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Cyclic neutron activation analysis of large samples with a pulsed 14 MeV neutron source

11.-15. April 2016 | RANC-2016 Budapest

Frank Mildenberger | Eric Mauerhofer
Institute of Energy and Climate Research – Nuclear Waste Management and Reactor Safety
Forschungszentrum Jülich GmbH
D-52425 Juelich

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Introduction

Motivation: Non-destructive characterization of toxic (non-radioactive) elements and water pollutants in radioactive waste.

- Repository "Konrad"
- Declaration of toxic elements
- Reducing risks to human health and environment
- Product quality control
- MEDINA facility

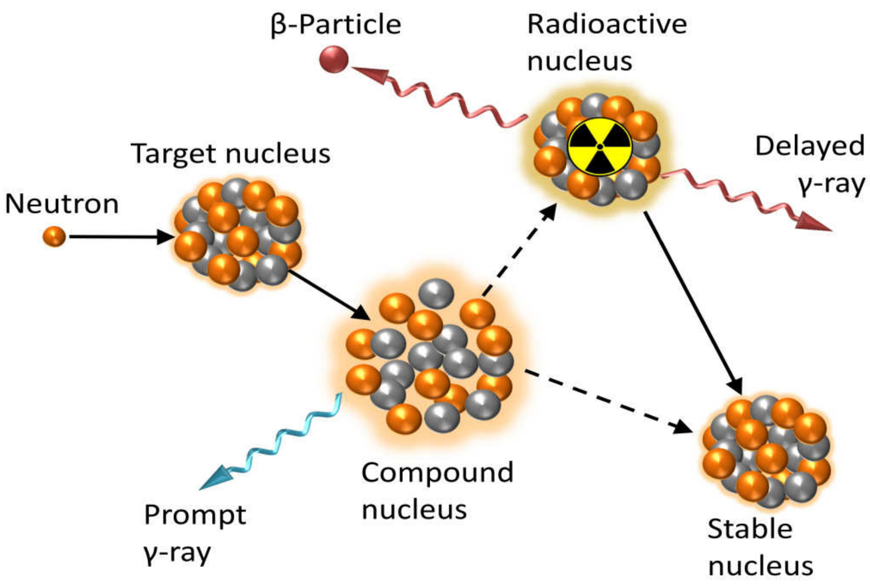
Source: Hamburger Abendblatt

Aim: The elemental composition of waste may be obtained measuring the delayed gamma rays of short-lived radionuclides (e.g. ^{16}N, ^{24m}Na, ^{28}Al, and ^{207m}Pb) induced by fast and thermal neutron reactions.

Introduction

Physical fundamentals

Prompt & Delayed-Gamma-Neutron activation analysis (P&DGNAA)

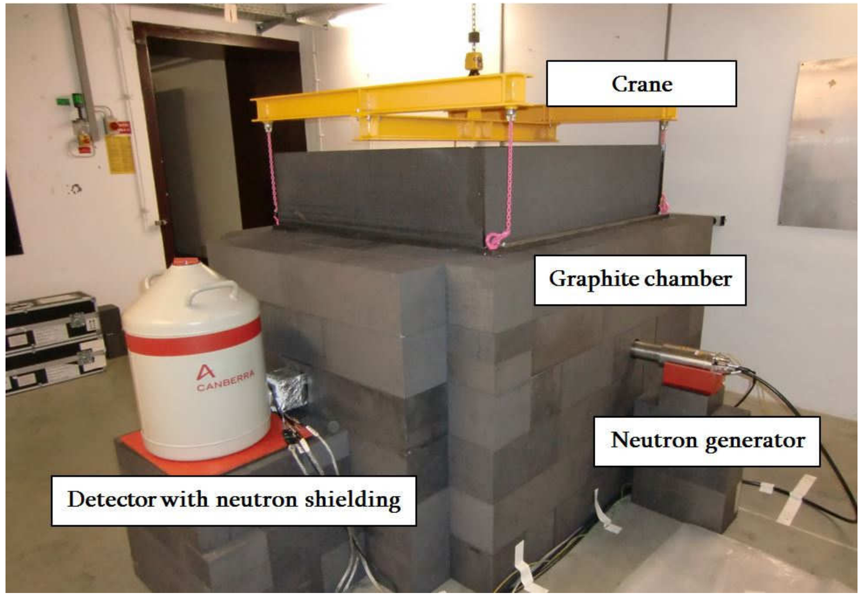


Basics

- *Non-destructive*
- *Multi-element analysis*
- *High sensitivity*

MEDINA facility

Multi-Element-Detection based on Instrumental Neutron Activation



Specification

- *14.1 MeV D-T Neutron generator*
- *HPGe Detector (rel. Eff. 100%) with a thermal neutron shielding*
- *Rotary table*

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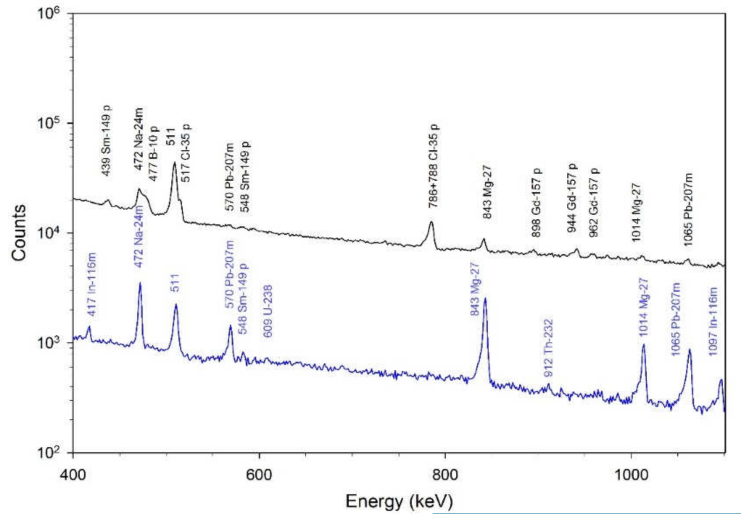
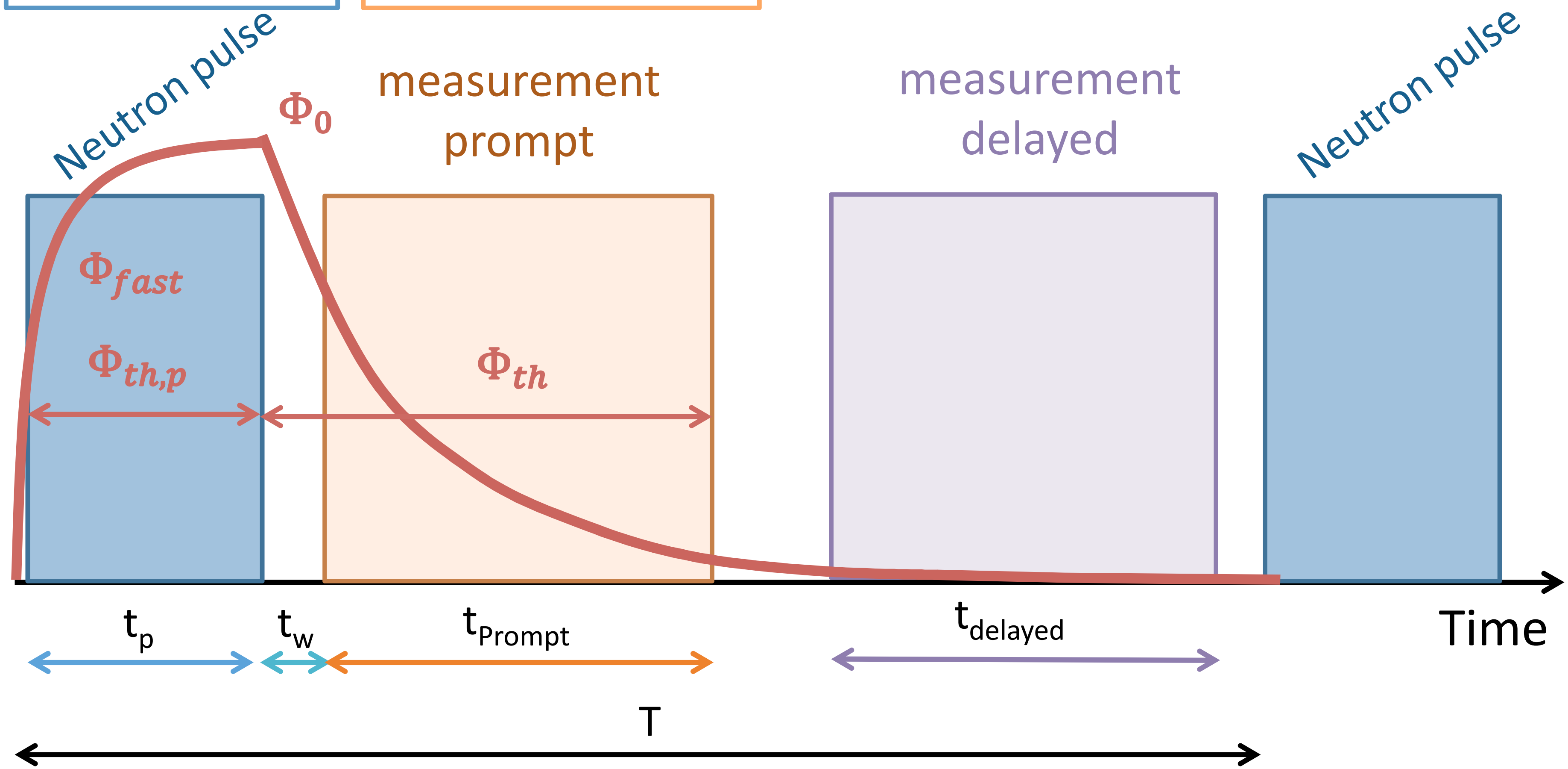


Counts
Energy (keV)
439 Sm-149 p
472 Na-24m
477 B-10 p
511
517 Cl-35 p
570 Pb-207m
548 Sm-149 p
786+788 Cl-35 p
843 Mg-27
898 Gd-157 p
944 Gd-157 p
962 Gd-157 p
1014 Mg-27
1065 Pb-207m
417 In-116m
609 U-238
912 Th-232
1097 In-116m

Prompt- & delayed-gamma activation analysis (CNAA)

Prompt-γ by fast neutrons	Prompt-γ by thermal neutrons	Delayed-γ by fast neutrons Delayed-γ by thermal neutrons

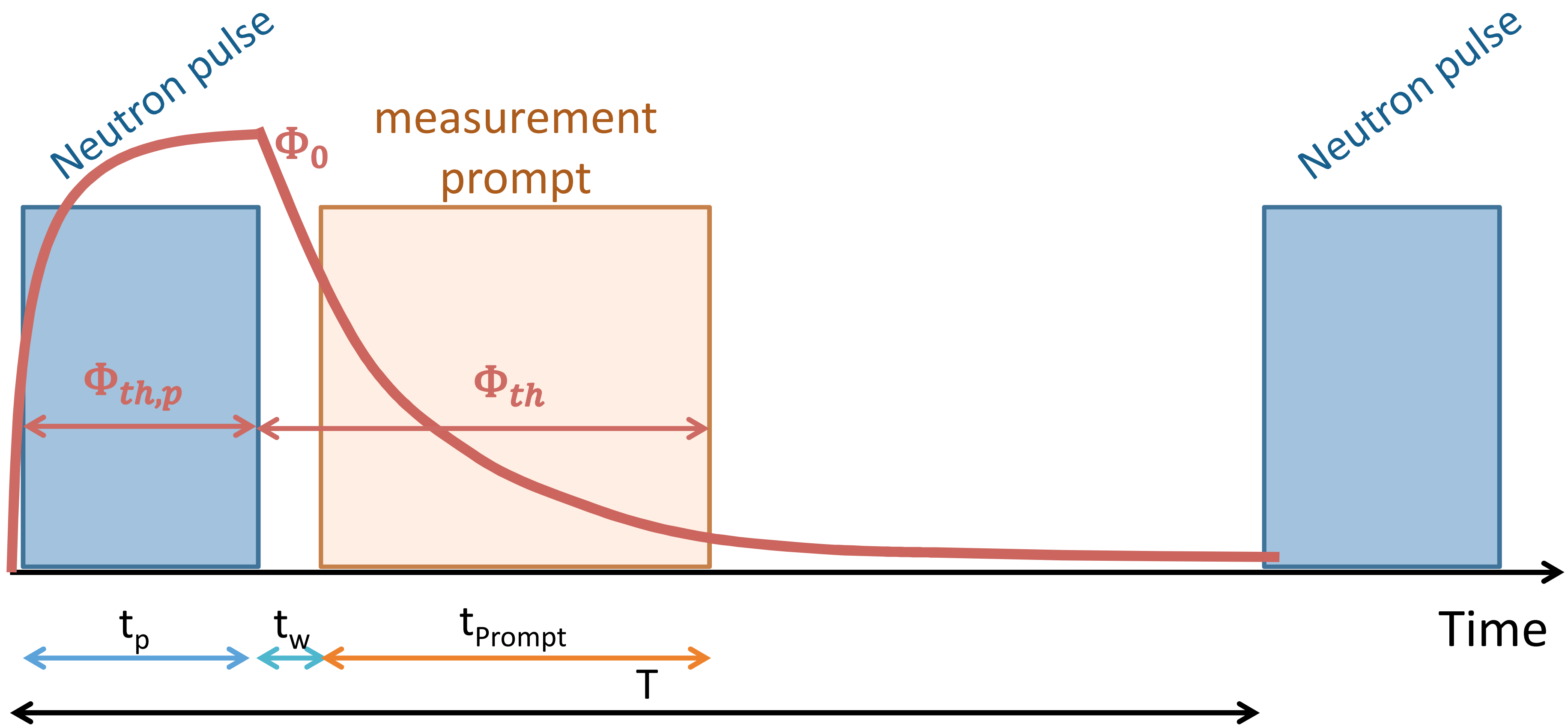


CNAA-Prompt-Gamma

Basic equation

Based on the results of the analyzed PGNAA spectra, the amount of elements can be quantified.

$$m = \frac{Z(E_\gamma) \cdot M}{N_A \cdot \varepsilon(E_\gamma) \cdot \Phi_{th} \cdot \sigma(E_\gamma)}$$



CNAA-Prompt-Gamma

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Interference correction of the prompt-gamma count rate for quantification needed using the thermal neutron die-away time [1]:

$$Z_{E\gamma cor} = Z_{E\gamma} - \frac{\Lambda_{E\gamma}}{\Lambda_{E\gamma back}} Z_{E\gamma back}$$

Corrected count rate — Count rate sample — Count rate background

Isotope	Eγ (keV)	Facility	$\Lambda_{E\gamma back}$ (ms)	$\Lambda_{E\gamma}$ (ms)
^{1}H	2223.2	CFRP	2.59 ± 0.01	0.60 ± 0.05
^{10}B	477.6	Graphite & CFRP	3.56 ± 0.25	2.37 ± 0.04
^{28}Si	3538.9	Neutron shielding	2.71 ± 0.01	2.00 ± 0.02

[1] F. Mildenberger, E. Mauerhofer (2015) *Thermal neutron die-away times in large samples irradiated with a pulsed 14 MeV neutron source. Nucl. Chem, J Radioanal. doi: 10.1007/s10967-015-4178-2*

CNAA-Delayed-Gamma

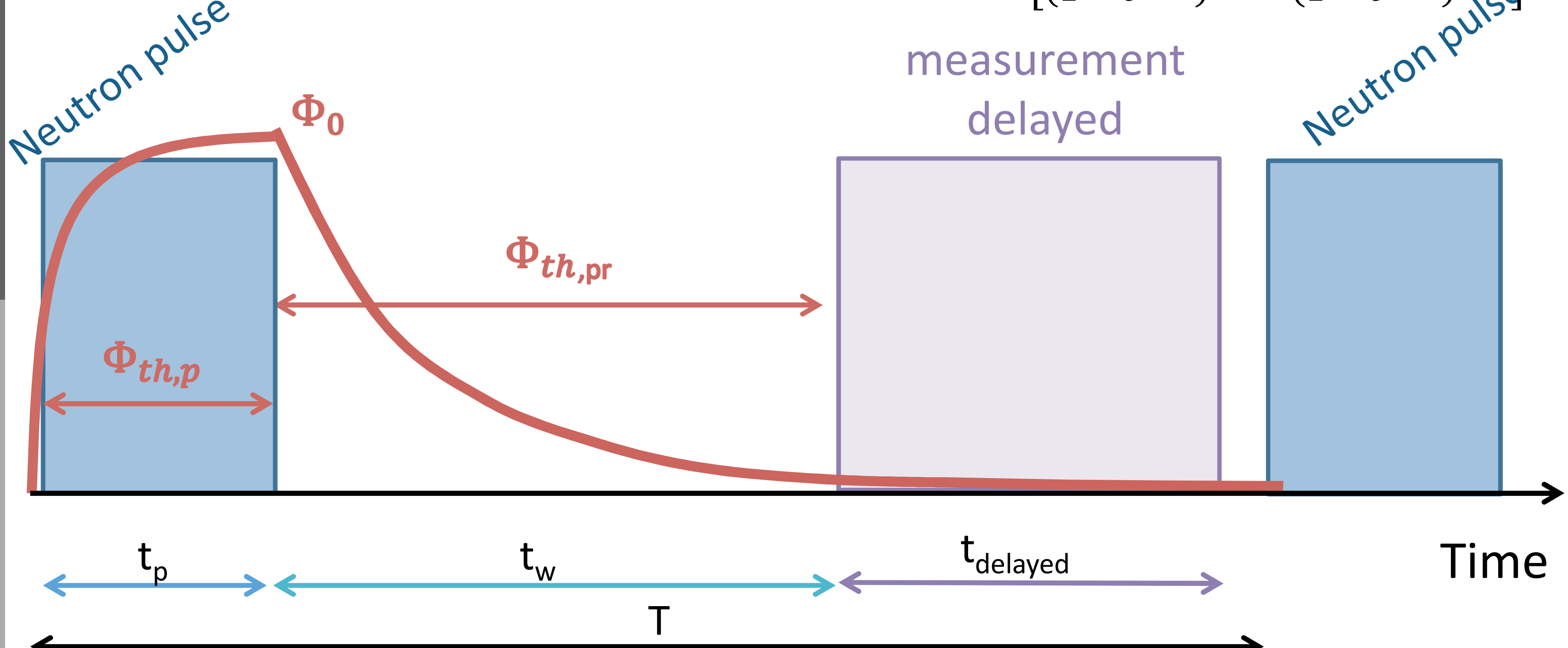
Delayed gamma-ray activation products by **fast** neutron activation:

$$P(E_\gamma) = \frac{m}{M} N_A \varepsilon \Phi_{th} \sigma h \left(1 - e^{-\lambda t}\right)\left(e^{-t_{pr}}\right)\left(1 - e^{-\lambda t_{dl}}\right) \frac{1}{\lambda}\left[\frac{n}{\left(1 - e^{-\lambda T}\right)} - \frac{e^{-\lambda T}\left(1 - e^{-n\lambda T}\right)}{\left(1 - e^{-\lambda T}\right)^2}\right]$$

Delayed gamma-ray activation products by **thermal** neutron activation:

$$P_{E\gamma} = \frac{m}{M} N h \sigma_{th} \varepsilon_{E\gamma} I_{E\gamma}\left(1 - e^{-\lambda t_{dl}}\right)\left(e^{-\lambda t_{pr}}\right)$$

$$\left[\Phi_{th,pr}\left(1 - e^{-\lambda t_{pr}}\right) + \Phi_{th,p}\left[1 + (0.44 + I/\sigma_{th})R\right]\left(1 - e^{-\lambda t_p}\right)\right] \frac{1}{\lambda}\left[\frac{n}{\left(1 - e^{-\lambda T}\right)} - \frac{e^{-\lambda T}\left(1 - e^{-n\lambda T}\right)}{\left(1 - e^{-\lambda T}\right)^2}\right]$$



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Sample

200 L drum filled with concrete bodies

Specification:
Drum with Concrete

m_{Drum}	52.3 kg
$m_{Concrete}$	195.5 kg
$\rho_{Concrete}$	1.62 g cm^{-3}
$\rho_{Filling}$	1.02 g cm^{-3}

Measurement parameters

- $n_{Emission} = 7.2 \pm 0.9 \cdot 10^7 \mathrm{n\ s}^{-1}$
- $t_{Pulse} = 2\ ms$
- $T_{Repetition} = 40\ ms$
- $t_{Gate,prompt} = 18\ ms\ (Acquire)$
- $t_{Gate,delayed} = 20\ ms\ (Acquire)$
- $t_{Livetime} = 3600\ s$
- *After 12 ms after the neutron pulse almost all thermal neutrons have vanished [3].*

[3] F. Mildenberger, E. Mauerhofer (2015) Thermal neutron die-away times in large samples irradiated with a pulsed 14 MeV neutron source. Nucl. Chem, J Radioanal. doi: 10.1007/s10967-015-4178-2

Neutron flux

Thermal neutron flux determination

The average **thermal** neutron flux in the concrete matrix is monitored by the steel drum and calculated from the count rates of the ^{54}Fe & ^{56}Fe prompt gamma-rays [2].

$$\bar{\Phi}_{th,Matrix} = (1.4 \pm 0.3)10^3 \, n \, cm^{-2} s^{-1}$$

Fast neutron flux determination

The average **fast** neutron flux in the steel drum is monitored by the steel drum and calculated from the count rates of the delayed gamma-rays of ^{56}Fe [$^{56}Fe(n,p)\,^{56}Mn$ – 1811 keV] by fast neutron activation.

The average **fast** neutron flux in the concrete matrix is calculated with the following formula using the a priori information of the elemental composition by the prompt gamma-ray analysis:

$$\bar{\Phi}_{fast,Matrix} = \bar{\Phi}_{fast,Drum} \, e^{-\Sigma_{14,5MeV} \, d}$$

$$\bar{\Phi}_{fast,Matrix} = (14.8 \pm 0.4)10^3 \, n \, cm^{-2} s^{-1}$$

[2] Mauerhofer E, Kettler J International Patent Application WO 2012/010162 A1, Australian Patent AU201128018, Chinese Patent ZL201180035866.0

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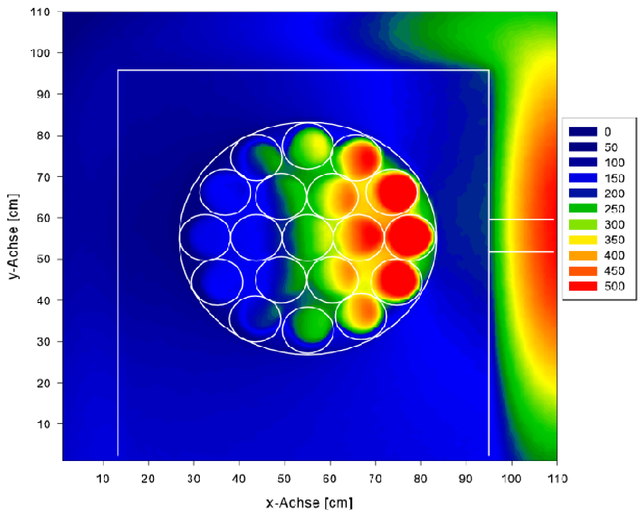

Result – Quantification

Element / Isotope	PGNAA Small sample [4]	CNAA-Prompt Massive sample	CNAA-Delayed Massive sample
H / ^{1}H *prompt*	1.40 ± 0.07 %	1.4 ± 0.1 %	-
B / ^{10}B *prompt*	95 ± 2 ppm	92 ± 10 ppm	-
O / $^{16}O(n,p)^{16}N$	47.3 ± 2.5 %	-	48.5 ± 0.7 %
Na / $^{23}Na(n,\alpha)^{20}F$	0.52 ± 0.11 %	-	0.6 ± 0.1 %
Al / ^{27}Al *prompt*	4.9 ± 0.1 %	4.9 ± 0.8 %	-
Al / $^{27}Al(n,\alpha)^{24m}Na$	4.9 ± 0.1 %	-	4.7 ± 0.6 %
Si / ^{28}Si *prompt*	17.4 ± 0.2 %	17.1 ± 0.8 %	-
Si / $^{28}Si(n,p)^{28}Al$	17.4 ± 0.2 %	-	18.7 ± 1.1 %
K / ^{39}K *prompt*	1.38 ± 0.06 %	1.40 ± 0.08 %	-
Ca / ^{40}Ca *prompt*	23.3 ± 0.6 %	22.4 ± 1.1 %	-
Ca / $^{48}Ca(n,\gamma)^{49}Ca$	23.3 ± 0.6 %	-	21.1 ± 1.2 %

[4] Zsolt Révay: Results of the PGAA Measurements of three CFK Samples and three Cement Samples, Hungarian Academy of Sciences, Institute of Isotopes, Budapest, Konkoly-Thege Miklos utca 29-33. 1121 Hungary, 12.07.2010.

Limit of detection - LOD

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Limit of detection (3σ) for chemotoxic elements for the massive concrete samples (homogeneous distribution):

Element	Eγ (keV)	LOD Prompt	LOD Delayed
Cd	558.3	3.2 ± 0.3 ppm	-
Hg	1693.3	146 ± 13 ppm	-
Pb (prompt)	7367.8	8.1 ± 0.7 %	-
Pb (delayed)	567.7 1064.7	-	0.58 ± 0.10 %

→ Better LOD for Lead (factor 10) using delayed gamma-rays.

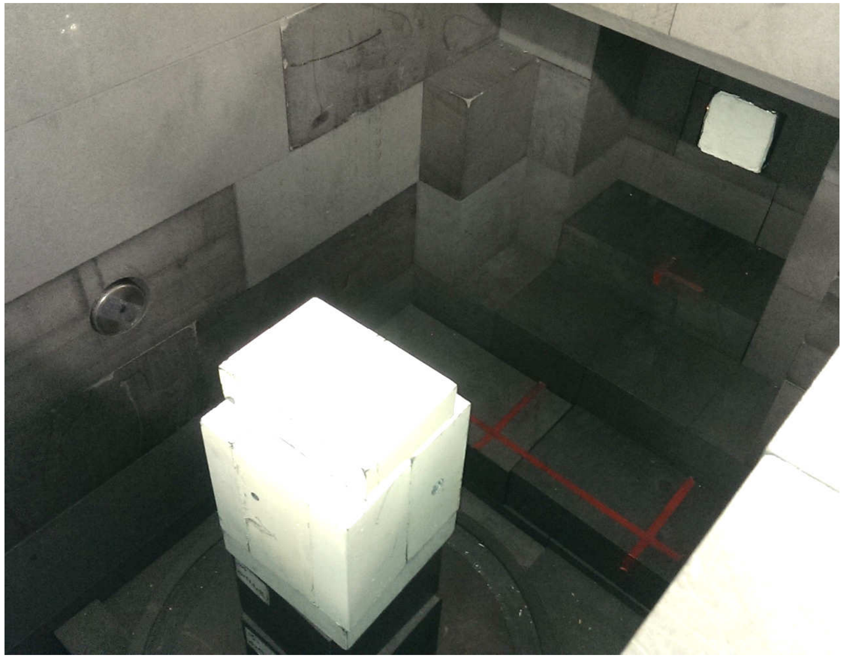
Results – Massive Lead Sample

Characterization of a large lead sample using delayed gamma rays of the short-lived isotope ^{207m}Pb induced by (n,2n)-reaction with fast neutrons.

Sample description:

m_{Pb} = 101.4 kg

H x W x D = 300 x 200 x 200 mm



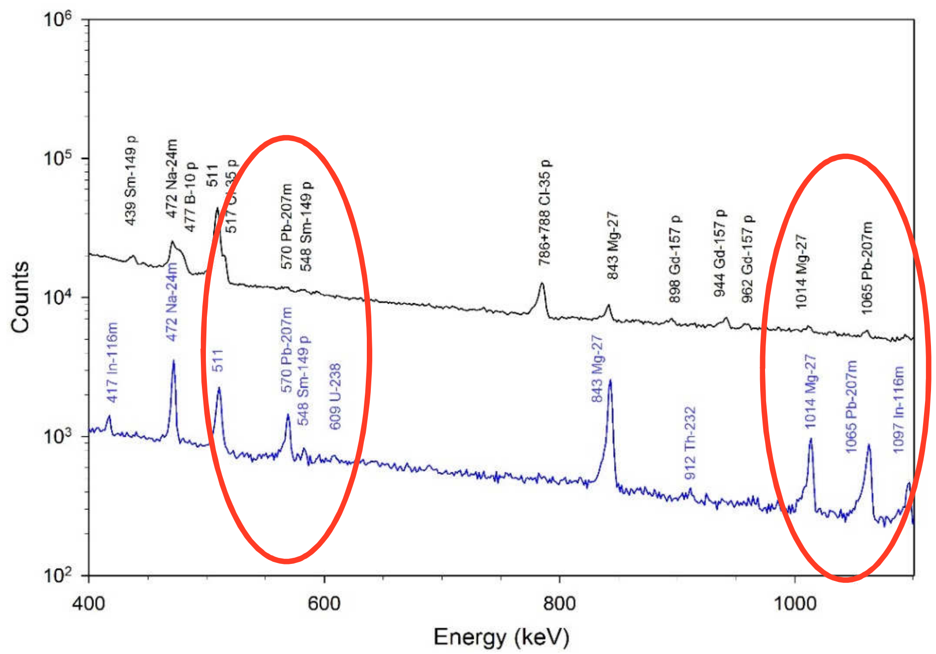
Measurement parameters

- $n_{Emission} = 7.2 \pm 0.9 \cdot 10^{7} \mathrm{n\,s^{-1}}$
- $t_{Pulse} = 2\,ms$
- $T_{Repetition} = 40\,ms$
- $t_{Gate,prompt} = 18\,ms\ (Acquire)$
- $t_{Gate,delayed} = 20\,ms\ (Acquire)$
- $t_{Livetime} = 3600\,s$

Results – Massive Lead Sample

Qualitative results of the characterization of a large lead sample.

Reaktion	E_γ (keV)	Peak-to-Back Prompt	Peak-to-Back Delayed
$^{208}Pb(n,2n)^{207m}Pb$	569.7 d	0.06	0.48
$^{208}Pb(n,2n)^{207m}Pb$	1064.7 d	0.05	0.39
$^{207}Pb(n,\gamma)^{208}Pb$	7367.8	0.04	-



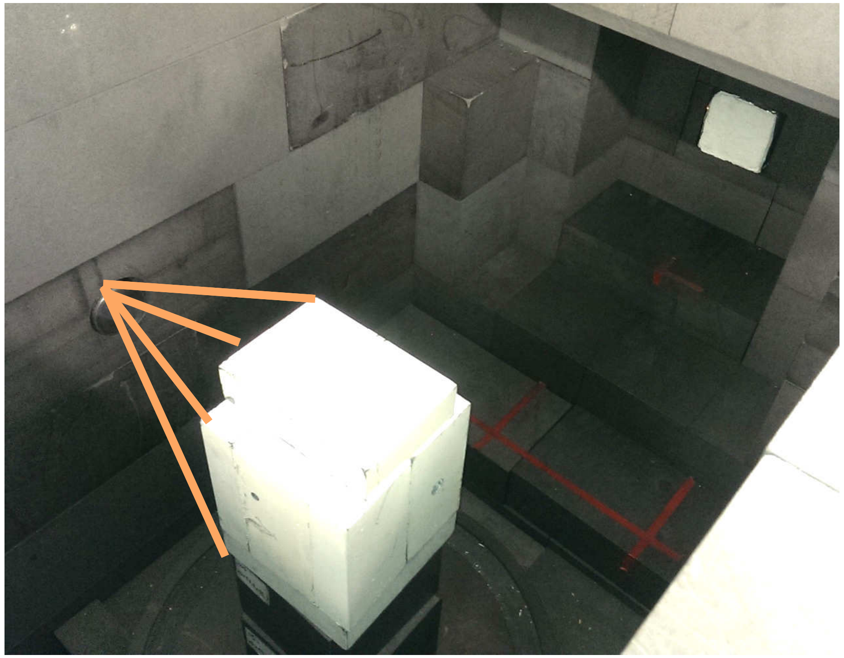
→ Peak-to-Background ratio could be increased for the delayed gamma-rays up to a factor of 8.

Mitglied der Helmholtz-Gemeinschaft

Results– Massive Lead Sample

Simple model for quantification:

- Assuming the fast neutron flux at the sample.
- Gamma-Self-Shielding for a plate [5].
- Neutron-Self-Shielding for a plate [6].
- Photopeak-efficiency of a point source in the middle of the sample.



Result:

$m_{Pb,det} = 128 \pm 11$ kg
(26 % overestimated)

[5] C. Agarwal, S. Poi, A. Goswami, M. Gathibandhe, R.A. Agrawal: A simple numerical method for gamma-ray self-attenuation correction for samples of common geometries, Nuclear Instruments and Methods in Physics Research A 597 page 198–202, 2008.

[6] A.Trkov, G. Zerovnik , L. Snoj, M. Ravnik: On the self-shielding factors in neutron activation analysis, Nuclear Instruments and Methods in Physics Research A, 610, page 553–565, 2009.

Contents

Conclusion

- CNAA (with prompt & delayed gamma-rays) provides additional information on the elemental composition.
- Die-Away Time is required for PGNAA to correct background interferences.
- LOD of Lead improved using (n,2n)-reactions with fast neutrons.
- First attempt to quantify a massive lead sample with (n,2n)-reactions using a simple assumption gives reasonable results.

Outlook

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Work done:

✓ Quantification of mixed waste samples (concrete and PE) [7].

In work:

- Development of an <u>analytical model</u> for the prediction of the thermal neutron die-away-time for mixed waste samples.
- Measurements of <u>local concentrated</u> toxic elements like Cadmium in mixed waste samples (concrete and PE).

[7] F. Mildenberger, E. Mauerhofer (2016) Prompt gamma neutron activation analysis of large heterogeneous samples composed of concrete and polyethylene, J Radioanal Nucl Chem. doi 10.1007/s10967-016-4743-3

Any questions?