$ ratios determined by AMS measurements and the calculated original ratios in concrete samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dilution factor</th>
<th>$^{36}\text{Cl} / {^{35}\text{Cl}}$</th>
<th>AMS measurement</th>
<th>Calculated original ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>60</td>
<td>$(5.43 \pm 0.19) \times 10^{-12}$</td>
<td>$(3.26 \pm 0.11) \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>$(4.60 \pm 0.28) \times 10^{-12}$</td>
<td>$(3.43 \pm 0.21) \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>$(3.99 \pm 0.35) \times 10^{-12}$</td>
<td>$(3.30 \pm 0.29) \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>No.2</td>
<td>2036</td>
<td>$(5.11 \pm 0.31) \times 10^{-12}$</td>
<td>$(1.04 \pm 0.06) \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2036</td>
<td>$(5.18 \pm 0.31) \times 10^{-12}$</td>
<td>$(1.05 \pm 0.06) \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>No.3</td>
<td>1</td>
<td>$(7.46 \pm 0.59) \times 10^{11}$</td>
<td>$(7.46 \pm 0.59) \times 10^{11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33.5</td>
<td>$(2.36 \pm 0.13) \times 10^{12}$</td>
<td>$(7.90 \pm 0.44) \times 10^{11}$</td>
<td></td>
</tr>
<tr>
<td>No.4</td>
<td>134</td>
<td>$(9.51 \pm 0.42) \times 10^{-12}$</td>
<td>$(1.27 \pm 0.06) \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>192</td>
<td>$(7.16 \pm 0.63) \times 10^{-12}$</td>
<td>$(1.37 \pm 0.12) \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>No.5</td>
<td>37.4</td>
<td>$(4.02 \pm 0.14) \times 10^{11}$</td>
<td>$(1.50 \pm 0.05) \times 10^{9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>331</td>
<td>$(4.86 \pm 0.22) \times 10^{-12}$</td>
<td>$(1.61 \pm 0.07) \times 10^{-9}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2  Depth profiles of $^{36}\text{Cl} / {^{35}\text{Cl}}$ ratios and specific radioactivities of $^{152}\text{Eu}$ and $^{60}\text{Co}$ induced in the shielding concretes of SF cyclotron (Center for Nuclear Study, the University of Tokyo)

- $^{36}\text{Cl} / {^{35}\text{Cl}}$
- $^{152}\text{Eu}$
- $^{60}\text{Co}$
CHANGES IN THE FILTERABLE FRACTIONS OF $^{60}$Co, $^{125}$Sb, $^{137}$Cs AND $^{241}$Am FROM A CONTAMINATED AQUIFER: A LABORATORY STUDY

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The migration of radionuclides in groundwaters depends on the element itself, the aqueous species, the nature of the soil as sorbent material, etc., to name a few factors. In shallow subsurface waters containing radionuclides from a shallow land burial site, several geochemical considerations influence the aqueous speciation. Most radionuclides are minor or trace components of the total load of ions, and hence the geochemical conditions will dictate the dominant aqueous species of these trace elements. In addition, some radioisotopes (e.g., $^{60}$Co) are likely outnumbered on a mole or atom basis compared to the stable element, such that there is mixing between the active and non-active isotopes. Other radiocontaminants (e.g., $^{241}$Am) are not subject to this, but they are nevertheless minor constituents of groundwaters. It is difficult to determine a priori whether mixing of active and non-active isotopes takes place, because this depends upon the rate of mixing and the natural cycling of elements. But in all likelihood, radiocontaminants that have been in soils for long periods of time (a few decades), due to inadvertent spillage or in old shallow radioactive burial sites, are probably well mixed with the natural components of groundwaters. These sites provide the opportunity to determine the major species of radionuclides that are mobile in soils.

Previous studies done in the vicinity of a former waste disposal area at a nuclear research centre (Chalk River, ON) have suggested that dissolved organics play a key role in the speciation and the mobility of radionuclides [1-6]. The nature and origin of these organics is uncertain, i.e., they could be man-made complexing agents released simultaneously with the wastes, degradation compounds of the latter by geochemical processes, or Natural Organic Matter (NOM). Because of the unknown origin of the organics, the term Total Organic Carbon (TOC) will be used henceforth.

A follow-up study in the same area was subsequently done [Caron and Mankarios, submitted], using a different separation scheme to pre-assess the aqueous species of selected radionuclides ($^{60}$Co, $^{125}$Sb, $^{137}$Cs and $^{241}$Am). A groundwater sample was extracted by ion exchange, reverse phase solid support (C$_{18}$), and it was submitted to ultrafiltration (5kDa membrane cartridge). Cesium-137 and $^{241}$Am were in the fraction containing the larger-sized material (>5kDa), whereas $^{60}$Co and $^{125}$Sb were found in the 5kDa filtrate. The radionuclides were likely associated with TOC, with the potential exception for $^{125}$Sb. It was suggested that $^{137}$Cs was associated with TOC, however, this was without direct measurement. This behaviour was consistent with previous work in the vicinity of the sampling site of the study, but a direct and dominant association of Cs with TOC has not been reported elsewhere. Furthermore, there is some experimental evidence that $^{137}$Cs in solution (colloidal-sized or otherwise) is unstable, and its dominant character can change in the time frame of a few days [5].
In this work, further processing of this sample will be presented, along with the analysis of a second sampling. The re-processing was done with a 1kDa pore size filter, to further characterize the associations of the target radionuclides in three size fractions: larger than 5kDa material; intermediate fraction (smaller than 5kDa but larger than 1kDa), and the “dissolved” fraction (i.e., smaller 1kDa material). In addition, the intermediate fraction was re-processed with inert water of similar ionic composition to the groundwater, to isolate the radionuclides in the 1kDa retentate material. This process is similar to harvesting cells from cultures, and we use it to isolate and characterize the retentate (for TOC and radionuclides).

We found that the TOC was distributed almost equally between the 3 fractions of interest (Figure 1a). Cobalt-60 had a similar distribution, whereas 125Sb and 137Cs were predominantly in the “dissolved” fraction. The 241Am was detected only in the retentate fraction (>1kDa; note that in the graph, the bar represents only the detected fraction, and the value “below detection limit” is not shown). There was a substantial change for 137Cs, which was associated with the large (>5kDa) fraction in the earlier study (Figure 1b). The >1kDa retentate re-processing with inert solutions indicated that some of the 56Co, 125Sb and 137Cs were no longer associated with the TOC fraction of interest (Figure 2). In contrast, the TOC was conservative, which was expected, while 241Am distribution did not appear to change (see above). The radionuclide losses (56Co, 125Sb and 137Cs) indicated that the association with TOC was not strong, whether this association was direct (complexation or electrostatic) or not. The discussion of a re-sampling will be presented and discussed as well.

References


Figure 1: Size distribution of elements and radionuclides in contaminated groundwater. (a), this study; (b) previous study of Caron and Mankarios [7]. Note that Am-241 was detected only in the retentate, and it is marked with an asterisk (*).

Figure 2: Size distribution of elements and radionuclides in contaminated groundwater, after re-processing with inert water. Note that Am-241 was detected only in the retentate, and it is marked with an asterisk (*).
UPTAKE OF THORIUM BY WHEAT AT DIFFERENT STAGES OF PLANT GROWTH

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Introduction
Generally soils and plants contain all naturally occurring radioactive elements with half-lives comparable to the age of the Earth, though their concentration in plants may be rather low. Geochemistry of uranium and thorium appears to be of particular interest for the radioecological studies. Fundamental knowledge of biogeochemical behaviour of these metals and processes involved in their environmental migration are also of practical importance for power generation, water supply, agriculture, sewage disposal, environmental protection and remediation. Although there are reports in literature on biogeochemistry of both elements [1, 2, 3], the number of publications on uranium prevails. The typical concentration range of Th in soils is 2 – 12 mg kg\(^{-1}\) [4]. Th concentration in plants can vary depending on part of the plant, but it is significantly lower than in soil.

The aim of the present study is to assess thorium uptake by plants grown in soil supplemented with this radionuclide. The effects of Th accumulation on distribution of other trace elements and macro-nutrients in the plants were also studied. The data of multi-element interrelations may be useful for an assessment of thorium toxicity for plants.

Materials and methods
Seeds of wheat were divided into two groups and germinated at room temperature. One group of the seeds was treated with thorium nitrate, and second group served as a control. After germination, wheat seedlings were transferred to pots filled with soil. The control seedlings were divided into two groups. One group of the seedlings was grown in soil supplemented with thorium, and second group of the seedlings was grown in normal (non-supplemented) soil. The seedlings germinated in solution enriched with thorium were transferred to normal soil. After seven days the plants were harvested, soil samples from the surface of the plant roots were also collected in each case and the plant and soil samples were dried at room temperature to constant weight. Instrumental neutron activation analysis and ICP-MS were used to determine elemental composition of the soil and plants.

Results and discussion
The transfer of the control wheat seedlings after germination to normal soil favoured the uptake of different elements by roots and transfer of the elements from roots to other plant parts. Germination of seeds in medium where thorium was added resulted in a significant increase of Th content in all parts of the wheat seedlings. The thorium uptake differed depending on the part of the plant. Transfer of the wheat seedlings germinated in Th supplemented medium to normal soil and growth of the seedlings in the soil led to a significant decrease of Th content in roots and in leaves. Cultivation of the control wheat
seedlings (germinated in absence of Th) in soil supplemented with Th also resulted in accumulation of this metal in roots and in seeds. In plants grown in clean (control) soil the highest concentration of Th was observed in roots, and the lowest Th content was typical for leaves. Similar distribution of Th in the wheat seedlings was found after adding Th to soil. In this case, however, differences between Th concentrations in different plant parts were more significant. Although after adding Th to soil its content in the soil increased, the change was not statistically significant. A decrease of thorium in the soil where wheat seedlings previously germinated in thorium supplemented medium were grown was rather surprising for us because the concentration of Th in the plants also decreased. We can assume that this loss of Th might be due to vaporization of thorium from the leaves together with transpired water.

The accumulation of Th in wheat seedlings caused variations in uptake of other elements. Although Th concentration in leaves was rather stable in all experiments and in the control, the most suffering part of the plants was just leaf. In the plants grown in soil artificially contaminated with Th concentrations of Rb, La and Sm in the leaves were lower than in the control plants. In the leaves of the plants germinated in Th amended medium and then grown in normal soil concentrations of Na and Rb were higher, and concentrations of Ca, Fe, La, and Sm were lower as compared to those in the control plants. Variations in seeds and in roots were not so significant. As a result of germination in Th enriched medium, concentration of Ca in seeds and in roots of the seedlings grown after the germination in normal soil decreased in comparison with Ca content in the seeds and roots of the control plants. Addition of Th to soil resulted in decrease of La in roots of the wheat seedlings grown in the soil. Thus, first and the most important reaction of the young wheat seedlings on the germination in Th enriched medium was efflux of calcium from all parts of the seedlings.

The variations in uptake of main mineral nutrients such as potassium, calcium, and sodium may provide a valuable information about the toxic effects of thorium. In particular, K/Na+ ratio is an important characteristic of physiological state of a plant [5]. We found that potassium is preferentially accumulated in all parts of the plants. The K/Na ratio in leaves is much higher than in seeds and in roots because of the higher K content and lower concentration of Na in the leaves. As was mentioned above, leaves of the seedlings germinated in the presence of thorium showed higher Na values which consequently decreased the K/Na ratio in the leaves.

The question arises, could the sodium influx be toxic for the plants? We did not observe any significant variation in the leaf biomass when the seedlings were grown in the presence of Th. The lengths of the leaves were comparable both in the control plants and in plants affected by thorium. It is necessary to note that in our study the growth time was rather short (seven days) and we can not exclude the possibility of certain physiological changes in the further stages of the plant growth.

**Conclusions**

Wheat seedlings were treated with thorium nitrate solution at two stages of their growth: (1) during germination in nutritive medium; (2) during growth in soil, after germination. Both treatments resulted in an increase of Th concentration in roots and in seeds. The leaf Th content remained rather low. The highest Th concentration was observed in seeds of the seedlings treated with Th during germination. The accumulation of Th in the wheat seedlings resulted in variations in concentrations of some other nutrients and trace elements. Although
there were no significant variations in Th concentrations in leaves, the most suffering part of the plants was just leaf. The first and the most important reaction of the young wheat seedlings on the germination in Th enriched medium was efflux of calcium from all parts of the seedlings.

References
DISTRIBUTION OF $^{238}\text{Pu}$, $^{239}+^{240}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$ RADIONUCLIDES IN CHERNOBYL FALLOUT BY SOIL ORGANIC MATERIAL FRACTIONS

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The interaction of radionuclides with natural organic species is a subject of high interest [1 – 4]. Soil is the main place accumulating radionuclides of Chernobyl fallout on the underlying surface. Radionuclides may be present in soil in a variety of physical and chemical forms, ranging from simple ions and molecules to larger molecular weight forms, such as compounds with soil organic matter. During the prognosis of migration in soil and entrance of $^{239}\text{Pu}$, $^{239/240}\text{Pu}$, $^{241}\text{Am}$, and $^{244}\text{Cm}$ to plant, it is necessary to consider specific character of distribution of radionuclides on different fractions of soil organic matter. The radionuclides have extensive, complex and organo-metallic chemistry. To investigate the extent of association of $^{239}\text{Pu}$, $^{239/240}\text{Pu}$, $^{241}\text{Am}$, $^{90}\text{Sr}$ and $^{137}\text{Cs}$ with soil organic matter, gel filtration was applied to the soil solution obtained from the top layers of forest soil within the 10 km zone of the nuclear reactor at Chernobyl [5]. Not enough information is available about interaction of $^{239}\text{Pu}$, $^{239/240}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$ of Chernobyl origin with humic and fulvic acids in soil.

Samples of different types of soil (sand, peat and meadow), most typical of exclusive zone of Chernobyl NPP (ChNPP), were collected from northwest direction at 5-10 km from ChNPP. The main physical and chemical characteristics of soils are presented. For extraction of humic material a suitable amount of soil was stirred in a beaker with 0.1 M NaOH in the ratio 1 g soil / 10 ml NaOH. After extraction, the sample was allowed to settle, centrifuged, and the supernatant was decanted. The solution was acidified to pH 2 by adding 6 M HCl and the humic acid (HA) precipitate centrifuged off, the fulvic acids (FA) remain in solution. Soil organic material fractions were obtained by Turin’s scheme (a suitable amount of soil sequential stirring in a beaker with 1-0.025 M H$_2$SO$_4$; 2-0.1 M NaOH; 3-0.5 M H$_2$SO$_4$; 4-0.1 M NaOH). Measurements of $^{238}\text{Pu}$, $^{239/240}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$ in soils and organic matter were conducted radiochemically, which allows doing it simultaneously from one sample. The maintenance of radionuclides of Pu, Am and Cm was measured at the eight-channel $\alpha$-spectrometer OCTETA PC ORTEC with semi-conductor Si- detector. Contents of radionuclides (Bq g$^{-1}$) in the top layers of soils are present in Table 1.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth, cm</th>
<th>$^{137}\text{Cs}$</th>
<th>$^{90}\text{Sr}$</th>
<th>$^{241}\text{Am}$</th>
<th>$^{244}\text{Cm}$</th>
<th>$^{239}\text{Pu}$</th>
<th>$^{239/240}\text{Pu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy sod-podzol</td>
<td>0 – 1</td>
<td>970 ± 20</td>
<td>260 ± 30</td>
<td>12 ± 1</td>
<td>0.81 ± 0.09</td>
<td>4.7 ± 0.5</td>
<td>9.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>860 ± 20</td>
<td>210 ± 30</td>
<td>14 ± 2</td>
<td>0.97 ± 0.11</td>
<td>5.6 ± 0.4</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>Sand</td>
<td>0 – 1</td>
<td>1130 ± 30</td>
<td>550 ± 40</td>
<td>17 ± 2</td>
<td>1.1 ± 0.1</td>
<td>6.8 ± 0.6</td>
<td>14 ± 2</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>850 ± 20</td>
<td>410 ± 40</td>
<td>18 ± 2</td>
<td>0.82 ± 0.11</td>
<td>5.9 ± 0.6</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>Meadow</td>
<td>0 – 1</td>
<td>1550 ± 30</td>
<td>430 ± 40</td>
<td>31 ± 4</td>
<td>1.5 ± 0.2</td>
<td>12 ± 1</td>
<td>25 ± 2</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>660 ± 20</td>
<td>350 ± 30</td>
<td>15 ± 1</td>
<td>0.77 ± 0.12</td>
<td>6.2 ± 0.6</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>Peat</td>
<td>0 – 1</td>
<td>4840 ± 60</td>
<td>95 ± 11</td>
<td>13 ± 2</td>
<td>0.55 ± 0.08</td>
<td>4.7 ± 0.5</td>
<td>10 ± 1</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>1490 ± 40</td>
<td>110 ± 10</td>
<td>1.6 ± 0.4</td>
<td>0.07 ± 0.02</td>
<td>0.66 ± 0.8</td>
<td>1.3 ± 0.2</td>
</tr>
</tbody>
</table>
This paper presents measurement results of radionuclide contents in fulvic and humic acids. For example, Table 2 contains the distribution of radionuclides $^{238}\text{Pu}$, $^{239+240}\text{Pu}$, $^{241}\text{Am}$, and $^{244}\text{Cm}$ of Chernobyl origin between fulvic and humic acids as percent of total content in soil sample.

Table 2: Distribution of $^{238}\text{Pu}$, $^{239+240}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$ of Chernobyl origin between fulvic and humic acids isolated by 0.1 M NaOH from soil

<table>
<thead>
<tr>
<th>Soil type</th>
<th>C_org (%)</th>
<th>$^{238}\text{Pu}$</th>
<th>$^{239+240}\text{Pu}$</th>
<th>$^{241}\text{Am}$</th>
<th>$^{244}\text{Cm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy sod-podzol</td>
<td>1.1</td>
<td>6.7</td>
<td>39</td>
<td>7.6</td>
<td>41</td>
</tr>
<tr>
<td>Meadow</td>
<td>19</td>
<td>4.8</td>
<td>28</td>
<td>4.5</td>
<td>29</td>
</tr>
</tbody>
</table>

The results show that $^{238}\text{Pu}$, $^{239+240}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$ are tied with all groups of organic compounds in various types of soils. At the same time, $^{244}\text{Cm}$ and $^{241}\text{Am}$ are basically associated with fulvic acids. It indicates the possibility of $^{244}\text{Cm}$ and $^{241}\text{Am}$ migration under the condition of fulvic complex compounds. Distribution of $^{241}\text{Am}$ and $^{244}\text{Cm}$ on the fraction organic matter with measurement uncertainty consideration is equal. For $^{238}\text{Pu}$ and $^{239+240}\text{Pu}$ it is typical association with humic acids and their compounds with chemical elements. Distribution of radionuclides $^{239+240}\text{Pu}$ and $^{241}\text{Am}$ of Chernobyl origin between six fractions is given in Table 3.

Table 3: Distribution of $^{239+240}\text{Pu}$ and $^{241}\text{Am}$ between six fractions of natural organic species isolated from sand and peat soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>0.025 M H$_2$SO$_4$</th>
<th>0.1 M NaOH</th>
<th>0.5 M H$_2$SO$_4$</th>
<th>0.1 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pu Am (I)</td>
<td>FA (II)</td>
<td>HA (III)</td>
<td>Pu Am</td>
</tr>
<tr>
<td>Sand</td>
<td>2.8 27</td>
<td>11 13</td>
<td>34 20</td>
<td>15 32</td>
</tr>
<tr>
<td>Peat</td>
<td>0.19 2.9</td>
<td>2.7 3.5</td>
<td>5 18</td>
<td>1.7 49</td>
</tr>
</tbody>
</table>

The association of $^{238}\text{Pu}$ and $^{239+240}\text{Pu}$ with higher molecular weight material impedes radionuclide uptake to plants, thereby helping to explain the low soil-to-plant concentration ratio. Contribution of soil organic matter to migration of radionuclides is under discussion.

References

750
WHITE SEA RADIOACTIVITY ASSESSMENT

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The aim of the present work is to estimate potential sources and chronology of pollution of the White Sea (Russia) by artificial radionuclides. White Sea is semi-closed water body connected with Barents Sea by a narrow strait. Thus, pollution of White Sea may be caused by highly polluted Barents waters [1] and river (mainly Northern Dvina) run-off. This is the first detailed investigation of radioactivity of White Sea sediment records.

Sampling was performed during 49 cruise of RV "Professor Shtokman" (August 2001) and cruise of RV "Ekolog" (September 2002) by Niemistö gravity corer. Sampling location is presented in Table 1.

Table 1. Sediment sampling location

<table>
<thead>
<tr>
<th>Station</th>
<th>Date</th>
<th>N</th>
<th>E</th>
<th>Sea depth, m</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>4697</td>
<td>13.08.01</td>
<td>65°17'</td>
<td>38°55'</td>
<td>89-96</td>
<td>Central part</td>
</tr>
<tr>
<td>4698</td>
<td>13.08.01</td>
<td>65°25'</td>
<td>38°40'</td>
<td>100-107</td>
<td>Central part</td>
</tr>
<tr>
<td>4706</td>
<td>15.08.01</td>
<td>65°05'</td>
<td>36°06'</td>
<td>60</td>
<td>Central part</td>
</tr>
<tr>
<td>4729</td>
<td>18.08.01</td>
<td>65°57'</td>
<td>35°53'</td>
<td>290</td>
<td>Central part</td>
</tr>
<tr>
<td>4727</td>
<td>21.08.01</td>
<td>65°28'</td>
<td>39°21'</td>
<td>56.5</td>
<td>Central part</td>
</tr>
<tr>
<td>4</td>
<td>04.09.02</td>
<td>67°08'</td>
<td>32°23'</td>
<td>40</td>
<td>Kandalaksha Bay</td>
</tr>
<tr>
<td>32</td>
<td>07.09.02</td>
<td>64°07'</td>
<td>37°35'</td>
<td>16</td>
<td>Onega Bay</td>
</tr>
<tr>
<td>78</td>
<td>18.09.02</td>
<td>65°05'</td>
<td>39°44'</td>
<td>32</td>
<td>Dvina Bay</td>
</tr>
</tbody>
</table>

137Cs and 210Pb were determined by γ-ray spectrometry using coaxial and planar HPGe detectors, respectively. In some cases 210Pb was determined by a radiochemical method [2]. Sedimentation rates calculated by 210Pb constant initial specific activity model and 137Cs inventories are presented in Table 2. Vertical profiles of 137Cs are shown in Fig.1.
Fig. 1. $^{137}$Cs profiles in White Sea sediments

The results allow to reconstruct chronology of radioactive contamination of the White Sea. It is evident that the activity of $^{137}$Cs in most cases slowly decreases. In some cores the horizons corresponding to maximum bomb $^{137}$Cs fallout and Chernobyl accident can be identified.
Table 2. Sedimentation rates, calculated from $^{210}$Pb and inventories of $^{137}$Cs in sediments

<table>
<thead>
<tr>
<th>Station</th>
<th>Sedimentation rate, g/cm²/y</th>
<th>$^{137}$Cs inventory, Bq/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4698</td>
<td>0.13±0.02</td>
<td>1120±40</td>
</tr>
<tr>
<td>4697</td>
<td>0.11±0.05</td>
<td>460±30</td>
</tr>
<tr>
<td>4720</td>
<td>0.09±0.02</td>
<td>650±40</td>
</tr>
<tr>
<td>4727</td>
<td>0.14±0.05</td>
<td>1720±50</td>
</tr>
<tr>
<td>4706</td>
<td>Not determined</td>
<td>900±100</td>
</tr>
<tr>
<td>32</td>
<td>Not determined</td>
<td>790±40</td>
</tr>
<tr>
<td>4</td>
<td>Not determined</td>
<td>340±20</td>
</tr>
<tr>
<td>78</td>
<td>Not determined</td>
<td>3030±70</td>
</tr>
</tbody>
</table>

References


MODELLING COLLOID GENERATION WITH PLUTONIUM: 
THE EFFECT OF pH AND REDOX POTENTIAL

Claude Degueldre, Magdalena Bolek

NES, Paul Scherrer Institute, 5232 Villigen, Switzerland

An analytical expression that evaluates the effect of pH and the redox potential (E) was used to study the colloid generation of plutonium. It includes surface complexation with one type of surface sites (>SOH) and its formulation leads to a distribution coefficient (Kd) as a function of the pH (hydrolysis) and E (redox sensitive species; such as recently published for Np and Am [1,2]. The effect of the redox potential at the surface has been taken into account considering the following reactions:

\[
> \text{SOH} + \text{MO}_x(\text{OH})_{y}^{-(2x+i)i} + \text{H}^+ \rightleftharpoons \text{SOMO}_x(\text{OH})_{y}^{-(2x+i-1)i} + n\text{e}^- + (2x - 2y + i - j)\text{H}^+
\]

\[
> \text{SOH} + \text{MO}_x(\text{OH})_{y}^{-(2x+i)i} + \text{H}^+ \rightleftharpoons (x - y + i - j)\text{H}_2\text{O} + (x - y + i - j)\text{H}_2\text{O} + n\text{e}^- + (2x - 2y + i - j)\text{H}^+.
\]

The surface complexation constants K_{SOH} were related with the stepwise stability constant K_{pH} using correlations between both constants since both surface complexation and hydrolysis reactions are analogous and based on similar exchange mechanisms e.g. onto Al₂O₃, FeOOH and SiO₂ colloids [3]. These K_{pH} constants were found in the literature for each of the selected oxidizing and reducing species.

The Kd formulation also considers the values of the stability and hydrolysis constants for all species present in solution and associated at the surface. The adequate semi-empirical correlations between hydrolysis and surface complexation constants reported in literature have been applied for each colloid system. The presence of complexing ligands in solution (such as carbonates) was also taken into account.

The distribution coefficient for the metal complexation with a ligand (L^9) was written in terms of the redox potential E:

\[
K_d = \frac{\sum_{i,k} K_{s,i} \cdot \beta_i \cdot [L_k]^4}{\sum_{i,k} [L_k]^4 \cdot \exp \left( \frac{(E^0 - E) \cdot nF}{RT} \right) \cdot [\text{SOH}]} \cdot \sum_{j,j'} K_{s,j,j'} \cdot \beta_{j,j'} \cdot [L_{j'}]^4 \cdot \exp \left( \frac{(E^0 - E) \cdot nF}{RT} \right) \cdot [\text{col}] 
\]
where the site concentration [\text{SOH}] is given by their distribution function. For total ligand concentration \([L]_T \gg [M]\), the free ligand concentration \([L]\) also has to be written in terms of its total concentration.

The model was applied to study the association of plutonium onto \(\text{Al}_2\text{O}_3\), \(\text{FeOOH}\) and \(\text{SiO}_2\) coloids, in the absence (Fig. 1, for \(\text{Al}_2\text{O}_3\)) or in the presence (Fig. 2, \(\text{Al}_2\text{O}_3\)) of carbonates in solution. The tests performed with the model suggest that the oxidation of \(\text{Pu}(\text{III})\) to \(\text{Pu}(\text{IV})\) has the potential to increase the sorption, as demonstrated by the increased \(K_d\) values. Under the natural conditions \(\text{Pu}\) may be present at oxidation states of (III), (IV), (V) and (VI), and the effect of redox potential is significant because of the differences in the sorption of each oxidation state. When carbonates are present in the solution, the calculated values of distribution coefficient were lower than those calculated in the absence of carbonates, particularly in case of \(\text{Pu}(\text{VI})\).

\[\text{Pu - Al}_2\text{O}_3\text{ colloid generation}\]

\[\begin{array}{c}
\text{pH 12} \\
\text{pH 10} \\
\text{pH 8} \\
\text{pH 6} \\
\text{pH 4} \\
\text{pH 2}
\end{array}\]

\[\begin{array}{c}
\text{1} \\
\text{3} \\
\text{5}
\end{array}\]

\[\begin{array}{c}
\text{E (V)} \\
\text{log Kd (ml g\textsuperscript{-1})}
\end{array}\]

Fig. 1 \(K_d\) values as a function of redox potential at different pH values for the sorption of plutonium onto 200 nm \(\text{Al}_2\text{O}_3\) coloids without carbonates in solution.
Fig. 2: $K_d$ values as a function of redox potential at different pH values for the sorption of plutonium onto 200 nm Al$_2$O$_3$ colloids considering carbonate concentration of [CO$_3^{2-}] = 0.02$ M.

The $K_d$ values obtained with the developed model are in agreement with experimental values reported for the sorption of plutonium onto colloids in the CRR program. This model can equally be applied to study the sorption of other redox sensitive elements.

References

BEHAVIOR OF RADIOACTIVE CESIUM, PLUTONIUM AND AMERICIUM IN BOREAL FOREST ECOSYSTEMS

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Lisa Outola, Michael Tillander and Reijo Pehrman

Laboratory of Radiochemistry, P.O.Box 55 FIN-00014 University of Helsinki,
Helsinki, Finland

In 1997-2003 a large number of environmental samples have been collected from the Muddusjärvi area in Finnish Lapland. These samples include soil, water, sediment, vegetation and fish. Radioactive contamination in this sub-arctic environment has mainly resulted from the nuclear weapons tests fallout in the 1950's and 1960's. Chernobyl accident did not considerably increase the contamination level in this area. Laboratory of Radiochemistry, University of Helsinki has been studying the behaviour of fallout radionuclides in the environment and in food chains in Lapland from the beginning of 1960's. The study area lies in the middle of northern reindeer hearding area where accumulation of radioactive cesium and plutonium has been observed in food chains. A special accumulating chain has been transfer of $^{137}$Cs from lichen via reindeer to reindeer-hearding sami people.

In this paper we report on the behaviour of radioactive cesium, plutonium and americium in soil columns and their transfer into several vegetation species (berries, mushrooms, hay and birch leaves). The soil in this area is typically nutrient-poor podzolic soil. Altogether thirty-six soil columns were collected and they were divided into horizons (litter, organic and mineral layers). The activity concentrations of cesium in the horizons were determined by gamma spectrometry. The total fallout of $^{137}$Cs in this area is somewhat above 2 kBq/m$^2$. In general, cesium has concentrated mainly in the litter and organic layers, but in some cases it had migrated considerably to mineral layers even below 20 cm. The $^{137}$Cs activities in the six soil columns collected in 2001 are presented in Figure 1 for each individual profile and as average values in Figure 2.
Figure 1. $^{137}\text{Cs}$ activities in various soil layers.

Figure 2. Distribution of $^{137}\text{Cs}$ in various layers in soil columns. Percentages are standard deviations of six soil samples.

Aggregated transfer factors for cesium transfer from soil plants were highest with mushrooms, between 0.1 and 1 m$^3$/kg (Table I). With other plants the values were an order of magnitude lower.

For the determination of plutonium and americium activity concentrations, samples of the soil horizons and the plants were ashed in oven and leached with acids. The radiochemical separation procedures were carried out using both anion exchange and extraction
chromatographic methods. Plutonium and americium have been considerably less mobile and they were found more or less in the litter and especially in the organic layer. The activity of $^{137}$Cs in the soil was found to be around 2 kBq/m². Corresponding value for $^{239,241}$Pu was 46±17 Bq/m² and for $^{241}$Am 19±6 Bq/m². The $^{241}$Am to $^{239,240}$Pu ratio in soil was on average 0.42±0.03. For plutonium and americium the transfer factors for the transfer from soil to plants were several orders of magnitude lower than in case of cesium (Table II).

Table I. Aggregated transfer factors for the transfer of $^{137}$Cs from soil to plants

<table>
<thead>
<tr>
<th>Plant</th>
<th>Samples</th>
<th>Average activity (Bq/kg)</th>
<th>Standard deviation (Bq/kg)</th>
<th>Transfer factor from soil to plants (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mushrooms</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suillus variegatus</td>
<td>6</td>
<td>1785</td>
<td>205</td>
<td>0.90</td>
</tr>
<tr>
<td>Leccinium versipellis</td>
<td>5</td>
<td>200</td>
<td>7.4</td>
<td>0.10</td>
</tr>
<tr>
<td>Russula padulosa</td>
<td>6</td>
<td>1000</td>
<td>106</td>
<td>0.51</td>
</tr>
<tr>
<td>Russula</td>
<td>5</td>
<td>917</td>
<td>12</td>
<td>0.46</td>
</tr>
<tr>
<td>Lactarius rufus</td>
<td>7</td>
<td>1209</td>
<td>2057</td>
<td>0.61</td>
</tr>
<tr>
<td>Berries</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crowberry</td>
<td>7</td>
<td>68</td>
<td>0.8</td>
<td>0.034</td>
</tr>
<tr>
<td>Crowberry twig</td>
<td>8</td>
<td>51</td>
<td>0.5</td>
<td>0.026</td>
</tr>
<tr>
<td>Blueberry</td>
<td>7</td>
<td>122</td>
<td>1.7</td>
<td>0.062</td>
</tr>
<tr>
<td>Blueberry twig</td>
<td>8</td>
<td>103</td>
<td>3.1</td>
<td>0.052</td>
</tr>
<tr>
<td>Lingonberry</td>
<td>6</td>
<td>44</td>
<td>0.1</td>
<td>0.022</td>
</tr>
<tr>
<td>Lingonberry twig</td>
<td>8</td>
<td>49</td>
<td>0.6</td>
<td>0.025</td>
</tr>
<tr>
<td>Other plants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hay</td>
<td>5</td>
<td>49</td>
<td>0.7</td>
<td>0.025</td>
</tr>
<tr>
<td>Birch leaves</td>
<td>8</td>
<td>32</td>
<td>0.3</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table II. Aggregated transfer factors (m²/kg) for the transfer of $^{239,238}$Pu and $^{241}$Am from soil to plants.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Pu-239,240</th>
<th>Am-241</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russula</td>
<td>0.00000505</td>
<td>0.0005015</td>
</tr>
<tr>
<td>Crowberry</td>
<td>0.0000275</td>
<td>0.0000947</td>
</tr>
<tr>
<td>Crowberry twig</td>
<td>0.0002599</td>
<td>0.0001964</td>
</tr>
<tr>
<td>Blueberry</td>
<td>0.0000626</td>
<td>0.0001241</td>
</tr>
<tr>
<td>Blueberry twig</td>
<td>0.0002428</td>
<td>0.0003602</td>
</tr>
</tbody>
</table>

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DEVELOPMENT OF NUCLEAR ANALYTICAL TECHNIQUES IN ANALYSIS OF SOME POLLUTANTS IN PLANT LEAVES

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Institute of Nuclear Physics of Uzbekistan Academy of Sciences, Ulughbek, 702132 Tashkent, Uzbekistan, kadyrova@inp.uz

Today Uzbekistan has a highly developed industry, with more than a hundred branches, including power engineering, machine-building, metal smelting, the production of chemicals, oil, gas, textiles, and food-processing. Cotton-growing, gold and uranium mining processing are the main branches of the national economy at present. But it is evident that industrial and agricultural progress in human life has resulted in creating serious ecological problems. The sources of environmental pollution with radioactive and toxic elements and also heavy metals in Uzbekistan can be industrial objects of ore and mine processing, metallurgical works, chemical fertilisers plants, automobile industry and exhaust gases from automobiles, etc. All of these make it vitally important to elaborate highly sensitive analytical techniques capable of controlling degree of environmental pollution and determining pollutant sources. Highly sensitive, precise and reliable instrumental neutron activation analysis (INAA) and X-ray radiometric techniques have been developed in the Institute of Nuclear Physics for the determination of about 30 major and minor elements in such environmental samples, as leaves and seeds of plants, with detection limit of 0.0001 - 1 mg/kg by using a nuclear reactor and \(^{109}\)Cd, \(^{241}\)Am sources. Characteristics of developed INAA techniques are given in Table 1.

### Table 1. Characteristics of developed INAA techniques

<table>
<thead>
<tr>
<th>Determined elements</th>
<th>Sample mass, g</th>
<th>Neutron flux density and spectrum, n cm(^{-2}) s(^{-1})</th>
<th>Time of irradiation</th>
<th>Cooling</th>
<th>Measuring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, K, Mn, Cu, Sr</td>
<td>0.1</td>
<td>6.5×10(^{10}) thermal</td>
<td>16 h</td>
<td>2 - 3 h</td>
<td>5 min</td>
</tr>
<tr>
<td>Ti, As, Se, Br, Rb, Cd, Sb, Ba, La, U</td>
<td>0.2-0.3</td>
<td>5.3×10(^{13}) fission spectra</td>
<td>20 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc, Cr, Fe, Co, Ni, Zn, Zr, Mo, Ce, Cs, Hg, Th</td>
<td></td>
<td></td>
<td>20 d</td>
<td></td>
<td>10 min</td>
</tr>
</tbody>
</table>

The explored area was an urban city in Uzbekistan with industrial estate involving a mining processing plant, regions of Tadjik aluminum factory, Chirchik works of heatproof and refractory metals, Asaka automobile works and Tashkent nuclear reactor. Samples analysed were leaves and seeds of plants grown in the selected areas. INAA and X-ray radiometric technique experimental results of many kinds of leaves and seeds have been obtained. Results
of INAA of quince, tomato, peach, vineyard, apricot mulberry leaves collected from Dashnabad and Djarkurgan (control) sites of aluminium factory are given in Table 2. For example X-ray spectrum of vineyard leaves measured with Si (Li) detector and $^{109}\text{Cd}$ source is shown in Figure 1. Kα - lines of Ca, Fe, Cu, Sr and Zr will be seen. Ca concentration determined by X-ray method is 1500 mg/kg$^{-1}$.

Table 2. Results of INAA of some plant leaves growing near Tadjik aluminium factory

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration, mg/kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dashnabad</td>
</tr>
<tr>
<td></td>
<td>quince</td>
</tr>
<tr>
<td>Na</td>
<td>310</td>
</tr>
<tr>
<td>K</td>
<td>18000</td>
</tr>
<tr>
<td>Sc</td>
<td>0.052</td>
</tr>
<tr>
<td>Cr</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn</td>
<td>820</td>
</tr>
<tr>
<td>Fe</td>
<td>240</td>
</tr>
<tr>
<td>Co</td>
<td>6.55</td>
</tr>
<tr>
<td>Ni</td>
<td>29</td>
</tr>
<tr>
<td>Cu</td>
<td>9.7</td>
</tr>
<tr>
<td>Zn</td>
<td>16</td>
</tr>
<tr>
<td>As</td>
<td>7.2</td>
</tr>
<tr>
<td>Se</td>
<td>0.0065</td>
</tr>
<tr>
<td>Br</td>
<td>4.0</td>
</tr>
<tr>
<td>Rb</td>
<td>0.95</td>
</tr>
<tr>
<td>Zr</td>
<td>15</td>
</tr>
<tr>
<td>Mo</td>
<td>0.80</td>
</tr>
<tr>
<td>Cd</td>
<td>30</td>
</tr>
<tr>
<td>Sb</td>
<td>0.074</td>
</tr>
<tr>
<td>Cs</td>
<td>0.030</td>
</tr>
<tr>
<td>Ba</td>
<td>6.5</td>
</tr>
<tr>
<td>La</td>
<td>0.022</td>
</tr>
<tr>
<td>Sm</td>
<td>0.0031</td>
</tr>
<tr>
<td>Tb</td>
<td>0.012</td>
</tr>
<tr>
<td>Hg</td>
<td>0.84</td>
</tr>
<tr>
<td>Th</td>
<td>0.0067</td>
</tr>
</tbody>
</table>

Comparative assessment and reasons of variations in some element contents depending on location from the specific objects in investigated samples, have been considered in this work. Mild, average and highly polluted areas near these objects have been found.
Fig. 1. X-ray spectrum of vineyard leaves with source $^{109}$Cd

The capability of nuclear track techniques of imaging the analysed objects makes it possible to use them as additional tools for the study of environmental pollution with some toxic and radioactive elements. Boron is known to be a vitally important micro-component for most of the plants. However, excessive amount of boron affects the plants as a toxic element. Analysing surface distributions of the elements in the leaves of the plants it was possible to reveal a nature of pollution. The technique is based on the detection of $^{10}$B(n,α)$^7$Li reaction products using cellulose nitrate. The experimental procedure consists of irradiation of the detector strips, pressed to the surface of plant leaves, with thermal neutrons of WWR reactor. The alpha and $^7$Li particles, having energies of 1.47 MeV and 0.84 MeV, respectively, produce tracks in the detector. After irradiation in a mixed γ-neutron field with low cadmium ratio (~100) the optimum regime of chemical etching of the detector strips have been found. It was etched in 6N NaOH solution at 40°C for 35 min. After etching the detectors were washed in water and dried. Etching enlarges these tracks enough to be seen by an ordinary light microscope. Then after counting track densities, they will transform to $^{10}$B concentration.

The software for treatment of microscopic scanned photographic track images by application of digital image processing has been developed. All program modules are made in DELPHI execution environment by using Pascal object-oriented language.

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THE ENVIRONMENTAL ACTINIDE AND RADIOCHEMISTRY PROGRAM AT
CLEMSON UNIVERSITY

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Clemson University
342 Computer Court
Anderson SC 29625-6510
USA

This paper will review the environmental actinide and radiochemistry program at Clemson University as well as highlight the facilities, funding and research topics of the program. Clemson University, founded in 1889, is a public university in South Carolina with a strong heritage in environmental sciences. The 1,400 acre main campus is surrounded by 17,000 acres of University farms and woodlands with another 12,390 acres for engineering research land. Clemson currently has about 17,000 students and offers 112 graduate programs. Clemson ranks among the nation’s top 25 universities in revenue generated from marketing intellectual property. Since 1990, Clemson has completed over 100 projects totaling over $20M dealing with environmental effects at the Savannah River Site (SRS). The University was selected as Time Magazine’s Public College of the Year in 2001.

Clemson’s Environmental Engineering and Science (EE&S) graduate program has been in existence since 1961. EE&S is nationally ranked by US News and World Report as fourteenth out of over 300 environmental departments. Recently, Clemson re-organized its total environmental science and engineering programs through the formation of the School of the Environment. This program combines the resources from EE&S, Geological Sciences, and Environmental Toxicology academic departments.

EE&S is located in the L. G. Rich Environmental Research Laboratory. The nuclear facilities include a teaching laboratory with an array of radiation detection instrumentation, a low level counting laboratory for environmental samples, a radiation detection and measurement laboratory, and a radiochemical separation laboratory for sample preparation. Adjacent to the Rich Laboratory is the Clemson Environmental Technology Laboratory, which has two state-of-the-art analytical laboratories, two high bay laboratories for pilot-scale projects and a demonstration area. These facilities are specifically designed for research and treatment technologies related to hazardous, radioactive, and mixed wastes. Almost all radioisotopes, including the actinides and up to 200 grams of special nuclear material, can be handled in these facilities.

Through a partnership with the Department of Energy (DOE), SRS and DOE Office of Nuclear Energy, a program in environmental actinide and radiochemistry was started at Clemson in late 1999. The program addresses radioactive materials processing, nuclear waste management and environmental restoration issues, and contributes to ongoing actinide and radiochemistry research programs at DOE facilities in preparing students for careers in actinide and radiochemistry. Since 2000, most of the participating students have spent a summer doing research at SRS. The program is currently supporting several graduate students who are doing
thesis research on subjects related to SRS problems. The progress and results to date of the program are reflected in the research awards totaling more than $3.0M. The titles and dates of the grants are listed in Table 1. Another measure of success is the number of students graduated from the program as well as visiting scholars and post-docs. The graduate students and their thesis titles are shown in Table 2. Currently there are four other graduate students enrolled in the program. In addition seven visiting scholars and post-docs, worked at Clenson during the last two years.

Table 1. Titles and Dates of Sponsored Research Projects
Radiochemistry Education Award Program (2000-04).
Polyvinyl Alcohol Technical Study (2000-01).
Radiochemistry and Actinide Chemistry (2000-03).
Graduate Student Fellowships in Radiochemistry and Actinide Chemistry (2001-04).
Graduate Student Internships in Radiochemistry and Actinide Chemistry (2003-04).
Improvement of Radiochemistry Methods for the International Atomic Energy Agency’s Safeguards Analytical Laboratory at Seiberdorf, Austria (2004).

Table 2. Graduate Students and Thesis Titles/Dates

During the past four years the basic infrastructure of the program was developed. Specific accomplishments include the hiring of a new faculty member, the development of an actinide chemistry course, the expansion of the environmental radiation laboratory, the establishment of an environmental radiochemistry focus area, the recruitment of graduate students, the initiation of a summer program for recruiting undergraduates into the field, the addition of new laboratory space, and the acquisition of equipment to support both the instructional and research programs. With the infrastructure now in place, the focus has turned to ensuring the long-term viability of the program by
expanding the student base, especially at the PhD level, by continuing the very successful undergraduate student recruiting program, and by adding post-doctorates who can assist the faculty in expanding the research base.

Research projects in the following areas are available: Actinide chemistry; Chemical aspects of environmental restoration, spent nuclear fuel processing, nuclear waste management, materials deposition, and isotope production; Chemistry of radionuclides in the environment; and Separations related to environmental management and the nuclear fuel cycle. Research assistantships and fellowships are available through a variety of sources including the following:
- REAP: DOE Radiochemistry Education Awards Program
- SCUREF Internships (SC Universities Research & Education Foundation)
- Radiochemistry Internships from DOE-Savannah River Operations Office
- Research Associates at Savannah River
- International Atomic Energy Agency

Reference

RADIONUCLIDE X-RAY FLUORESCENCE METHOD OF DETERMINATION OF TOXIC METAL CONTENT IN ENVIRONMENT OBJECTS


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The problem of environmental protection in each country is solved according to peculiarities of its social structure and the level of production development. Even in countries with high level of economic development, there are technological cycles that not exclude discharge of harmful substances in surrounding air. If from the viewpoint of strategy maximum scientific efforts must be paid to the development of non-waste technologies, with complex processing of raw materials in closed production cycles, protection of environment quality, requires the development of effective objects for purification and decontamination of industrial wastes, discharges and strict standardisation of toxic materials emission in the biosphere.

One of the most important problems of environmental monitoring is estimation of different objects of pollution (air, water, soil) with minute quantities of toxic materials. When the content of toxic elements in them is known, it is possible to estimate the quantity of environment and to choose a suitable method of improving its characteristics.

At present almost all methods used in analytical chemistry are employed for monitoring of environmental state.

Radionuclide and X-ray fluorescence analysis (RRFA) that was used for determination of heavy metals (lead, cadmium, chromium) in surface water and soils of Kharkiv and Kharkiv region plays an important part among methods of determination of minute quantities (10^{4} — 10^{8} per cent) of toxic elements in environmental objects.

Employment of radioactive sources has a number of advantages over X-ray tubes application; these are a wide range of nonchromatic electromagnetic radiations produced by available radionuclide set, stable intensity of radionuclides radiation and simple equipment used in analysis. They are also easy to handle.

Besides RRFA allows to determine up to twenty elements simultaneously. The time of one sample analysis is up to 30 minutes. Sensitivity of metals determination in water is 10^{5} kg/l (samples preparation is included) and that one in soils — 10^{8} kg/kg (without preparation of samples).
APPLICATION OF SIMPLE ENVIRONMENTAL MODEL FOR NATURALLY OCCURRING TRACE ELEMENTS TRANSFORMATION IN SURFACE WATER

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Analytical Chemistry Department, Hot Labs Center, Atomic Energy Authority, Cairo, Egypt.

Several studies on the anthropogenic radionuclides artificial elements, Sr-90, Cs-137 and Pu239+240, were performed in the water column of the Japan Sea [1], which might add more contaminants to the environment. Therefore, studying the transportation using naturally occurring radioactive elements is better from the environmental point of view. Adsorption and desorption rates and retardation factors of radionuclides based on U-238 and Th-232 series nuclide activities have been studied [2]. Knowledge of the ability of sediment to retard the surface water transport of toxic or radioactive ions can be inferred from the analysis of surface water and the bottom sediments for radionuclides 239+240Pu, 232Th. A statistical evaluation of the concentration of different radioisotopes in both water and contacting sediments was performed to correlate the chemical transportation in such system. Compartment model is widely used and is found appropriate for problems requiring long time scales for prediction. In this respect, retardation factors were evaluated based on the distribution coefficient of the dispersal radioactivity in surface water. It is a generic model requiring few sites details. Some basic results for this model type and its effectiveness are presented revealing that uranium dispersion is higher than thorium and/or potassium, which indicate the dependence of retardation on sediment.

Determination of naturally occurring uranium, thorium and potassium in the sediments and water of Ismailia canal were calculated as shown in Table 1, where the activities were calculated based on Bq/L for water and Bq/Kg for sediments. In general, the data revealed that the increase in natural radioactivity levels within 30 km from the first site Moustorod to Menayer, Table 1 also reveals the increase in thorium activity compared to uranium one in some of the investigated locations.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Uranium</th>
<th>Th/U ratio</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moustorod (S1)</td>
<td>57.3±3</td>
<td>1.00</td>
<td>618±80</td>
</tr>
<tr>
<td>Fertilizer Factory (S2)</td>
<td>58.7±2.9</td>
<td>1.18</td>
<td>774±60.8</td>
</tr>
<tr>
<td>Insas (S3)</td>
<td>93.3±12</td>
<td>1.26</td>
<td>323±50.2</td>
</tr>
<tr>
<td>Menayer (S4)</td>
<td>101.0±8.1</td>
<td>0.72</td>
<td>1020±112</td>
</tr>
<tr>
<td>El-Tal el Keboor (S6)</td>
<td>36.8±4.8</td>
<td>0.72</td>
<td>982±55</td>
</tr>
<tr>
<td>El-Kassasien (S7)</td>
<td>36.8±3.5</td>
<td>0.79</td>
<td>579±37.2</td>
</tr>
<tr>
<td>Abu Sour (S8)</td>
<td>78.0±5.9</td>
<td>0.68</td>
<td>736±12.1</td>
</tr>
<tr>
<td>El-Galaa(S9)</td>
<td>59.8±11</td>
<td></td>
<td>514±13.4</td>
</tr>
</tbody>
</table>
Table 2 shows that the mean concentration levels of natural radionuclides along Ismailia canal in water (in Bq/L) are within the range 0.76-2.94 for U-238, 0.1-1.6 for Th-232 and 0.31-8.3 for K-40.

Table 2. Mean activity of uranium, thorium and potassium of water from Ismailia Canal

<table>
<thead>
<tr>
<th>Sites</th>
<th>Uranium-238</th>
<th>Thorium-232</th>
<th>Potassium-40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moutord (S1)</td>
<td>1.39±0.31</td>
<td>0.1±0.09</td>
<td>8.3±2.1</td>
</tr>
<tr>
<td>Fertilizer Factory (S2)</td>
<td>1.82±0.21</td>
<td>0.13±0.3</td>
<td>7.3±0.3</td>
</tr>
<tr>
<td>Inshas (S3)</td>
<td>2.94±0.53</td>
<td>0.14±0.01</td>
<td>6.5±1.5</td>
</tr>
<tr>
<td>Menaiyer (S4)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>El-Tal el Atbaa (S6)</td>
<td>1.41±0.33</td>
<td>0.2±0.008</td>
<td>3.1±0.5</td>
</tr>
<tr>
<td>El-Kasrari (S7)</td>
<td>2.02±0.08</td>
<td>0.23±0.04</td>
<td>6.3±1.1</td>
</tr>
<tr>
<td>Abu Sour (S8)</td>
<td>0.76±0.03</td>
<td>1.6±0.01</td>
<td>0.31±0.01</td>
</tr>
<tr>
<td>El-Galaa (S9)</td>
<td>0.85±0.05</td>
<td>1.2±0.05</td>
<td>0.94±0.02</td>
</tr>
</tbody>
</table>

Differences in the concentration levels in both systems can be referred to the existing differences in sediment water interface characteristics, which may lead to the adsorption of different radionuclides and other metallic pollutants with subsequent removal from aquatic media. This is best exemplified by the results of both sediment and water samples collected from El-Menaiyar area (27 km far from Cairo) where the water samples proved to be void of any measurable levels of U-238, Th-232 and K-40 while the sediment samples from the same area have the highest concentration levels of these radionuclides among all other analyzed samples. Statistical evaluation using unpaired “t” test and correlation coefficient “r” values are derived to investigate the relationship between the individual activity of each radionuclide in both sediment samples and the respective contacting aquatic media. Based on the calculated mean values (as shown in Tables 1, 2) of uranium in both sediment and water compartment, it is shown that there is a high significant difference in activity levels ( t = 7.97) which is mainly attributed to the high retardation factor of sediment to uranium as a result of complexation process.

As shown in Table 3, the high correlation coefficient ( r = 0.5679) indicating the presence of steady distribution pattern of uranium between sediment and contacting aquatic phase. As is evident from Table 3, very high correlation coefficient ( r = 0.844) was observed between the activity levels of uranium and thorium in sediment which mainly related to the natural decay process in a relatively steady phase, i.e. low rate of dissolution and high retardation capacity.

Table 3. Unpaired “t” test and correlation coefficient “r” between uranium and thorium in sediment and water media.

<table>
<thead>
<tr>
<th>Statistical Parameter</th>
<th>U_{sediment-water}</th>
<th>Sediment U/Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>0.5679</td>
<td>0.844</td>
</tr>
<tr>
<td>p</td>
<td>&lt; 0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>t</td>
<td>7.97</td>
<td>0.0816</td>
</tr>
<tr>
<td>p</td>
<td>&lt; 0.001</td>
<td>&lt;0.45</td>
</tr>
</tbody>
</table>
In this regard, the dimensionless distribution coefficient for uranium, thorium and potassium have been determined by assuming steady state condition using the following model.

\[ K_d = \frac{\text{concentration in sediment}}{\text{concentration in water}} \]

The model used here to describe the behavior (i.e. adsorption-desorption and retardation) of radionuclides in surface water is that employed by Krishnaswami et al [2]. The model neglects the role of coprecipitation and colloidal transport. It assumes steady state and first order kinetics of adsorption and desorption. A complete mixing is assumed to take place within a volume, from which radioactivity is lost by a combination of water exchange, decay and sediment interaction. The simplified model of this process makes use of the distribution factor \( K_d \).

Table 4. Distribution coefficient of natural radioactivity uranium, thorium and potassium.

<table>
<thead>
<tr>
<th>Site</th>
<th>Distribution coefficient of natural radioactivity in Ismailia Canal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uranium-238</td>
</tr>
<tr>
<td>Moustrod (S1)</td>
<td>41.2</td>
</tr>
<tr>
<td>Fertilizer Factory (S2)</td>
<td>32.6</td>
</tr>
<tr>
<td>Inshas (S3)</td>
<td>32.2</td>
</tr>
<tr>
<td>Menayer (S4)</td>
<td>--</td>
</tr>
<tr>
<td>El-Tal el Kebeer (S6)</td>
<td>26.3</td>
</tr>
<tr>
<td>El-Kassassin (S7)</td>
<td>18.4</td>
</tr>
<tr>
<td>Abu Soir (S8)</td>
<td>102.6</td>
</tr>
<tr>
<td>El-Galas (S9)</td>
<td>70.3</td>
</tr>
</tbody>
</table>

Retardation factor was calculated as given in ref [2]

\[ R_t = 1 + K_d \]

From Table 4, the data reveal that the transport of thorium is very slow which indicate that the retardation effect of the sediment is very high. However, in case of uranium and potassium, the transfer of both elements is very fast, while the retardation effect of the sediment to them is very slow. However, in case of thorium the distribution coefficient ranged from 575 to 33.8 while in case of uranium and potassium it is 32.2-102.6 and 50-2453, respectively.

Sediment scavenging is influenced by particulate sedimentation rates and by the distribution of radionuclides between solid and aqueous phases, thus even in this simple case we have need for soil-specific knowledge to incorporate the loss to sediment. In general, compartmental models are widely used in modeling the long-range dispersal of pollutant over long time scale. Because they deal in average concepts for both level and space and are not based directly on the analytical solution of advection-diffusion equation, they require less detail. The transformation of the natural radioactivities was also studied.

References


STUDY OF POLONIUM-210 RADIOACTIVITY IN INDIAN AND GERMAN TOBACCO

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The carcinogenic effect of tobacco is well known to man for years. It is said that besides the chemical carcinogens the radioactive carcinogens play a major role in bringing about significant increase in the incidence of lung cancer [1-3]. In recent years the content of other carcinogens in tobacco have been considerably reduced by employing modified tobacco processing methods and use of modern cigarette filters but these have proved to be of little help in lowering the polonium radioactivity levels.

It is now a well established fact that the naturally occurring uranium series radionuclides contribute significantly to the radiation dose received by man. It has been estimated by the United Nations Scientific Committee on Effects of Atomic Radiation [4] that seven percent of the total effective dose received by man from ingested natural internal radiation comes from one of the members of the above mentioned series: namely the alpha emitting 210Po which is descendent of the beta emitting 210Pb. The polonium isotopes are therefore regarded as one of the most radionuclides.

There have been several estimates of the 210Po content in the mainstream cigarette smoke [5-8] but one can safely presume that nearly fifty percent of the 210Po present in tobacco leaves ends up as smoke, around thirty five percent remains in the butt and approximately fifteen percent ends up as ash.

The main source for 210Po and 210Pb in the atmosphere is the ubiquitous radioactive gas 222Rn. It is presumed that the radionuclide so produced precipitates out with snowfall and rainfall on land surface, plants and in oceans. Tso et al [9] suggested that the tobacco plants enrich this radionuclide as a result of uptake into roots from soil and phosphate fertilizers. On the other hand Francis et al. [10] suggested that deposition of 210Pb by rainfall is the principal mechanism of 210Po entry in plants. Papastefanou [11] in his findings on radioactivity in tobacco leaves states that the properties and distribution of trichomes (hairs) on tobacco leaf surfaces suggest that they are effective collectors of small Aitken (nuclei) particles by means of diffusive deposition due to Brownian motion of the particles. Therefore one can safely state that the long growing time and special leaf hairs present on the big surface of the tobacco leaves play an important role in the 210Po enrichment process.

India is the third largest producer of tobacco in the world. It is estimated that sixty five percent of the men use some form of tobacco either in the form of smoking or chewing or both. India has one of the highest incidences of oral cancers and tobacco related cancers account for almost half of all the cancers among men and one fourth among women.

Singh and Nilekan [12] measured the polonium activity in Indian tobacco way back in mid seventies and found that the Indian tobacco products had 10 to 15 times less 210Po in comparison to the US tobacco products. A number of publications related to 210Po content of tobacco leaves can be found in literature [5,6,8,13-16]. The recent publication of Khater [8] in which polonium level determined in cigarettes from different countries were compared showed that the 210Po level (4 mBq per cigarette) in Indian tobacco is still the lowest in the
world whereas cigarettes from Germany, Japan and France, have the highest respective polonium levels (19-23 mBq per cigarette).

In the present work a comparative study of German and Indian tobacco is reported with a view to find if in the intervening years the modern methods of agriculture have had any effect on the polonium content. The Indian tobacco leaves were procured from Nipani located in the state of Karnataka whereas the German Tobacco was obtained from Bergheim close to Juelich.

Material and methods

10 g of freeze dried tobacco leaves from Nipani in India and Bergheim in Germany were assayed directly using gamma ray spectrometry to estimate the radioactive level in the sample compared to the natural background level. In addition, we investigated stems of the locally grown specimen as well as beedi leaves used in India for wrapping the tobacco instead of using paper along with commercially available tobacco and cigarette samples. Determination of $^{210}\text{Po}$ was carried out in triplicate by leaching it out from 5 g samples by nitric acid, followed by TTA extraction. The extracts were either directly assayed after mixing with scintillation cocktail in our liquid scintillation counter (Guardian 1414, Wallac) or after spontaneous deposition of polonium on a nickel disk using PIPS detectors. The chemical yield was determined by adding known amounts of isotopic Polonium tracer to the sample.

Results and discussion

Measurements in our gamma-ray spectrometer (Canberra-Eurysys) showed no significant differences of the content of $^{210}\text{Po}$ between the tobacco samples and the ambient background during counting times of 24 h. We could not observe activities exceeding background radiation in a significant way.

Typical radiochemical yields of $^{210}\text{Po}$ are $85 \pm 10\%$. In some separations we co-extracted $^{210}\text{Bi}$ along with the polonium for control. Table 1 shows our results for the specimens investigated. Fig. 1. depicts a typical alpha-particle spectrum. Measurement uncertainties are given as one standard error. We cannot corroborate the finding of Khater [8] that German cigarettes contain significantly higher polonium concentrations. Our samples show lower concentrations in $^{210}\text{Po}$ than tobacco samples watered with the effluent of a uranium processing plant as recently assayed in Hungary [17].

It may be noted, that the Indian cigarettes investigated by us contain only ca. 0.7 g of tobacco whereas German cigarettes contain ca. 1g.

We are further investigating our samples with our new ultra-low-level gamma-spectrometer to corroborate our data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{210}\text{Po}$ concentration ( mBq / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bergheim tobacco leaves</td>
<td>5 ± 3</td>
</tr>
<tr>
<td>Bergheim tobacco stem</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>Nipani tobacco leaves</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>Beedi leaves</td>
<td>2 ± 2</td>
</tr>
<tr>
<td>Cigarettes Brand 1 (G)</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>Cigarettes Brand 2 (G)</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>Cigarettes Brand 3 (G)</td>
<td>17 ± 4</td>
</tr>
<tr>
<td>Cigarettes Brand 4 (G)</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>Cigarettes Brand 5 (G)</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Cigarettes Brand 6 (I)</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>Cigarettes Brand 7 (I)</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>Cigarettes Brand 8 (I)</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>Cigarettes Brand 9 (I)</td>
<td>5 ± 3</td>
</tr>
</tbody>
</table>

References


Figure 1: Typical a-particle Spectrum of an investigated sample
STUDY OF AIRBORNE RADIOACTIVITY AROUND OPEN CAST COAL MINES IN JUELICH REGION

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2Panjab University, Department of Chemistry, Chandigarh, India

The study of atmospheric deposition of radionuclides has been a subject of investigation for a number of years [1-4] because of its importance from the point of view of geochemistry and radioprotection. The region of Juelich (52°N 10°E) is surrounded by several open cast lignite mines. Most of the coal excavated is transported to several local thermal power stations which produce some 20% of the electrical energy in Germany.

The mineral coal is known to consist of one percent trace elements and radionuclides and according to the United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR) Report [5] the mean natural radionuclide concentration ranges between 16-110 Bq.kg⁻¹ for ²³⁵U, 17-60 Bq.kg⁻¹ for ²²⁶Ra, 11-64 Bq.kg⁻¹ for ²³²Th and 140-850 Bq.kg⁻¹ for ⁴⁰K.

In the fall of 2003 environmental activists claimed a high risk of cancers caused by airborne fine dust originating from coal mining for its inherent high radioactivity levels. As there were only few data available (measured by the authorities) we started to collect fine-dust fractions and measure their activity. Gross alpha, gross beta and specific isotopic analyses were carried with a view to study the general background radiation level as well as to further investigate the apprehension of local communities. The data are being compared to permissible limits of radioactivity and fine dust concentrations.

The collection of airborne radionuclides was carried out on glass fiber filters using a commercially available high volume air impactor. The samples were collected at two different locations: Niederzissen, the affected town located between two mining sites and near a local freeway, and Juelich located farther away from the mining site. We collected “total dust” samples besides respirable suspended particulate matter with a mean aerodynamic diameter of 10 μm (PM10) according to EN 13284-1. The latter is known to be more injurious to human health. Collection times varied between 10 and 100 h. All samples were collected with a constant flow of 2.3 m³/h.

Dry glass fiber filters were weighed before and after the collection of sample to estimate the amount of suspended particulate matter present in a cubic meter of air. The background radioactivity of each filter paper was determined in advance to ensure that the inherent radioactive level did not introduce any bias to the measured radioactivity level. Typical results for our Low-Level-α-/β-proportional counter (Berthold LB770) are 5 mBq and 25 mBq for α- and β-activities, respectively. These data are consistent with the certified potassium content of the filters.
The samples were counted without any further preparation for a time period ranging between 3 to 100 hours for decay analyses and to determine gross alpha and beta activities. In addition, we counted the samples in our 120 cc HP Germanium detector shielded by 20 mm lead and coupled to an 8K multi channel analyser. Some samples were also measured with PIPS-detectors for α-spectrometric identification of the radionuclides. Data were analysed with Genie 2000 software (Canberra-Eurysis). Some filters were further investigated by microscopy to specify the type of particulate matter.

Results and discussion

The masses accumulated during collection were typically 2.0 – 4.0 mg total dust and for PM10, 0.1-2.0 mg according to concentrations of 30 – 50 µg/m³ and 3 – 30 µg/m³, respectively.

We identified the radionuclides $^{214}$Pb, $^{214}$Bi, $^{210}$Po, $^{212}$Pb, $^{212}$Bi, $^{208}$Tl, along with $^7$Be by gamma-ray spectrometry. In time-resolved alpha-spectrometric measurements we were able to identify $^{214}$Po, $^{210}$Po, $^{211}$Bi, and $^{212}$Po. $^{210}$Po was observed only during the first three hours of counting, $^{210}$Po only in long-term measurements.

These findings were corroborated by half-life analyses using data from our LL-α-β-proportional counter revealing activities with half-lives of 27 min, 61 min, and 10.6 h.

Activities extrapolated to the end of the collection period were similar for the two short-lived radionuclides: 0.2 - 11 Bq, respectively, in the alpha-channel, and 2.5 - 28 Bq, respectively, in the beta-channel. The 10.6 h-activity showed typical initial activities in the range of 1 - 5 Bq (α) and 3.8 – 12.8 Bq (β). The activities tended to be slightly higher during periods of rainfall.

After the decay of these components we could not distinguish the α- and β-activities from the background given by the potassium-content in the glass-fiber filters. Studies with our new ultra-low-level gamma-spectrometer are still being pursued.

The microscopic inspection of the filters revealed a large variety of particle types. The samples of total dust contained a large number of pollen originating from different species as already could be perceived macroscopically by yellowish patterns on the filter.

The concentration of PM10 particles collected is well below the legal permissible limits of 250 µg/m³. However, a new regulation based on European legislation allows to exceed 50 µg/ m³ only 35 times/year. During our sampling period the concentrations have never exceed this limit. The state environmental agency is measuring continuously and publishes the results on their website (www.lua.nrw.de/luft/immissionen/Disko-Immissionen-2003.xla). Our data are in good agreement with data published there.

The radionuclides identified could be shown to be of cosmogenic origin ($^7$Be) or progeny of the radon isotopes $^{220}$Rn and $^{222}$Rn. The activities show some correlation to the mass of dust particles collected, but vary in a small range, only. They can be understood by local (low) concentrations of Radon in the ambient air. Some environmentalists claim that the dust particles originating from coal would absorb and enrich Radon like activated charcoal cannot be substantiated on the basis of our data.
We conclude that fine dust particles with mean aerodynamic diameter of 10 μm (PM10) have been well below legal limits during our sampling period. Their radioactivity resembles the ambient Radon concentrations which are low in the region around Juelich.

References


OPTIMIZATION OF ELECTROCHEMICAL SOIL DECONTAMINATION

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Introduction
The operation or malfunctions of nuclear facilities and development or testing of nuclear weapons caused environmental contamination by fission nuclides at many places all over the world. Remediation and/or decontamination procedures are necessary for the restoration of the environment. The treatment processes for the contaminated soils can be divided into two categories. The first one is “in situ” decontamination and it is used mainly for remediation of large areas. The second category groups techniques for treatment of soil, that has been removed from its original location, in special treatment devices [1]. These techniques are used namely for high active soils from localized contaminations, such as those from the Jaslovske Bohunice nuclear power plant (NPP), where some leaks from liquid waste tanks occurred in 1977 and fission products, mainly caesium-137, contaminated the neighbouring soil. Several decontamination procedures were described for treatment of such soils - classic leaching, soil fractionation, biological methods (e.g. phytoextraction), thermochemical and electrochemical (electrokinetic or electrolytic) methods [1].

At the Czech Technical University in Prague, soil decontamination techniques have been studied for several years. The leaching procedures (batch or “sorption” leaching) [2,3] did not allow to achieve more than 30% caesium desorption. Caesium thermodesorption was demonstrated not to be very efficient either; quantitative caesium separation could be achieved only from solutions resulting from fusion of the soil with special fluxes [3,4]. The most promising results were achieved by electrolytic decontamination. In preliminary experiments [5], more than 97% of caesium was released from soils contaminated long time ago. The aim of this study was to perform optimisation of the parameters of this method.

Experimental
Soil samples with specific activities ranging from 700 to 900 Bq/g from Jaslovske Bohunice NPP waste storage depots were used for the experiments. These soil samples had a relatively high content of caesium adsorbing minerals; their average mineralogical characteristic is given in Table 1. Caesium speciation in the soil was obtained by Tessier’s sequential leaching method and it showed that almost 83 wt% of caesium is not leachable and it is bound inside the crystalline detritus of soil minerals [2].

Before the electrolysis, the soil was dried and homogenized. Then, a small quantity of the soil (about 3 g) was treated in an electrolytic cell consisting of a glass crucible with porous glass frit bottom. This frit enabled the necessary ion migration and supported the soil in the vicinity of the anode. The anode electrode was placed as close as possible to the soil surface, to enable
the action of the aggressive environment on the soil and agitation or even suspension of the soil in the electrolyte by the electrolytic gases.

Table 1: Exception from the mineralogical composition of the studied soil samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Illite</th>
<th>Kaolinite</th>
<th>Chlorite</th>
<th>Plagioclase</th>
<th>Orthoclase</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content wt%</td>
<td>13-23</td>
<td>2-4</td>
<td>2-4</td>
<td>7-11</td>
<td>5-16</td>
<td>4-10</td>
</tr>
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</table>

During the method optimisation, influence of the following parameters was studied: current, type of electrolyte, and regime of the electrolysis. As the electrolytes, 0.5 molar solutions of ammonium phosphate and phosphoric acid, distilled water, ammonium chloride with hydrochloric acid, or ammonium carbonate were used. The basic experimental process was carried out in batch mode without electrolyte exchange. The soil was always electrolysed for several (5-10) hours, then the glass crucible with the soil was drained, dried, and measured by γ-ray spectrometry; from the soil activity decrement, the level of decontamination was calculated. Each treatment run lasted for 35 - 50 hours of the net electrolysis time. During the treatment, any losses of the electrolyte were compensated for only by refills of distilled water. Platinum anode and stainless steel cathode were used.

Results and discussion
The results obtained for different electrolysis parameters are compared in Fig.1. It can be seen that the decontamination level depends significantly on the current used. When the electrolysis current is increased, the amount of caesium released increases and also the decontamination accelerates (compare the curves in Fig. 1A for 0.5, 1, 1.5 A, and the resumption curve, where the current was elevated to 1.5 A after the end of electrolysis at 1 A). However, from the practical point of view, higher currents cause problems with precipitation of the low soluble salts of the major soil elements, and also, potentially, problems with cathode instability.

Fig.1: Dependence of the total caesium desorption on the electrolysis time or energy input into the system.

The next parameter tested was the change of the decontamination efficiency with the electrolyte exchange. The exchanges were found to suppress the precipitation; they also enabled the study of the course of the caesium (or soil elements) release. However, no noticeable effect on the decontamination efficiency was observed (cf. Fig. 1A, curves 1 A and 1 A-exchanges).
The influence of soil relaxation between two successive electrolysis steps was also tested. The soil was electrolysed for 32 hours without interruption at 1 A current, the results were compared with a standard experiment performed also at 1 A. For better estimation of the influence of soil relaxation, the sample from continuous treatment was electrolysed 3 times again after 14, 7, and 20 days relaxation in dry state at room temperature. The results show (cf. Fig. 1A, curves 1 A and 1 A-continuous), that the decontamination process is significantly influenced by breaks between the successive electrolysis steps. It is supposed that this effect is caused by caesium speciation re-distribution during the relaxation period.

In Fig.1B, the caesium desorption curves are re-drawn relative to the energy input into the system to show whether the above discussed effects should be ascribed to the current used or the energy input. It can be seen that it is not only the overall energy input, but also (to some extent) the rate of its delivery - i.e. the current - that determines the efficiency of the decontamination process. The results obtained at 1 A (any electrolysis mode) and at 1.5 A do not differ dramatically. However, at a low current, the decontamination is much less effective (see Fig. 1B). The plausible explanation of this effect is connected with the decrease of the "in statu nascendi" electrolytic products concentration in soil caused by their slower transport from the anode to soil and also by lower electrolytic gases production - soil agitation. In the experimental set-up used, the energy needed for the release of 99% of caesium is about 300 Wh/g at the electrolysis current of 1 A or higher.

Conclusions
The experiments demonstrated high efficiency of the electrolytic decontamination of soils contaminated long time ago. Further optimisation will be required before scaling up the procedure.

References
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A SYSTEMATIC STUDY ON CESIUM SORPTION ON A SEDIMENTARY ROCK TOWARDS RELIABLE SAFETY ASSESSMENT METHODOLOGY FOR HLW DISPOSAL

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There is a demand to ensure the reliability of high level radioactive waste (HLW) repository technology and establish safety assessment methodology in Japan. The Horonobe underground research laboratory (Horonobe URL) is one of the facilities under construction to meet the demand, and the aim is to study the subsurface environment in sedimentary rock[1], one of the potential host rocks for the disposal in Japan. To match the demand, a sorption study is making a small step toward establishment of reliable safety assessment methodology for HLW Disposal. Being linked to site-specific conditions, a systematic sorption study on cesium, one of the key radionuclides in the safety assessment, was conducted on the sedimentary rock from cores of borehole drilled at the site of the Horonobe URL. It included characterization of the sedimentary rock and groundwater from the same borehole, batch sorption tests with various parameters, and analysis of the sedimentary rock after the sorption tests with multi-analytical techniques. Such a systematic study allowed a mechanistic understanding and provided fundamental data for eventually modeling prediction of the sorption in a sedimentary rock/saline groundwater environment based on the groundwater chemistry and rock mineralogy.

The sorption tests were conducted to the sedimentary rock samples (SRS) and three aqueous phases, including deionized water (DIW), natural ground water (NGW) and synthetic groundwater (SGW), under various parameters in a low-oxygen glove box. The SRS were classified as group A, B, C, and D, according to depths of core. Characterizations of the SRS included mineralogy and some important physicochemical properties for sorption. Major minerals were identified to be quartz, feldspars, clay minerals, carbonates, pyrite and trace of other unknown minerals. Clay minerals were determined mainly to be smectite, illite, chlorite, halloysite, somewhat muscovite and kaolinite. Chemistry of the SGW was modeled thermodynamically by geochemical
computer code (PHREEQC) with JNC-Thermodynamic Data Base (JNC-TDB)[2], based on the major chemistry of the NGW, except for the content of organic matter. The parameters investigated were time, pH, liquid-solid ratio (L/S), organic matter, initial concentration of Cs, [Cs\(^+\)], and ionic strength.

The distribution coefficients, \(K_d\), were determined at equilibrium. No significant pH dependence of the \(K_d\) values could be observed. Values of \(K_d\) at high L/S (500 mL/g) showed several times higher than that at relative low L/S (50, 5 mL/g), but no significant difference at the low L/S. The \(K_d\) values decreased with increase of [Cs\(^+\)], as shown in Fig.1, suggesting the existence of heterogeneous sorption sites and saturation of these sites. Additionally, no significant difference in the \(K_d\) value was observed between the SGW case and the NGW case. This suggested less effect of organic matter. Since the major difference in the chemistry of the SGW and the NGW was that no organic matter was present in case SGW, but 52.8 mg/L TOC in case NGW.

![Graph showing distribution coefficients of Cs on sedimentary rock as a function of the initial concentration of Cs, at various ionic strengths (I\(_{\text{DIW}}\)=0.003, I\(_{\text{SGW}}\)=0.41).](image)

Large effect of ionic strength on the sorption is obvious. The \(K_d\) values in case SGW were in the range of 0.01~0.55 m\(^3\)/kg, one order of magnitudes lower than that under DIW’s. Ionic strength in the former, \(I_{\text{SGW}}\), was 0.41, more than two orders of magnitudes higher than that in the latter, \(I_{\text{DIW}}\), 0.003. These data suggested that sorption competition was significant between Cs\(^+\) and major cations at higher ionic strengths. For further discussing the competition, sorption was conducted in solution containing
one of the four major cations, NH$_4^+$, K$^+$, Na$^+$, and Ca$^{2+}$ at the same ionic strength. The descending sequence of the competition was found to be NH$_4^+$ > K$^+$ > Na$^+$ > Ca$^{2+}$.

Clay mineral, illite in the sedimentary rock, was founded to be a key mineral affecting the Cs sorption at higher ionic strength. In case of DIW, values of $K_d$ for group A were obviously lower than the others, possibly due to relevant low contents of smectite, which has been confirmed in the characterizations of sedimentary rock. However, as shown in Fig.1, the difference in $K_d$ values among the groups became insignificant and tended to be a similar value for each group in case of SGW. This revealed that although both smectite and illite were important for the sorption at lower ionic strength, only illite was essential to sorption at higher ionic strength. Illite showed high affinity to Cs even at high ionic strength, while smectite became less important, because of easier desorption of Cs on it. It was further proved by the analyses of the SRS after the tests with EPMA and SEM/EDS techniques. Selective and aggressive sorption of Cs on illite under SGW condition was observed, as illustrated in Fig.2.

![typical_sem_images](image_url)


Fig.2. Typical SEM images, showing the selective sorption of Cs on illite.

The conclusions were that the ionic strength as well as the competitive cations and illite were the key factors affecting Cs sorption at higher ionic strength. With the data sets and results obtained in the present study, modeling prediction will be conducted based on sorption on illite by ionic exchange mechanism, as a step from laboratory towards site for establishing the reliable safety assessment methodology. Comparison between the measured data and the results predicted by the model will be also presented.

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   Extended Abstracts of Papers presented at the Sixth International Conference on
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   ISBN: 3-89336-362-9
This book contains extended abstracts of papers presented at the 6th International Conference on Nuclear and Radiochemistry (NRC 6), held from 29 August to 3 September 2004 in Aachen, Germany. It comprises in a compact form some of the recent advances in all branches of this broad and interdisciplinary field. An account of fundamental studies on nuclear reactions, actinides and transactinides is followed by a description of recent developments in radioanalytics and nuclear technology. The applications of radiochemistry in both energy and non-energy related research areas are discussed, with particular reference to nuclear fuel cycle, life sciences, geological and environmental sciences, and industry.