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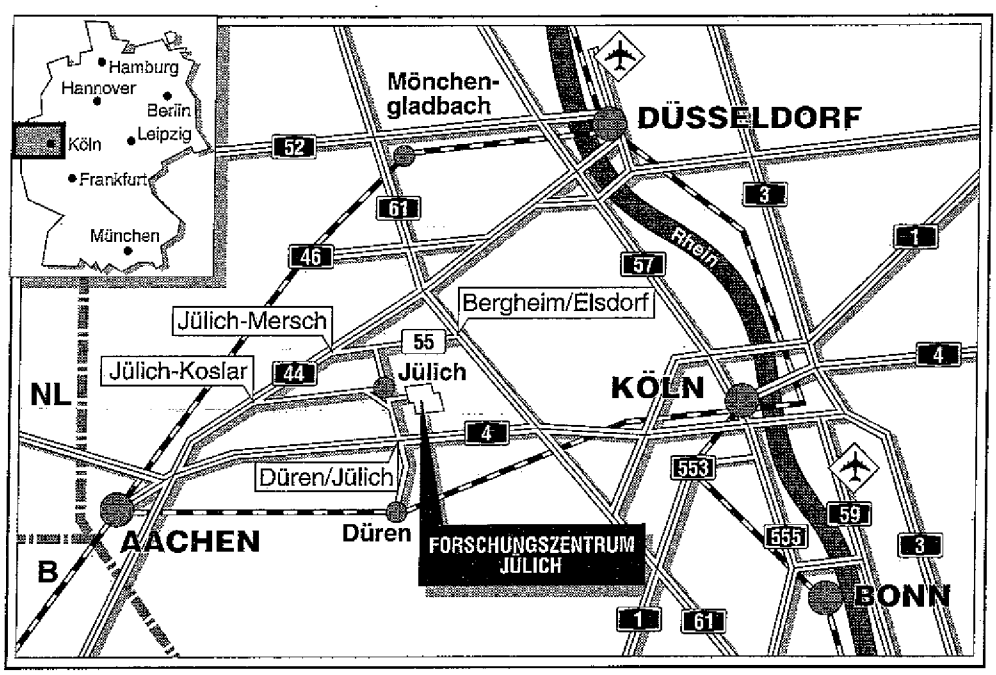
Applications of Instrumental Neutron Activation Analysis in the Analytical Division of the Research Center Jülich (KFA)

Gerhard Erdtmann



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Gerhard Erdtmann

Manuscript of an Invited Lecture at the International Workshop on Neutron Activation Analysis in Dubna/USSR, September 18-20, 1990

Anwendungen der Instrumentellen Neutronenaktivierungsanalyse in der Zentralabteilung für Chemische Analysen des Forschungszentrums Jülich (KFA)

Gerhard Erdtmann

Kurzfassung

Die Abteilung Radiochemische Analytik hat, als Teil der Zentralabteilung für Chemische Analysen, die Aufgabe, Analysenverfahren für den Bedarf des Forschungszentrums KFA zu entwickeln und im Analysenservice für die Institute und für Kunden außerhalb des Zentrums einzusetzen. Dabei werden ausschließlich nukleare Analysenmethoden angewendet. Der größte Teil der Analysen sind Spurenelementbestimmungen mit Neutronenaktivierungsanalyse, wobei der Forschungsreaktor FRJ-2 als Bestrahlungsquelle benutzt wird. Das Verfahren für die Instrumentelle Aktivierungsanalyse wird beschrieben und vor allem praktische Aspekte werden detailliert dargestellt. Es handelt sich um ein Absolutverfahren, bei dem die Analysenergebnisse aus den Peakflächen der γ-Linien, den Neutronenflüssen und aus k_0- und Q_0-Faktoren, wie sie von Simonits, De Corte et al. gemessen worden sind, berechnet werden. Eine neue Variante mußte entwickelt werden, nachdem ein anderes Verfahren zur Analyse der γ-Spektren eingeführt worden war, das eine bessere Ausnutzung der Information in überlagerten Linien ermöglicht. Dabei erhält man anstelle der einzelnen Peakflächen die absoluten Zerfallsraten der Radionuklide. Diese neue Variante des Analysenverfahrens wird ebenfalls beschrieben. Einige Beispiele von Analysen, die in letzter Zeit im Analysenservice ausgeführt wurden, werden dargestellt und vor allem im Hinblick auf die Richtigkeit der Ergebnisse und die erreichbaren Nachweisgrenzen diskutiert.

Applications of Instrumental Neutron Activation Analysis in the Analytical Division of the Research Center Jülich (KFA)

Gerhard Erdtmann

Summary

The Radioanalytical Chemistry Section, as a part of the Central Division of Chemical Analysis of the Research Center KFA Jülich, has the task to provide and to apply nuclear methods in the analytical service for the institutes and projects of the KFA and to customers outside. A great part of this service is trace element determinations by neutron activation analysis using the research reactor FRJ-2. The procedure for the instrumental technique is described and mainly practical aspects are reported in detail. It is based on the k_0-method developed by Simonits and DeCorte. The results are calculated from the peak areas of the γ-lines and the corresponding k_0-factors. A new variant of this procedure is required, if the program used for the deconvolution of the γ-spectra provides absolute decay rates of the radionuclides instead of the γ-emission rates. This variant is also described. Some examples of analyses carried out in the analytical service are presented and discussed mainly with respect to accuracy of the results and detection limits.

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1. The place and the task of the Central Division of Chemical Analysis (ZCH) in the Research Center (KFA).

The KFA is one of the large research centers in the Federal Republic Germany. It has about 4.500 employees. The research profile ranges from basic research to applied research and includes with some projects also cooperation with industrial firms. The fields of research are

- nuclear and non nuclear energy research
- health and environment
- biotechnology
- information science and technology
- materials research and properties of matter
- nuclear fusion and plasma physics
- basic nuclear research and
- general methods of science and technology.

In this last field, chemical analysis is included.

The research center consists of about 40 scientific institutes and about 10 central divisions. The latter are intended for the development, construction and maintenance of the experimental equipment of general importance such as the research reactor (FRJ-2), the large computers (2 × IBM 3081, CRAY X-MP/22, CRAY X-MP/48) and also chemical analysis is one of these central divisions. It has to carry out analyses for all other institutes as far as they cannot do it in their own laboratories. Presently the institute is mainly engaged in analyses of materials (high- temperature resistant alloys and ceramics, high-purity and semiconductor materials), of products from biotechnological experiments and of samples for geochemical research. The institutes occupied with environmental research are usually well equipped with appropriate analytical methods, so that only a small part of such analyses are carried out in the ZCH.

The ZCH has about 35 employees. It operates a great number of different analytical methods and instruments and with every new inquiry for an analysis, with every new analytical problem, it has to be decided, which of the methods

can be optimally applied. There are several other instrumental multielement methods of trace analysis, e.g. XRF (X-ray fluorescence spectroscopy, including total reflection XRF), OES-ICP (optical emission spectroscopy with inductively coupled plasma), MS-ICP (mass spectroscopy with ICP), and SS-MS (spark source mass spectroscopy), which are in competition with activation analysis.

The Radiochemical Analysis Section is a part of the ZCH with presently a staff of 6 people. The largest share in the work is devoted to activation analysis. It is, at the present time, preferably carried out by neutron activation techniques using the research reactor FRJ-2. Since such powerful research reactors are operated only in a few places in Germany, inquiries for analyses are received also from industrial firms, universities and scientific research institutes outside the KFA. For charged particle activation analysis (CPAA) a compact cyclotron with high currents at variable energies for protons, deuterons, ^{3}He- and ^{4}He-ions with a pneumatic tube to one of our laboratories can be used.

According to the large diversity of the research projects very different analytical problems have to be solved. Thus, the work is mainly characterized by the large variety of sample types, each requiring an own schedule of sample preparation and irradiation procedures. Small series of 1 to 5 samples have to be analyzed besides of larger series of some dozens up to a few hundred samples. In order to come up with such a complicated spectrum of tasks with a very limited number of personal staff it was necessary to introduce a widely automated and generally applicable, but versatile and flexible procedure of instrumental neutron activation analysis.

2. The analytical procedure

2.1 Basic considerations

The first idea was, many years ago, to introduce Girardi's single comparator method.[1] However, the large number of irradiation facilities with different neutron flux densities and flux spectra at our research reactors (the MERLIN reactor was still in operation at that time) made it a tremendous task to meas-

ure the analytical factors (single monitor constants) for all elements, for all irradiation facilities and positions, and for all detectors and their counting positions.

Therefore, as an interim solution, we applied an absolute method as well as the direct comparator method using home made single element standards or multielement reference materials as standards. The absolute method was, due to the lack of accurate nuclear data and because the neutron fluxes and spectra were not well known for the various facilities, not very accurate and could be used only for semiquantitative analyses. The reservations and objections against the use of reference materials as standards are often discussed and must not be recapitulated here. But also practical limitations make the direct comparator method ineffective. The most striking ones are

- Sample and comparator are enclosed in different vials and receive somewhat different fluxes during irradiation, which may lead to errors.

- The preparation of single or multielement standards is time consuming and, because of the many preparation steps, susceptible to mistakes

- Many elements in the reference materials are not certified or even not analyzed. Therefore, these materials are not useful for a true multielement method.

At that time we became aware of two inventions and developments made at the University of Gent, described by Simonits et al.[2,3] The first one was the introduction of analytical factors for activation analysis, the k_0-factors, which were generally valid, i.e. they could be applied with all nuclear reactors and all irradiation facilities for thermal neutron activation. This was possible by treating separately the contributions of thermal and epithermal neutrons. They also provided a set of equations which easily could be converted into a computerized and largely automatic procedure for the calculation of the analytical results.

It has to be admitted, that monostandard methods had been developed also by other groups, e.g. by Kim and Born [4] in Munich, but the great merit of

DeCorte and Simonits is, that they have measured accurate k_0-factors and the pertinent Q_0-values for nearly all elements important with neutron activation analysis.[5]

The other good idea from Gent was the introduction of zirconium as a double neutron flux monitor, i.e. for the simultaneous measurement of the thermal and the epithermal flux.[3] This work, done at Gent and Budapest, was the basis for the development of the instrumental neutron activation analysis procedure presently used for single and for multielement determinations in our laboratory.

2.2 The practical approach

The procedure is shown in the following list. For some of the steps we have developed apparatuses or procedures to facilitate or to automatize their execution and to make them more reliable.

PROCEDURE FOR INAA

Preparation, Irradiation, and Counting

Purification of sample containers

According to sample size and shape, the trace element levels to be determined and the irradiation conditions to be used (flux and time), different containments for samples are chosen. Most often used are polyethylene vials, graphite screw cap vials, ampoules from high-purity synthetic vitreous silica (quartz ampoules), and high-purity aluminium foils. The last ones are cleaned by short etching with nitric acid and rinsing with high-purity water. Graphite vials are rinsed with high-purity water and dried. PE-vials and quartz ampoules with large inner widths are soaked in hot nitric acid and rinsed with high-purity water. Quartz ampoules with small inner diameters (<6 mm) cannot be cleaned by this procedure, since, because of the surface tension and of the gas and steam bubbles produced during heating, the liquids used for cleaning will not or only partially enter the tubes and the inner walls are not completely wetted and cleaned. Therefore a rinsing machine has been built for automatic cleaning sets of 20 ampoules in one run .[6] A sketch of it is shown in Fig. 1.

Preparation of samples

powder samples: weighing into PE-vials, quartz ampoules or graphite vials

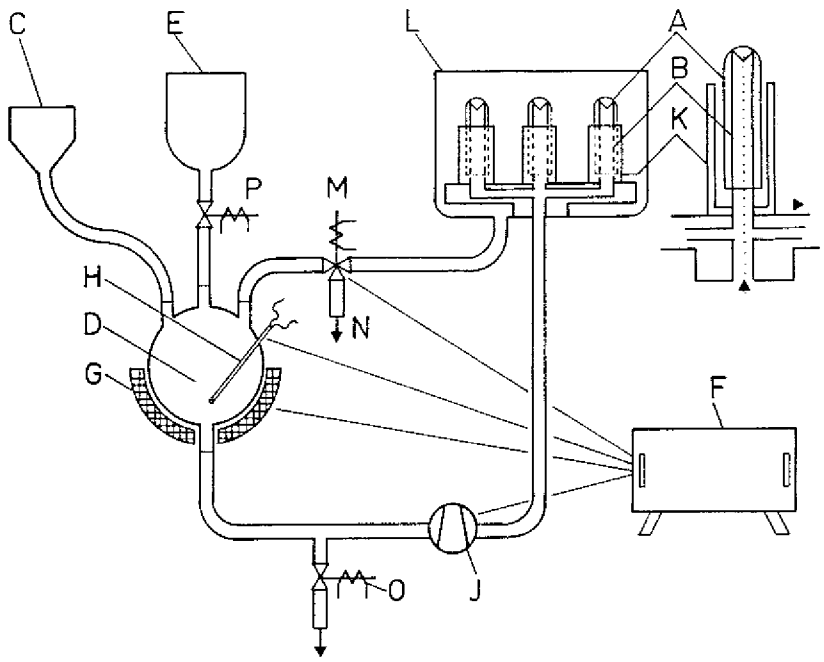

Fig. 1 - Apparatus for cleaning quartz ampoules

Ampoules A are placed on the rinsing nozzles B Via funnel C 500 ml conc. nitric acid are filled in the round flask D Vessel E is filled with 1000 ml high-purity water. The control unit F is started It controls all further functions At first the acid is heated to 95 °C (heating jacket G, thermocouple H). Then pump J is started It drives the acid through the nozzles B and the ampoules A The rinsing tubes K are filled so that the outside walls of the ampoules are also cleaned. The overflowing acid is collected in the vessel L and flows via the three-way valve M in the flask D. Here it is warmed up again and then recycled by the pump J. After 3 min rinsing time valve M is switched so that the acid flows via N to a waste container After another minute pump J is switched off and valve O is opened so that the acid which is still in the flask D, in the pump and in the pipes can flow off to the waste. Now valve O is closed and valve P is opened as long as 500 ml of the water need to flow in the flask D Here it is heated and then pumped through the ampoules. It is not recycled but flows directly via the valve M in the waste By opening valve O also the last residues of water are let off. Finally the second 500 ml water are pumped through the ampoules and the cleaning tubes K, but they are not heated
The flask D, the funnel C and the vessel E are made from quartz glass, tubings are from Viton®, the pipes, the valves, the vessel L with its inserts and the centrifugal pump J are made from PTFE The valves M, O and P are magnetically controlled

compact samples: etching and wrapping in high pure Al-foil or sealing in large PE-vials or quartz containers.

Preparation of flux monitors

In most cases zirconium is used, because the thermal and the epithermal flux can be determined with one single monitor. Another advantage is the low activation cross section of Zr, so that amounts of a few milligrams of wire, which can be accurately weighed with a microbalance, can be used even if high neutron fluences have to be measured. Furtherly, we often want to measure only long lived nuclides, and samples are very active with "short lived" nuclides, like ^{24}Na, and cannot be handled for some days or even weeks. During this time

^{198}Au, which is the usual monitor with the k_0-method, would have been decayed. Another disadvantage of gold is the high burn-up of ^{198}Au during long irradiation periods.

Zr-wire is weighed and packed in a separate container or, if contamination of the sample is negligible, placed inside the sample vial. Zr-foil can be used if low neutron fluences shall be applied and larger amounts of zirconium are required. ZrO_2-powder placed in a separate vial can be useful as monitor with powder samples. It has to be checked for stoichiometric zirconium content.

Filling in the "request for irradiation" form

The reactor operator has to be informed, what types of samples shall be irradiated, what type of containment is used and how long and at which flux they shall be irradiated. Several control boards have to be informed on the species and the activities of the radionuclides produced in the samples as well as in the packing material. To make faster and to simplify the calculation of expected activities for samples of complex composition a computer program (ABBA, "**A**ktivitäts**B**erechnung für **B**estrahlungs**A**nträge") has been developed.

Irradiation

The samples are irradiated together with flux monitors. According to sample types different arrangements can be used. Some are shown in Fig. 2 which also shows the flux gradients in the capsules of two of our irradiation facilities.

With the research reactor in Jülich we mainly use irradiation facilities with high fluxes and temperatures of more than 100 °C. Therefore, polyethylene vials, can seldom be used for packing samples. Quartz vials made from synthetic silica are most often used. The ampoules cannot be filled up to the top, because the heat produced during sealing would destroy the samples. If the ampoules are irradiated in a horizontal position, the distribution of the sample powder in the ampoules is uncertain and accordingly the fluxes cannot accurately be determined. This drawback can be avoided with screw cap or snap cap vials, which can be filled up to the top. Many types of samples can be placed in screw cap vials made from graphite. We use high pure spectral coal as it is used for electrodes in analytical emission spectroscopy. Such containers are shown with the example on the bottom of Fig. 2. If contamination of the sample is not suspected, the zirconium wire can be placed inside the sample and be taken out after irradiation to be measured separately.

If the samples all have the same shape, such as the aluminium disks shown in the middle of Fig. 2, then several flux wires can be distributed in the capsule and the flux for each sample be interpolated.

Waiting for decay

if disturbing short-lived nuclides are present

Unpacking of samples

The unpacking of samples and flux monitors cannot be done automatically, be-

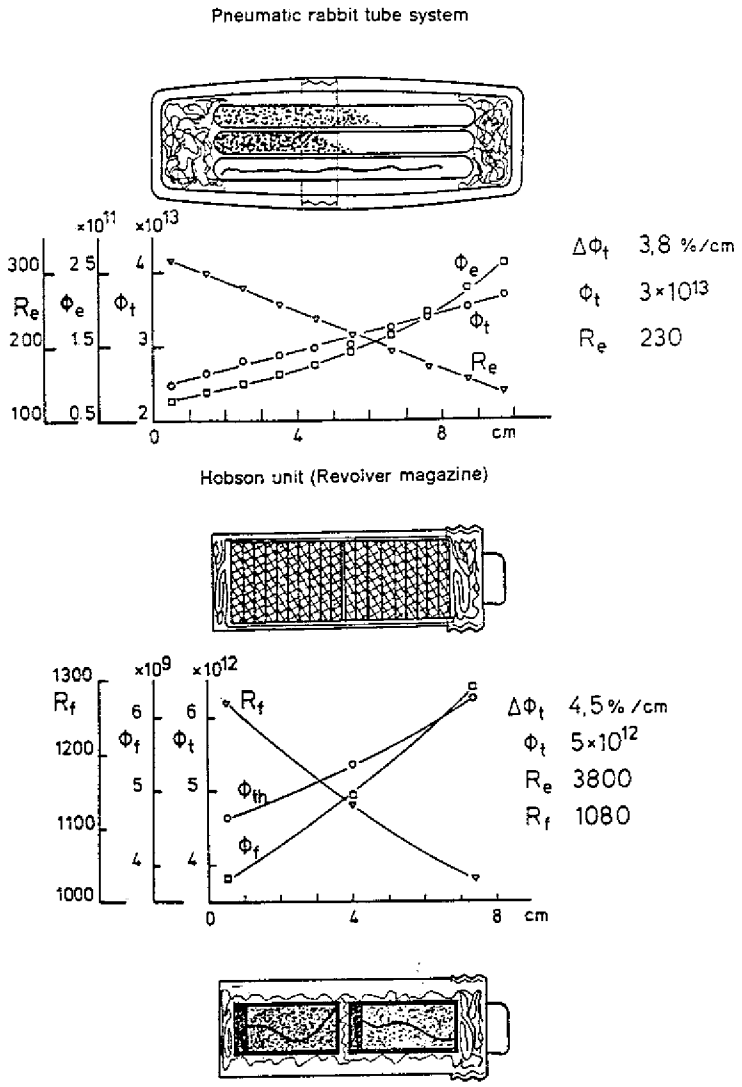

Fig. 2 - Containers for two irradiation facilities of FRJ-2 and flux gradients.

In both facilities the capsules are irradiated in horizontal position, so that when powders are irradiated in quartz ampoules (example on top of figure) the true shape and the situation of the samples are uncertain and the flux measured by a wire in a neighbouring ampoule is somewhat different from that in the sample. With the capsule shown on the bottom, screw cap or snap cap vials have been used. They can be filled up to the lid so that shape and situation of the samples are fixed. In this example, flux wires are placed inside the samples and removed and separately measured after irradiation. Such a procedure is admissible if contamination of the sample by the flux wire is negligible.) In the middle of the figure a set of disk shaped samples is shown as it was used with the analysis of VLSI aluminium Flux wires are placed at the bottom, in the middle and at the top of the stack., so that the flux can be interpolated for each disk. Under the capsules the flux distributions are shown: With the rabbit of the pneumatic system the thermal (Φ_t) and the epithermal (Φ_e) flux and with the Harwell capsule of the Hobson unit (revolver magazine) the thermal and the fast flux (Φ_f). $R_e = \Phi_t/\Phi_e$, $R_f = \Phi_t/\Phi_f$, $\Delta\Phi_t =$ mean thermal flux gradient.

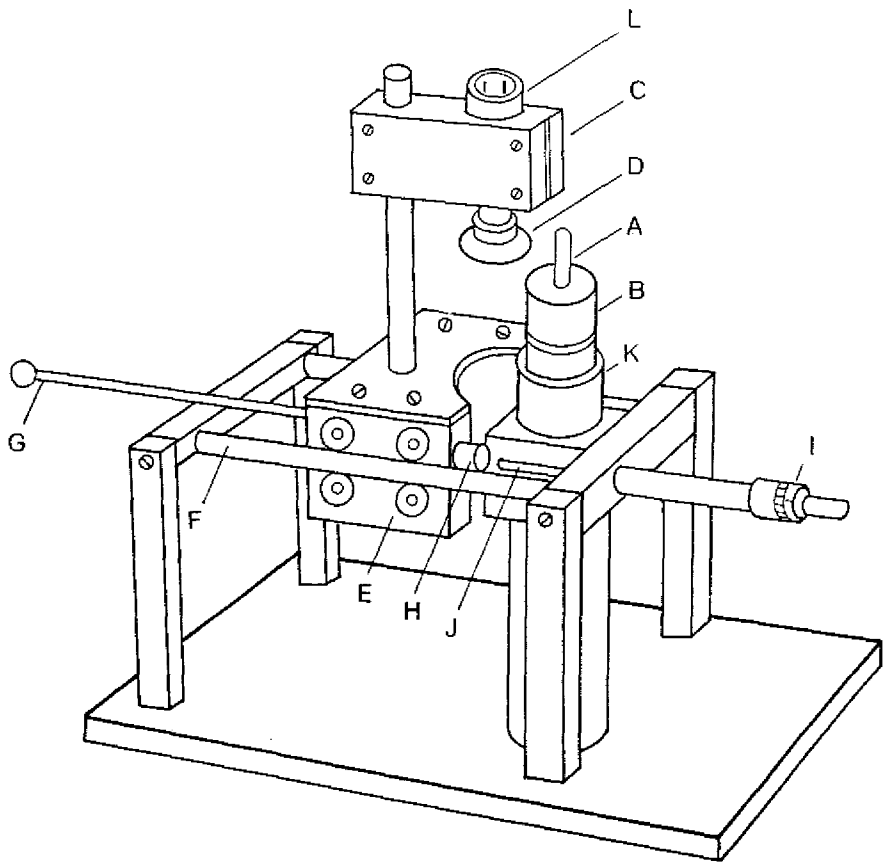

Fig. 3 - Diamond saw for opening irradiated quartz ampoules.

The opening machine is placed in a plexiglass box (not shown in the figure), the lid of which is closed during operation. The quartz ampoule A (usual size 6 mm diameter, 40 mm long) is fixed in the support B. The holder C is adjusted in height so that the saw D is 3 to 5 mm below the top of the ampoule. Then the box is closed and all further operations are done from outside. The cart E carrying the diamond saw can be moved along the rail-bars F by the push-rod G. H is a permanent magnet The micrometer screw I is adjusted so that the saw is about 1 mm from the ampoule when the magnet touches the bar J of the micrometer screw. The current is switched on, motor K slowly turns the ampoule clockwise and motor L fastly turns the diamond saw counterclockwise. The micrometer screw is slowly turned and moves the cart, which is magnetically fixed to its bar J, so that the saw reaches the ampoule. It is sufficient to cut a groove around the ampoule and the cap can be broken off by a grip (not shown in the figure) which also is handled from outside. In this way it is avoided that quartz dust from the saw comes into the sample. If an ampoule is under pressure then the sample powder may be ejaculated during opening or the ampoule explodes during sawing Such a sample is lost and the machine, but not the laboratory, is contaminated. Usually the box and the machine can be cleaned with a small vacuum cleaner, at least after some days, when short lived nuclides have decayed.

cause usually each sample has to be inspected if it is unbroken. We have built small mechanical devices for opening the irradiation vials. The machine shown in Fig. 3 is used to cut quartz ampoules in a closed box. In case that the ampoules explode during opening due to high pressure built up as a result of decomposition of the sample by heat or radiation or because of the generation

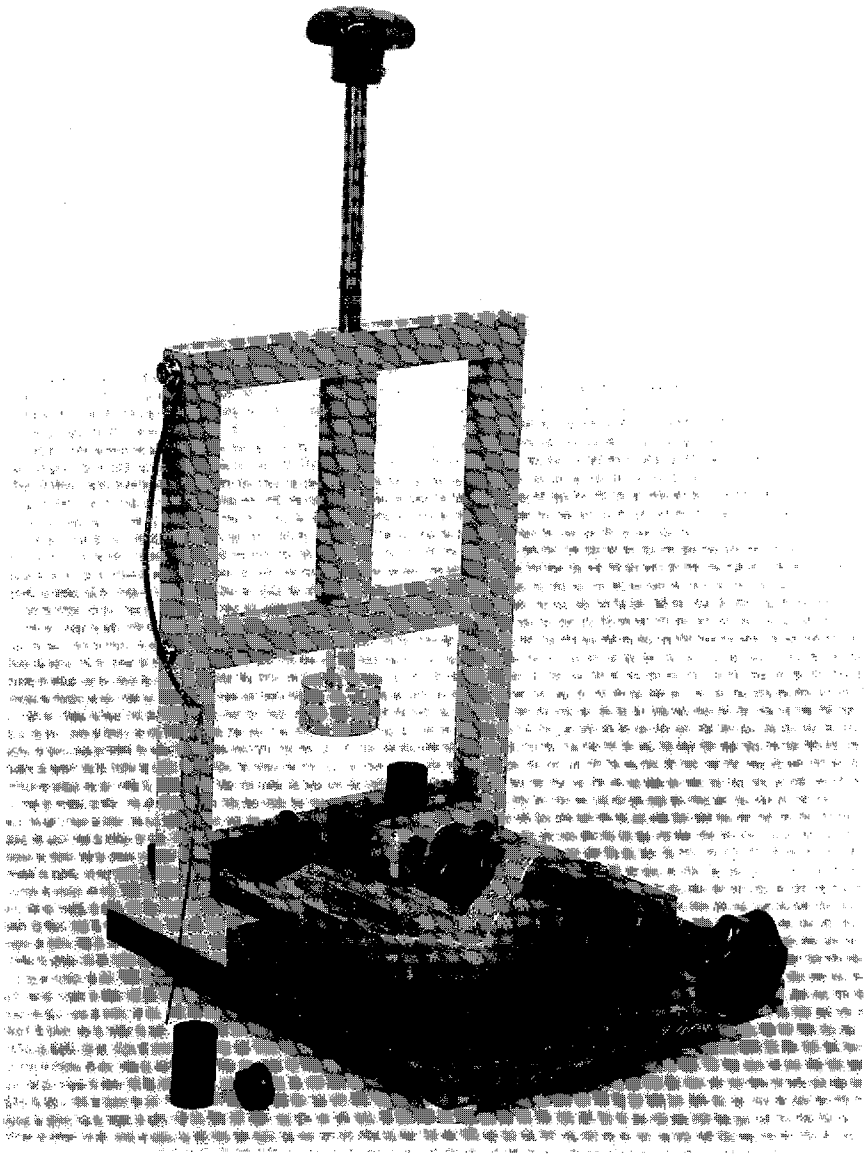

Fig. 4 - Device for opening screw cap vials.

The opening of irradiated screw cap vials by means of forceps and tongs is not very safe. Sometimes, samples are lost and the working place is contaminated The device provides much more safety and less radiation exposure to the operator

The graphite vial A is clamped in vice C. Then it is moved under the turnable rod D, which has at its lower end a metal cylinder E containing a rubber clutch. The rod is moved downward until the clutch grips the lid B of the vial (in the photo, the lid is scarcely to be distinguished from the body of the vial; an opened vial is shown aside). Then the rod is turned counterclockwise to screw off the lid

of an explosive mixture of hydrogen and oxygen, the box retains dust and splinters and prevents the working place from becoming contaminated. In Fig. 4 a device for opening graphite vials with screw caps is shown.

After unpacking samples are transferred to counting trays or vials. If the amounts of elements to be determined are in the range of 1 μg or above, unpacking is usually not necessary and samples can be measured in the irradiation containers after they have been cleaned outside with warm, concentrated nitric acid.

Placing samples for counting on a γ-ray spectrometer.

A calibration sample, the flux wires and the samples are measured in arbitrary sequence with the γ-ray spectrometer. An automatic sample changer can be used, which is controlled by the central computer of the γ-ray spectrometer system. These sample changers have been developed and built in the ZCH.

Selection and start of the counting procedure

We normally use 8000 channels to cover an energy range from 0 to 2000 MeV; lines of higher energy have only exceptionally to be considered.

To apply an automatic counting procedure controlled by the central computer (μVAX-II with operating system VMS) one has to

- enter a code name for the sample series
- select a counting position (sample - detector distance) and
- select the counting (life) time

When the procedure is started, the sample is moved from the storage plate of the automatic sample changer to the counting position, the analyzer is started and stopped when the counting time is elapsed. Then a file for this spectrum is opened in the VMS system. The file name consists of the series code name and a number for each spectrum. The file name and appertaining data like clock time, counting time, percentage life time, and counting position are the first data to be stored in that file. Then follows a list of the counts per channel. The file is closed but will be reopened later during the evaluation procedure. The measured sample is sent back to the storage and a new one is transferred to the counting position.

Evaluation

When all measurements are done, the operator has to start a "computer session".

Data input

At first, the required data for each sample and flux monitor (sample name, weight, and time of irradiation end) have to be entered.

Calibration

For calibration several ^{152}Eu solutions are provided with different volumes and shapes according to the sample types most often to be met with. The data of the

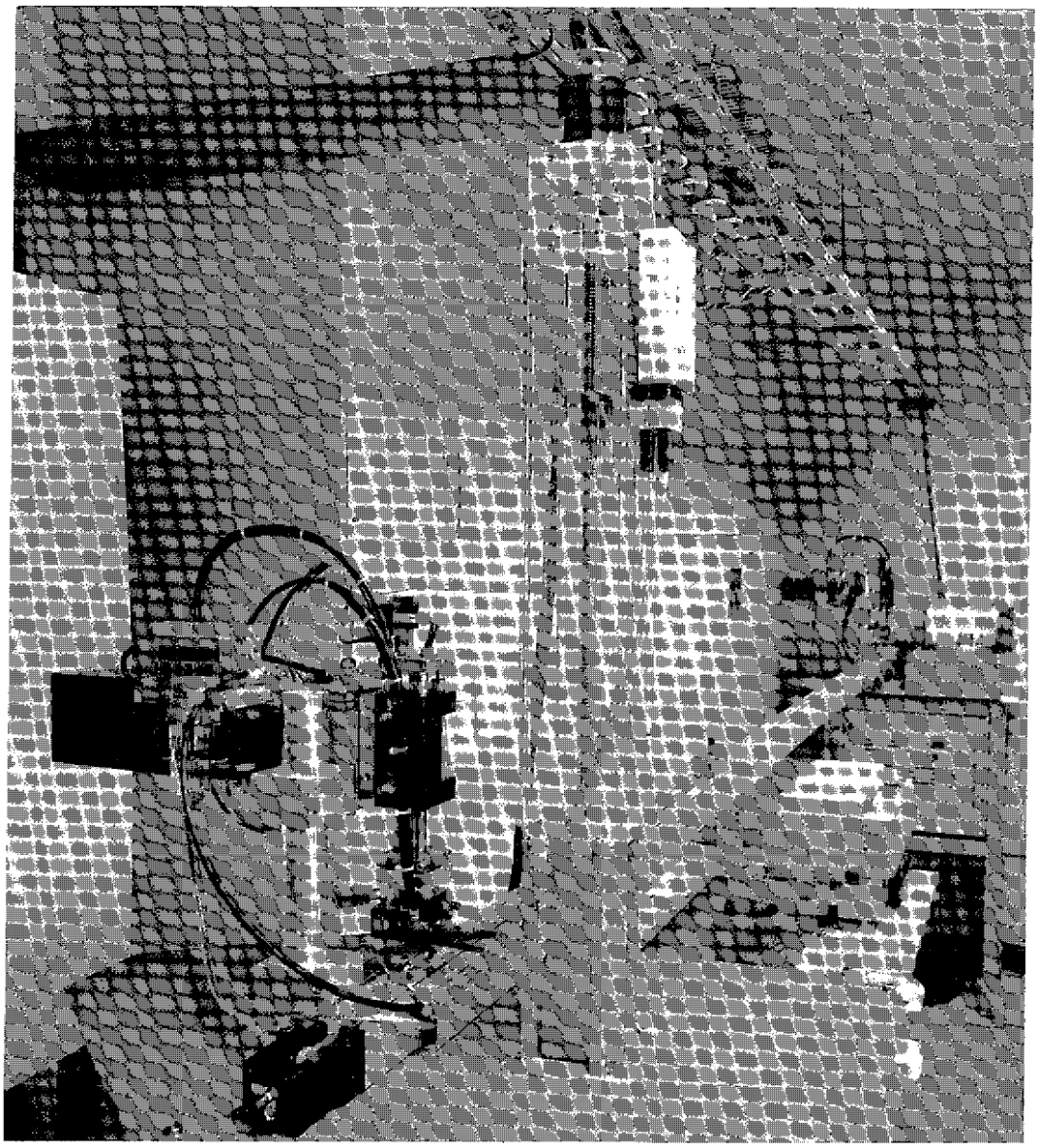

Fig. 5 - Automatic sample changer for the γ-ray spectrometer

The sample changer consists mainly of four parts:

1 The sample store and its handling unit (seen in the background)
2. The transport rail with the cart
3. The positioning device at the detector (foreground)
4. The control unit (background, under the sample store)

The sample store is arranged in a large distance from the γ-ray detector and it is shielded to prevent cross-talk of the radiation of the sample store with the detector. The store consists of a turntable with 16 positions for samples. The turntable can be rotated stepwise by a step motor Sample adapters, from which different types exist to handle different types of counting vials, are placed on the turntable. The adapters have ring-shaped

(Explanations continued on next page)

calibration sources (γ-energies and absolute emission rates) are stored in a certificate file in the computer and are called by the program which calculates the calibration curves.

The program is started and the operator is asked for and has to enter the file names of the calibration spectrum, the calibration source and of the calibration file to be created. Then the program calculates the parameters of the calibration curves for energy and intensity. The efficiency curve is shown on screen and plotted by the printer.

Peakfit procedure

The next step is starting the peak fit program for all spectra. It finds the peaks, their positions (channel numbers) and the peak areas. Before starting, some data have to be entered. Since the identification code for each file consists of a name (valid for the whole series) and a current number (for each spectrum) this procedure as well as the following can be started with only one command for all spectra of a series. The operator has to enter the series code name, the first and the last number of the spectra to be fitted, and the starting parameters for the approximation process used in the peakfit procedure (e.g. estimated half width). The list of peaks (position, area, FWHM (full width at half maximum), statistical errors and some other data) is created and connected to each spectrum file.

Flux calculation

The nuclear parameters of the zirconium isotopes ^{94}Zr and ^{96}Zr and their activation products used for flux determinations are stored as a data set in the

---

Explanation of Fig 5 (continued)

grooves which fit to a fork-shaped grip of the sample handling system. The sample handler takes a sample from the turntable and puts it on the cart, by which it is transported to the detector site. Samples coming back from the detector are set back to the turntable, which is then turned to the next position and the next adapter with a sample is moved to the cart. The cart, fixed on a transport-belt (cog-belt), is wheeled along a rail, and the motor, which drives the belt, is controlled by pulses from the control unit and by limit switches.

At the other end of the rail, near the detector, another sample handler takes the adapter with the sample from the cart and places it on the sample positioner, which is arranged vertically above the HPGe-detector, which is in the lead shield below the metal plate in the foreground. The sample holder of the positioner is fixed on a long thread-rod, which can be turned by a step-motor. Thus, the sample is moved downward and approaches the detector. The exact position, i.e. the distance between sample and detector, is determined by the number of revolutions of the thred-rod, which are registered by the control unit.

Usually, the sample changer is operated by an "autocycle" procedure, which can be composed via a menu at the main frame computer (μ-VAX II) of the γ-ray spectrometer system. When the autocycle is started, the control unit receives a starting pulse from the μ-VAX and sends the first sample to the detector. When the counting time is over, a pulse is sent to the control unit, which then starts the sample change cycle, i.e. the first sample is moved back to the store and the next one is moved to the detector.

computer and are called by the flux calculation program. The operator has to enter the file name of the spectrum of the flux wire, the irradiation time, the calibration file and the name of the flux file to be created, which contains the data of the neutron fluxes.

The flux calculation procedure has two options.

1. *Flux ratio Φ_{th}/Φ_e unknown.* In this case the flux ratio is calculated from the activities of ^{95}Zr and ^{97}Zr, and the wires have to be measured within about 2 days after irradiation end, before the 17-h-activity of ^{97}Zr has decayed.

2. *Flux ratio known,* which usually comes true. In this case, only the activity of ^{95}Zr must be known and the measurement of the wire can be done even after several weeks.

Another option of the flux determination procedure is the measurement of several flux monitors in one irradiation capsule and the interpolation of the flux for each sample position, such as it is shown in Fig. 2.

Calculation of results

When the peak list, the calibration and the flux file are prepared, then the last step of the evaluation procedure is executed. The names of the flux file and the calibration file have to be entered and the procedure is started: weights or concentrations of all elements found in the samples are calculated.

For this program, all k_0- and Q_0-values of DeCorte and Simonits and all other required data are stored in a library (data file "k0cat") in the computer. All elements from this library are checked, if fitting γ-lines are found in the spectrum, and if they are present, the amounts of elements are calculated. If more than one line is found, weighted mean values are calculated, but the individual results from the peaks are given also. Furthermore the program calculates the detection limits for all elements contained in the library including those which are not found in the spectrum. With many analytical problems, detection limits have the same importance as the contents of the elements positively detected; e.g. if a certain purity of a material has to be guaranteed or if the absence of some toxic elements from an environmental sample has to be confirmed. This feature is one of the important advantages of a single monitor or absolute method of analysis, because with a direct comparator method these values cannot be calculated, except for the elements present in the comparator.

As an example one page of a printout showing results for the elements titanium to gallium is presented in Fig. 6. The elements Ti, V, Mn, Cu, and Ga could not be found, because the nuclides had decayed. With iron all three lines of the k_0-catalogue have been found. The 192-keV-line gives a somewhat high value, but it has a low weight for the calculation of the weighted mean value due to its low γ-intensity. Detection limits ("Nachweisgr.") are given at the end of the result line. They were also calculated for elements not found (no example in the excerpt shown) except for those with half lives more then twenty times shorter than the decay time.

```
Titan        bestimmt ueber Ti-51
-----
Linien vom Ti-51   abgeklungen
-------------------------------------------------------------------------------
Vanadium     bestimmt ueber V-52
--------
Linien vom V-52    abgeklungen
-------------------------------------------------------------------------------
Chrom        bestimmt ueber Cr-51
-----
Pk/Ener:   61/  320.1  keV
p-Wert :         9.850    %
Gehalt :         29.63  ppm
------------------------------------------------------ ----------------------
Mittelwert:      29.63 +-  0.166 ppm rel.Fehl.:  0.5  % Nachweisgr.:  0.197 ppm
-------------------------------------------------------------------------------
Mangan       bestimmt ueber Mn-56
------
Linien vom Mn-56   abgeklungen
-------------------------------------------------------------------------------
Eisen        bestimmt ueber Fe-59
-----
Pk/Ener:   42/  192.3  115/ 1099.2  129/ 1291.6  keV
p-Wert :         2.640        56.100       43.800    %
Gehalt :         8365.         7912.        7922.  ppm
-------------------------------------------------------------------------------
Mittelwert:      7928. +-   71.2 ppm rel.Fehl.:  0.90 % Nachweisgr.:    8.9 ppm
-------------------------------------------------------------------------------
Kobalt       bestimmt ueber Co-60
------
Pk/Ener:  120/ 1173.2  134/ 1332.5  keV
p-Wert :       100.000      100.000    %
Gehalt :         1.779        1.790  ppm
-------------------------------------------------------------------------------
Mittelwert:      1.785 +- 0.0055 ppm rel.Fehl.:  0.31 % Nachweisgr.: 0.0126 ppm
-------------------------------------------------------------------------------
Kupfer       bestimmt ueber Cu-64
------
Linien vom Cu-64   abgeklungen
-------------------------------------------------------------------------------
Kupfer       bestimmt ueber Cu-66
------
Linien vom Cu-66   abgeklungen
-------------------------------------------------------------------------------
Zink         bestimmt ueber Zn-65
----
Pk/Ener:  117/ 1115.5  keV
p-Wert :        50.750    %
Gehalt :         38.99  ppm
-------------------------------------------------------------------------------
Mittelwert:      38.99 +-  1.689 ppm rel.Fehl.:  4.33 % Nachweisgr.:  0.598 ppm
-------------------------------------------------------------------------------
Zink         bestimmt ueber Zn-69m
----
Linien vom Zn-69m  abgeklungen
-------------------------------------------------------------------------------
Gallium      bestimmt ueber Ga-72
-------
Linien vom Ga-72   abgeklungen
-------------------------------------------------------------------------------
```

Fig. 6 - Excerpt of an INAA protocol as printed out by the program "GEHALT"
(Explanations see text)

Final check of results

The extensive automatization and computerization of the evaluation procedure up to the printout of the analytical results enables the treatment of a set of 20 to 30 samples within a session of about 30 minutes.

However, one should not blindly trust in the results automatically calulated. With γ-ray spectrometry two important sources of error are superposition of lines and spurious peaks. Such errors cannot completely be avoided by automatic evaluation procedures for γ-spectra. Another type of error is nuclear interference which occurs if the same radionuclide is produced from different elements. Therefore, a final test of the results by the operator, a plausibility test, is necessary, which indeed requires more skill and more time than entering the data for the automatic evaluation in the computer. To facilitate this task, the program package contains some further options including checking the peak fit by a computer plot or improving peak resolution by an interactive procedure.

2.3 The calculation of results using k_0-factors.

The calculation of the contents, c_x, of elements x by the procedure described above is based on the equation

$$c_x = \frac{1}{m_s} \times \frac{3.469628\, P_x\, Z_x}{\eta_x\, k_{0,x}^{Au}\, (\Phi_t + \Phi_e\, Q_{0,x})} \qquad (1)$$

which is derived from the equations of Simonits et al.[2] m_s is the sample weight, P_x is the number of counts in the γ-peak, $Z_x = \lambda e^{\lambda t_w}/[(1 - e^{-\lambda t_m})(1 - e^{-\lambda t_i})]$ is the factor containing the time dependent members for irradiation, waiting and measuring time, t_i, t_w and t_m. η_x is the counting efficiency, $k_{0,x}^{Au}$ is the k_0-factor for a γ-line of element x related to gold as the reference nuclide, Φ_t and Φ_e are the thermal and the epithermal flux and $Q_{0,x}$ is the epithermal-to-thermal cross-section ratio. The numeric constant is $3.469628 = M_{Au}/(a_{Au} h_{Au} \sigma_{t,Au} N_L)$, (M atomic weight, a isotopic abundance, h γ-ray abundance, σ_t thermal neutron activation cross section of gold, N_L Avogadro's number). For calculating the neutron fluxes from the peak areas in the spectrum of the flux wire the following equations are used:

$$\Phi_t = \frac{3.469628}{m_{Zr}\, (Q_{0,95} - Q_{0,97})} \left(\frac{P_{97}\, Q_{0,95}\, Z_{97}}{k_{0,97}^{Au}\, \eta_{97}} - \frac{P_{95}\, Q_{0,97}\, Z_{95}}{k_{0,95}^{Au}\, \eta_{95}} \right) \qquad (2)$$

$$\Phi_e = \frac{3.469628}{m_{Zr}\,(Q_{0,95} - Q_{0,97})} \left(\frac{P_{95}\,Z_{95}}{k^{Au}_{0,95}\,\eta_{95}} - \frac{P_{97}\,Z_{97}}{k^{Au}_{0,97}\,\eta_{97}} \right) \qquad (3)$$

where the subscripts 95 and 97 refer to the corresponding isotopes of Zr. In the equations for the calculation of element contents and for the fluxes we have neglected the deviation of the epithermal neutron spectrum from the 1/E-shape, which has been treated by DeCorte et al.[7] Because the contribution of epithermal neutron activation in a heavy water moderated reactor is very small - the flux ratios in the different irradiation facilities are between 1/200 to 1/4000 - the corrections for non-ideal epithermal flux spectra have practically no influence on the analytical results.[8] Meanwhile, we have started with the measurement of α-values in our irradiation channels in order to avoid errors with some elements where this correction is not negligible, and to enable analyses with accuracies better than those usually required with trace element analysis.

The calculation of results following Equation (1) is based on peak areas as they are calculated by a simple peakfit procedure. In some cases superposed lines cannot be resolved by this program and errors will occur with the element contents found.

2.4 The evaluation procedure based on the nuclide identification program

Therefore we are installing a new program which uses additional information for better deconvolution of peak clusters. The additional parameters are the γ-ray abundances of the radionuclides. Therefore, the program requires the identification of the radionuclides and it calculates for each double or multiple peak the contribution of each radionuclide emitting γ-rays of similar energy. The program "NUKID" follows with many respects the approach of Gunnink et al.[9] It yields a list of all radionuclides (activation products) and their absolute decay rates. That means, in contrast to the procedure described above, where the element contents are calculated from the peak areas and the pertinent k_0-factors, we now have to calculate the element contents from the absolute decay rates. For that purpose, we have to transform line-related k_0-factors into

isotope-related k_i-factors. We have done this [10] using the stored data set of k_0-factors and a computer program according to the equation

$$k_i = 3.469628 \frac{\sum_{j=1}^{n} \frac{h_j}{k_{0,j}^{Au}} w_j}{\sum_{j=1}^{n} w_j} \qquad (4)$$

where j is a running number of the γ-lines of a nuclide and w_j is a weighting factor considering the uncertainties in h_j and $k_{0,j}^{Au}$. I.e. the k_i-factor is a weighted mean of all k_0-factors of one nuclide, divided by the γ-ray abundances. It should be mentioned, that k_i-factors can also be calculated from the nuclear constants by

$$k_i = \frac{M}{N_L \, a \, \sigma_t} \qquad (5)$$

but, with the more accurate k_0-factors of DeCorte and Simonits more accurate k_i-values will be obtained.

With k_i-factors the element contents are calculated by the following equation:

$$c_x = \frac{1}{m_s} \times \frac{A_{0,x} \, k_{i,x}}{(\Phi_t + \Phi_e \, Q_{0,x}) \, B_x} \qquad (6)$$

Since the "NUKID" program calculates the absolute activities at irradiation end, $A_{0,x}$, i.e. the calculation of the activity from the number of counts in a peak and the counting time, and the correction for decay during the waiting time are included in the program, the time factor Z of Equation (1) is reduced to $B = 1 - e^{-\lambda_x t_b}$, the build-up factor during the irradiation.

The traceability of this method is mainly based on the nuclear constants, k_0^{Au} and h_j. The k_0^{Au}-values have been measured by DeCorte and Simonits and the corresponding experiments and procedures are well documented. The γ-ray abundances were taken from compilations.[5,12]. In both cases the data have

been traced down to the original publications by the authors. Where data did not agree, the "Nuclear Data Sheets" [13] and the "Table des Radionucléides" [14] were consulted. These collections are based on carefully evaluated data, the evaluations following strict rules and being controlled by a board of scientists, so that their generation seems indeed transparent, traceable and reliable according to the present state of knowledge. In most cases k_i-values calculated from k_0^{Au}-values and those calculated after Equation (5) are in very good agreement and confirm the accuracy of the h-values.

3. Results of analyses

3.1 Aluminium

Aluminium, which is a very suitable matrix for instrumental neutron activation analysis has been analyzed by hundreds of activation analysts and one would not expect news with it. But, after detection of the "soft errors" in microchips [15], caused by α-rays of natural radioactive trace impurities such as uranium and thorium in the materials used for their production, NAA got a new importance in this field. Presently, it seems to be the most sensitive and the most reliable method to determine these two elements in concentrations below 1 ng/g. In the production control of high-purity materials for VLSI applications, where meanwhile such low levels of impurities are required, it is often used for calibrating and checking analytical methods such as UV-fluorescence or GDMS, but several firms directly apply NAA as the routine method for measuring α-emitters.

We had been asked by an aluminium producer, VAW(Bonn), to analyze some samples of VLSI aluminium. At that time detection limits of about 1 ng/g could be attained only by radiochemical NAA.[16,17] In usual high-purity aluminium (99.9999%) several impurities contribute to the compton background level, which injures the detection limits for uranium and thorium, whereas in the VLSI aluminium it is mainly ^{24}Na, produced by fast neutrons from the matrix isotope ^{27}Al, which inhibits the detection of uranium and thorium contents below 0.5 ng/g.

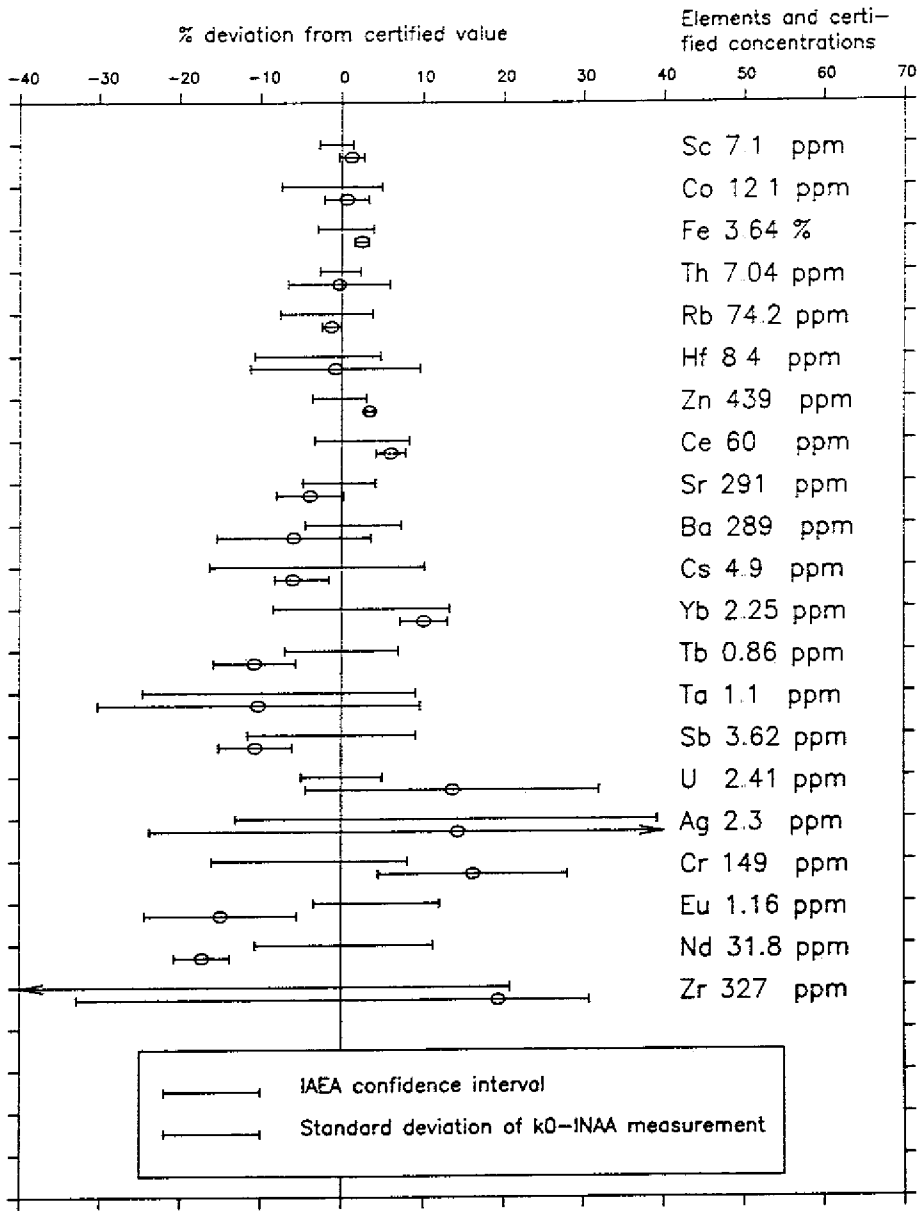

Fig. 7 - Analysis of reference material IAEA Sediment SD-N-1/2

In this respect, the research reactor at Jülich has a great advantage: Because it is moderated with heavy water, even in an irradiation facility with a comparatively high thermal flux of 1×10^{13} n $cm^{-2}s^{-1}$ the fast-to-thermal flux ratio is only $\simeq$ 1/1000, and the production of ^{24}Na is very low, so that detection limits of 0.1 ng/g U + Th and below can be attained even by a purely instrumental method.[18] The procedure has been optimized with respect to irradiation technique and throughput and the aluminium factory has installed

an own activation analysis laboratory where these analyses are carried out for production control.

3.2 Analysis of environmental samples

As has been mentioned above, environmental material and biological samples are not often analyzed in our laboratory. However, some institutes and clients outside the KFA required analyses of

- soils and plant ashes to investigate the influence of stable elements on the transfer factors of radioactive fallout nuclides from soils to plants,
- sewage sludge and ashes from incineration plants for sewage sludge and other wastes in order to investigate the path of heavy metals and other harmful elements,
- spruce needles in connection with investigations on the causes of "Waldsterben",
- plant materials in connection with the valuation and selection of analytical methods useful for the preparation of cadasters of trace element concentrations in ecosystems [21]

and for other purposes.

3.3 Analysis of IAEA Sediment SD-N-1/2

When working on these tasks we always have analyzed standard reference materials of similar composition. One example is shown in Fig. 4. It depicts the results with IAEA Sediment SD-N-1/2 for elements which were both certified by IAEA and found by INAA. For 15 elements (Sc, Co, Fe, Th, Rb, Hf, Ce, Sr, Cs, Yb, Ta, Sb, Ag, and Zr) the results are within the IAEA confidence interval. For another five elements (Cr, Zn, Ba, Tb, and U) at least the error bars for single standard deviation overlap. But with Eu and Nd our results are not in agreement. With Eu the thermal cross section strongly depends on the neutron

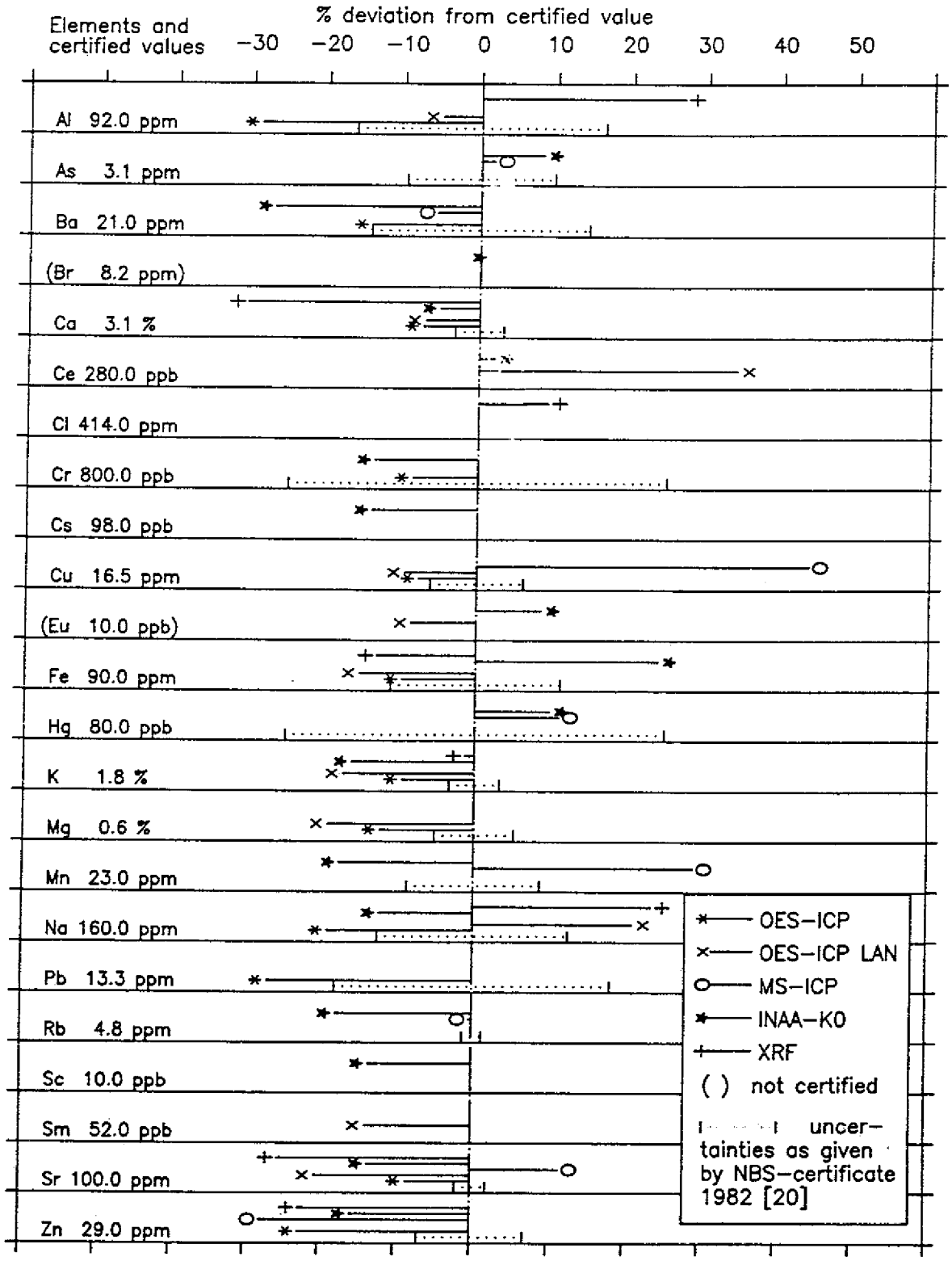

Fig. 8 - Comparison of Instrumental Analytical Methods

Sample: Citrus leaves NIST SRM 1572. Data from Markert [22]

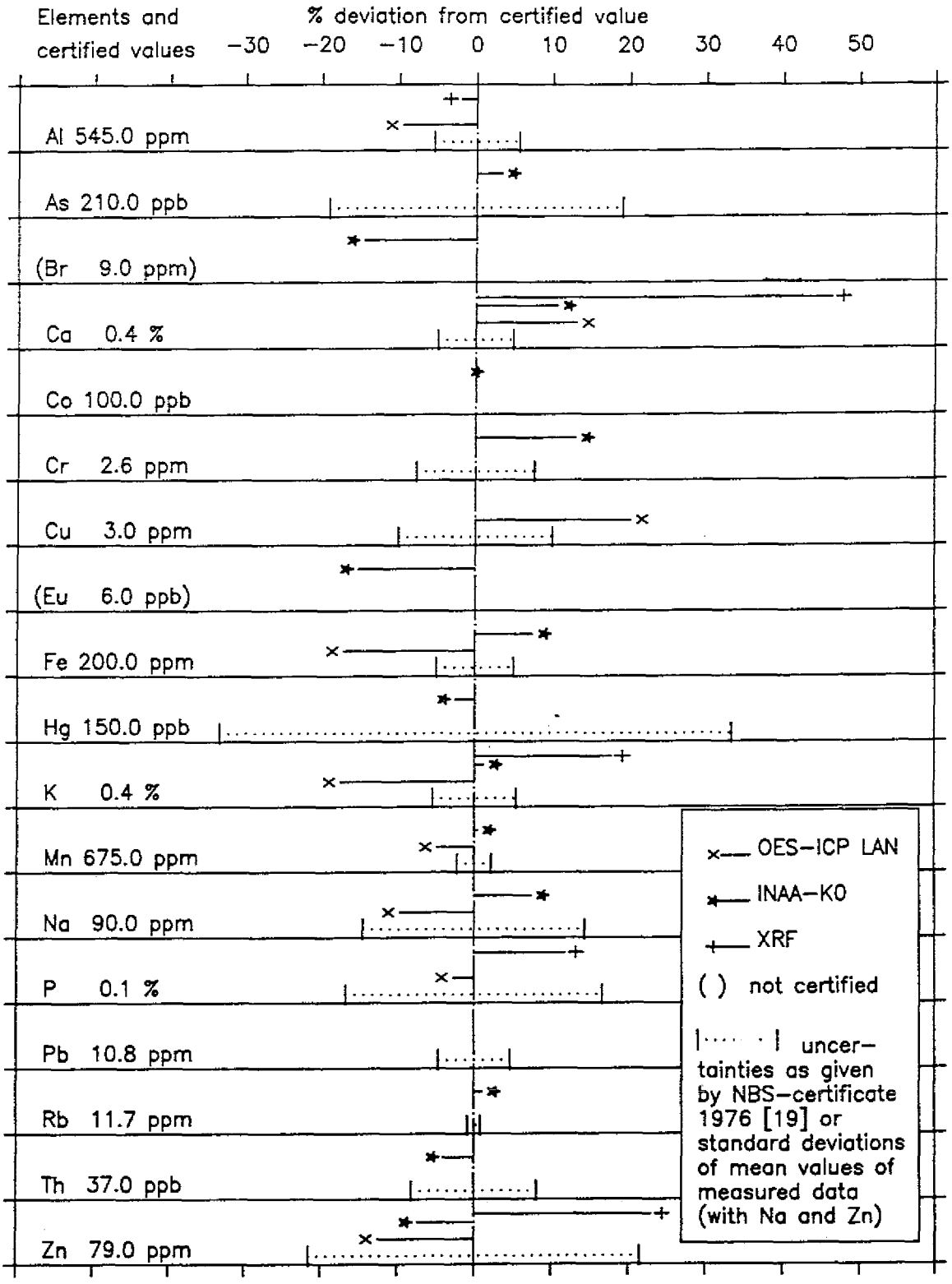

Fig. 9 - Comparison of Instrumental Analytical Methods

Sample: Pine needles NIST SRM 1575. Data from Markert [22]

temperature and we have not yet a reliable procedure to treat it within the k_0-method. Only calculated, not recommended k_0-factors are used. The discrepancy with neodymium is not yet investigated.

3.4 Comparison of several multielement methods.

With the aim to prepare a cadaster of element concentrations in ecosystems [21] a great number of analyses of plant materials have to be carried out. Instrumental multielement techniques will be preferably used and it has to be decided, which method or which combination of methods will be optimal to put into action such a tremendous task. In this connection Markert [22] has analyzed numerous plant materials including true samples from certain ecosystems and reference materials using the following multielement methods.

- OES-ICP in two versions: one purely instrumental and one with chemical separation of the rare earth elements
- MS-ICP
- XRF with a wavelength-dispersive instrument
- INAA with the k_0-method.

Results with two reference materials are shown in Fig. 8 (Citrus leaves NIST SRM 1572) and Fig. 9 (Pine needles NIST SRM 1575). They contain data of only those elements, which can be determined by INAA. The usual analytical procedure, following an irradiation time and a decay time of several hours either, allows only detection of fairly long lived isotopes with half lifes longer than about 2.5 hours. For short lived isotopes from Al, Cl, I, Mg, Ti, V and some other elements another irradiation-decay-measurement cycle is required, which has not applied with the analyses shown here. Cu is not evaluated because the 511-keV-line can be interfered by other nuclides. P and Pb, finally, cannot be determined by INAA because they don't yield useful activation products. It is often said INAA be not useful for environmental analyses because Pb and Cd, two elements which stood for a long time in the foreground of interests of environmental toxicologists, cannot be measured by this method.

Table 1 - INAA of Ashes from Spruce Needles and Branches [a)]

Element	Needles content [b)]		L_D [c)]		Branches content [b)]		L_D [c)]	
Na	30.4 ± 0 126	µg/g	0 04	µg/g	163 ± 0 261	µg/g	0 06	µg/g
K	1 17 ±0 0357	%	0.0003	%	1 12 ±0 0873	%	0 0005	%
Ca	1 52 ±0.0998	%	0 0048	%	1.15 ±0.0492	%	0 0170	%
Sc	45 9 ± 0 356	ng/g	0 250	ng/g	189 ± 0 266	ng/g	0.5	ng/g
Cr	1120 ± 80 6	ng/g	50.0	ng/g	4840 ± 137	ng/g	84 0	ng/g
Fe	179 ± 3.69	µg/g	2 4	µg/g	772 ± 24 1	µg/g	5 0	µg/g
Co	360 ± 3 84	ng/g	4 5	ng/g	1110 ± 4 68	ng/g	9.0	ng/g
Cu	not found		80.0	ng/g	not found		120	ng/g
Zn	68 7 ± 0 445	µg/g	0.17	µg/g	191 ± 0.967	µg/g	0 3	µg/g
As	111 ± 4 5	ng/g	4 2	ng/g	536 ± 38 6	ng/g	6 5	ng/g
Se	not found		85 0	ng/g	not found		130	ng/g
Br	1550 ± 14.4	ng/g	6 2	ng/g	4 49 ±0 0508	ng/g	0.009	ng/g
Rb	4.63 ± 0.268	µg/g	0 14	µg/g	7 37 ± 0 476	µg/g	0 22	µg/g
Sr	85 0 ± 5 36	µg/g	2.6	µg/g	92 4 ± 11.1	µg/g	4 8	µg/g
Zr	not found		3 0	µg/g	not found		3 5	µg/g
Mo	not found		175	ng/g	576 ± 210	ng/g	8 4531	ng/g
Ag	not found		34.0	ng/g	not found		61.0	ng/g
Cd	not found		180	ng/g	464 ± 271	ng/g	202	ng/g
In	not found		300	ng/g	not found		410	ng/g
Sn	not found		14.0	µg/g	not found		11 0	µg/g
Sb	125 ± 10.2	ng/g	6 0	ng/g	280 ± 57.3	ng/g	11.0	ng/g
Te	not found		0.2	µg/g	not found		0 12	µg/g
Cs	34.7 ± 11 7	ng/g	5 0	ng/g	129 ± 25 5	ng/g	11.0	ng/g
Ba	114 ± 7 77	µg/g	1.10	µg/g	186 ± 9 36	µg/g	2.0	µg/g
La	307 ± 17.1	ng/g	0.7	ng/g	992 ± 29 3	ng/g	1 3	ng/g
Ce	403 ± 64 6	ng/g	52.0	ng/g	1.65 ±0 093	ng/g	0.07	ng/g
Nd	not found		180	ng/g	719 ± 576	ng/g	210	ng/g
Sm	49.6 ± 12 6	ng/g	0 5	ng/g	149 ± 4.68	ng/g	0 65	ng/g
Eu	9 04 ± 0 595	ng/g	1.2	ng/g	21.8 ± 5.43	ng/g	2 4	ng/g
Tb	10 5 ± 2 03	ng/g	3 3	ng/g	13.1 ± 6.11	ng/g	4 6	ng/g
Yb	26 4 ± 3 28	ng/g	1 8	ng/g	56 1 ± 7.14	ng/g	3 1	ng/g
Hf	17.3 ± 8.31	ng/g	3 5	ng/g	98.2 ± 17 3	ng/g	6 0	ng/g
Ta	not found		6 0	ng/g	46 9 ± 33 0	ng/g	9 0	ng/g
W	47.2 ± 41 8	ng/g	7.0	ng/g	185 ± 44.5	ng/g	10.0	ng/g
Ir	not found		0.12	ng/g	not found		0 27	ng/g
Au	0.3± 0.13	ng/g	0.07	ng/g	2 45 ± 0.142	ng/g	0.11	ng/g
Hg	not found		23 0	ng/g	not found		35 0	ng/g
Th	39.5 ± 10 5	ng/g	5 0	ng/g	154 ± 93 0	ng/g	8.0	ng/g
U	42.7 ± 5 85	ng/g	15 0	ng/g	62.2 ± 38 8	ng/g	17 0	ng/g

Footnotes see next page

Indeed, out of the methods applied and as they were performed in the work of Markert [22] none gave results for Cd, and Pb was detected only by ICP-MS at the 10-μg/g-level. With all multielement methods the limit of detection for Cd has been obviously higher than 30 ng/g, the Cd-content of the Pine Needles SRM. Usually it is not possible with an instrumental multielement method to provide a procedure and instrument setting optimal for all elements and, maybe, some of the methods may yield results for cadmium if they are correspondingly optimized. The best detection limits for cadmium attained by INAA with environmental samples were $\simeq$ 200 ng/g, as is shown in the next example, but usually they are higher. The use of monoelement methods such as atomic absorption spectroscopy or polarography is usually more successful with the determination of Cd in environmental samples.

3.5 Analysis of spruce needles and branches

With the ashes of these materials higher neutron fluences could be applied, because the build-up of pressure in the sample ampoules due to radiolytic and thermal decomposition had not to be expected. Thus, detection limits of $\simeq$ 200 ng Cd/g could be attained (Table 1).

3.6 Sea sediments

These materials were analyzed mainly for uranium, thorium and potassium. α-tracks in mineral grains can be detected by thermoluminescence and used for age determinations. The contents of the α-emitting elements must be known. The α-tracks will be more or less extinguished by heat or by sufficiently

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Footnotes of Table 1

a) Experimental conditions: Irradiation at a thermal flux of 1×10^{13} n cm^{-2} s^{-1} for 48 h. Three measurements after decay times of $\simeq$ 80, 110 and 180 h with counting times of 15 to 18 h and a sample - detector distance of $\simeq$ 12 cm (efficiency at 1 MeV = 0 035 %).
b) Weighted mean of three results from one sample Error is three times standard deviation of the mean.
c) Detection limit is three times the standard deviation of the background in the γ-spectrum.

Table 2 - INAA of Deep Sea Sediment [a)]

Element	Content [b)]	L_D [c)]
Na	5370 ± 4.11 µg/g	1.10 µg/g
K	1.57 ± 0.257 %	0.0100 %
Ca	not found	1180 µg/g
Sc	10.3 ±0.0173 µg/g	0.0040 µg/g
Cr	100 ± 0.898 µg/g	0.500 µg/g
Fe	3.28 ±0.0632 µg/g	0.0040 µg/g
Co	11.9 ±0.0133 µg/g	0.0400 µg/g
Cu	1710 ± 14.4 µg/g	4.30 µg/g
Zn	80.7 ± 9.73 µg/g	4.20 µg/g
Ga	12.2 ±0.0876 µg/g	0.600 µg/g
As	11.7 ± 0.358 µg/g	0.0500 µg/g
Se	1.60 ± 3.00 µg/g	0.700 µg/g
Br	0.409±0.0788 µg/g	0.0400 µg/g
Rb	91.6 ± 3.74 µg/g	2.50 µg/g
Sr	not found	50.0 µg/g
Zr	495 ± 90.1 µg/g	31.0 µg/g
Mo	8.45 ± 1.30 µg/g	0.500 µg/g
Cd	not found	2.00 µg/g
In	not found	2.00 µg/g
Sn	259 ± 90.0 µg/g	30.0 µg/g
Sb	not found	0.200 µg/g
Cs	4.66 ± 0.588 µg/g	0.100 µg/g
Ba	288 ± 69.0 µg/g	10.0 µg/g
La	33.8 ± 0.612 µg/g	0.0200 µg/g
Ce	80.2 ± 0.460 µg/g	0.300 µg/g
Nd	not found	20.0 µg/g
Ce	5.28 ± 0.970 µg/g	0.0020 µg/g
Eu	0.763± 0.286 µg/g	0.0200 µg/g
Tb	677 ± 49.2 ng/g	35.0 ng/g
Yb	3.04 ± 0.443 µg/g	0.0200 µg/g
Lu	18.2 ± 0.235 ng/g	0.120 ng/g
Hf	14.4 ± 1.31 µg/g	0.0800 µg/g
Ta	0.653± 0.186 µg/g	0.0600 µg/g
W	1.99 ± 1.36 µg/g	0.100 µg/g
Au	3.55 ± 0.998 ng/g	0.700 ng/g
Hg	not found	0.250 µg/g
Th	11.4 ± 1.00 µg/g	0.0600 µg/g
U	2.03 ± 0.569 ng/g	0.150 ng/g

Footnotes see next page

high doses of γ-, β- or UV-radiation and consequently the thermoluminescence effect will be diminished. Therefore, also other radioactive elements have to be determined. The other trace elements shown in Table 2 were measured because they may be useful for further characterization of the sediments. Detection limits in this example are not as good as with the spruce samples, because the irradiation and the counting times were shorter.

3.7 Sewage sludge

This material was analyzed in air dried form. It could be irradiated for only 15 minutes to avoid excessive radio- and thermolysis. Consequently, the detection limits are high, but arsenic, which was the most interesting element for the customer, could be found in most of the samples (Table 3).

Acknowledgements - The author is indebted to Mr F Güldenberg, Dr G Küppers, Mr. H. Petri, Mr. M Rauschen and Mr W. Soyka, who were involved in the development and construction of the devices to facilitate sample handling and the development of procedures and programs to automatize the measurement of the samples and the data handling and who carried out most of the analyses (aluminium, soil, spruce samples, sediments and sewage sludge). Thanks are due to Dr B Markert for providing the unpublished analytical results obtained by different multielement methods.

Footnotes of Table 2

a) Experimental conditions: Irradiation at a thermal flux of 1.15×10^{13} n cm^{-2} s^{-1} for 24 h. Four measurements after decay times of $\simeq$ 80, 120, 150, and 400 h with counting times of 2.5, 6, 6, and 4 h, respectively. The sample - detector distance was $\simeq$ 18 cm with the first and $\simeq$ 12 cm with the other measurements. Efficiencies at 1 MeV were 0.023 % with the first and $\simeq$ 0.085 % with the other measurements.

b) Weighted mean of three results from one sample. Error is three times standard deviation of the mean.

c) Detection limit is three times standard deviation of the background in the gamma-spectrum.

Table 3 - Activation Analyses of Sewage Sludge [a)]

Values are in μg/g dry weight.

Element	n [b)]	Mean value [c)]	Median	Min. value	Max. value	L_D [d)]
Na	31	5520 ± 790	5240	3500	8940	3
K	31	6550 ± 651	6380	5130	9460	110
Sc	31	2.69 ± 0.397	3.00	1.50	3.50	0.1
Cr	31	110 ± 24.0	111	62.0	315	10
Fe	31	15400 ± 3120	16700	6840	36200	900
Co	31	18.1 ± 2.10	18.0	12.0	28.0	1.9
Zn	31	1560 ± 248	1430	918	2300	70
Ga	29	8.85 ± 1.48	8.70	3.50	14.0	2
As	24	6.15 ± 0.887	6.05	3.40	9.40	1.5
Se	0	not found	-	-	-	15
Br	31	22.1 ± 3.28	23.0	13.0	35.0	4
Ag	13	33.3 ± 7.40	31.0	17.0	48.0	8
Cd	0	not found	-	-	-	20
Sb	23	10.5 ± 1.41	11.0	5.80	16.0	3
Cs	0	not found	-	-	-	2
La	31	10.2 ± 1.86	9.70	4.50	15.0	1
Ce	22	35.5 ± 5.40	36.0	20.0	52.0	7
Nd	0	not found	-	-	-	35
Sm	30	1.39 ± 0.265	1.65	0.630	2.10	0.3
Eu	23	0.308 ± 0.0782	0.280	0.150	0.680	0.04
Tb	0	not found	-	-	-	1
Yb	2	1.55 ± 1.35	1.55	1.10	2.00	0.5
Hf	10	3.10 ± 0.716	3.30	1.90	4.20	0.8
Ta	0	not found	-	-	-	2
W	31	39.6 ± 14.7	34.0	14.0	126	2.5
Ir	0	not found	-	-	-	0.02
Au	31	0.894 ± 0.276	0.800	0.500	3.10	0.01
Hg	2	10.1 ± 17.5	10.1	4.30	16.0	3
Th	18	4.06 ± 0.737	3.75	2.20	5.90	1
U	0	not found	-	-	-	2

a) Experimental conditions: 31 different samples. Irradiation at a thermal neutron flux 9×10^{12} n cm^{-2} s^{-1} for 15 min; first measurement after 20 - 50 h decay time, counting time 3 h, distance $\simeq$ 18 cm (efficiency at E_γ 1 MeV $\simeq$0.04%); second measurement after 120 - 150 h decay time, counting time 6 h, distance $\simeq$ 10 cm (efficiency at E_γ 1 MeV $\simeq$0.18%).

b) Number of samples where the element was found.

c) Error is three times standard deviation of mean

d) Detection limit (three times standard deviation of background), approximate values because it slightly varied with the different samples

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