Ph. D. THESIS

by

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APPLICATION OF TIME-DEPENDENT PROCESSES IN THE PROMPT-γ ACTIVATION ANALYSIS

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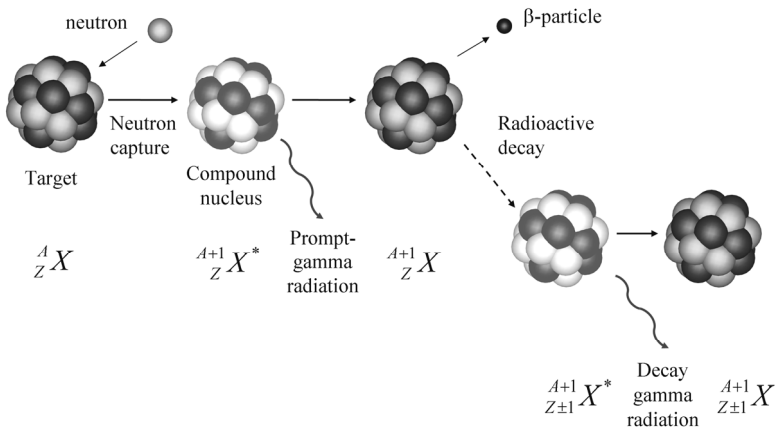
INTRODUCTION

Prompt-gamma activation analysis (PGAA, PGNAA) is a nuclear analytical technique for non-destructive determination of elemental and isotopic compositions. The sample is irradiated in a neutron beam and the gamma-rays from the radiative capture are detected. All elements can be analyzed, without any prior information on the analyte. Contrary to the conventional neutron activation analysis (NAA), the irradiation and the detection is simultaneous. The energies and intensities of the peaks are independent of the chemical state of the material; hence the analytical result is free of matrix-effects. Both neutrons and gamma-rays are highly penetrating, therefore – in contrast to many instrumental elemental analysis techniques – the average composition of the entire illuminated volume is obtained. Every step of the measurement and the evaluation can be described with statistical methods, and the uncertainties of the concentrations can be readily estimated from one measurement.

The prompt-photons are emitted in a very short time after the capture and their intensity is proportional to the actual neutron flux. Some secondary processes, like radioactive decay and the subsequent emission of delayed gamma-rays, are inherently time-dependent. These are also suitable for use in quantitative analysis, and sometimes offer even better sensitivities and limits of detection than the prompt peaks.



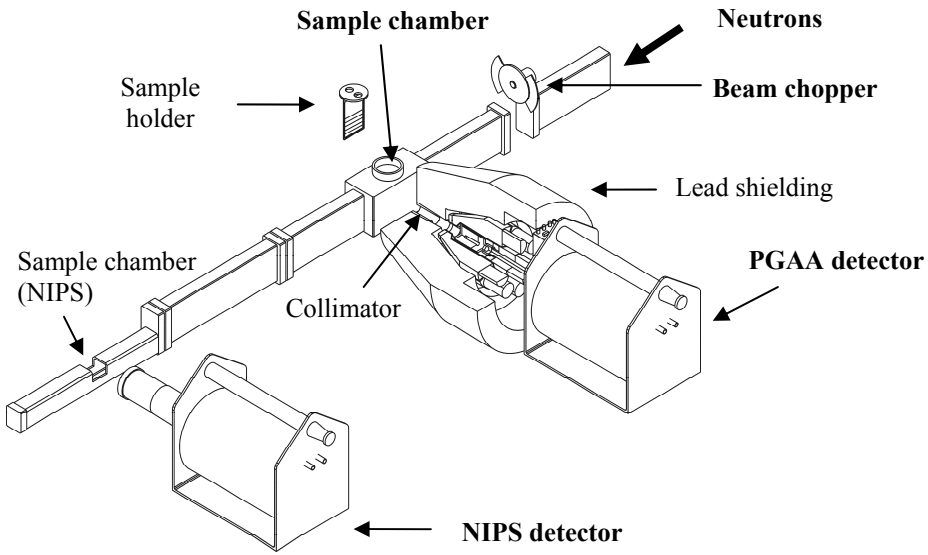
The sources of the analytical signal in PGAA

Following neutron capture on some light elements, charged particles may also be emitted. The most important case is with boron, where an energetic alpha particle and $^{7}Li^{*}$ are released [$^{10}B(n,\alpha\gamma)^{7}Li^{*}$ reaction]. Due to the Doppler-effect the peak of the photon emitted by the moving $^{7}Li^{*}$ gets broadened. The lifetime of the excited $^{7}Li^{*}$ and the deceleration time are comparable, and hence the matrix influences the actual peak shape. The high cross-section of this reaction makes PGAA a leading and very sensitive technique for determination of boron.

My Ph.D. work was to investigate time-dependent processes occurring in PGAA, and utilize them for better precision and a more reliable analysis. The characteristic times of the phenomena studied here varied between picoseconds to several hours; hence different methods were involved. The methodology used for the routine analyses had to be further developed or replaced.

EXPERIMENTAL METHODS

The PGAA laboratory at the Budapest Neutron Center was established in 1995. The neutrons from the research reactor pass through a "cold source" filled with liquid hydrogen, and than neutron guides transport them to the research instruments. Two detectors are installed at the PGAA facility. The first is a Compton-suppressed high-purity germanium (HPGe) detector with both active and passive shielding. This setup is used in the routine analyses. The other is a flexible arrangement with one or more detectors.



The sketch of the Budapest PGAA and NIPS facilities

The neutron flux at the sample position is approx. 3×10^7 $cm^{-2}s^{-1}$. Typically 0,5–2 gram of solids or liquids are measured. The acquisition times are between a few hours and 1 to 2 days, depending on the composition. The signals are processed with complex analogue electronics. The spectra are evaluated with the Hypermet–PC spectroscopy software, while the concentrations are calculated using an in-house developed Excel-macro.

The detection limits of the elements differ by many orders of magnitude. Constituents with high sensitivity (e.g. B, Cd, Hg, Sm, Gd) can be quantified at our facility even at the level of 0.01 ppm, while others with small cross-sections (e.g. Be, C, O) can be determined only as major components.

THESES

1. I investigated the performance of the digital signal processing in the PGAA.

The digital signal processing (DSP) is a recent technology in gamma-spectrometry. In contrast to the analogue electronics used for decades, the new devices digitize the output of the preamplifier signal and all further signal shaping is done on the data stream, using numerical algorithms. I tried to benefit from the advantages of this approach.

Since there were no published tests of the DSP modules with PGAA in the literature, my first task was to characterize their performances. The PGAA requirements are more demanding than most typical applications. The Inspector 2000, DSA-2000, DSP-2060 instruments made

by Canberra and the model Polaris of XIA were tested. Two series of measurements were done, with resolution- and throughput-optimized settings. The results were compared to those from the analogue system.

I investigated the energy-resolution of the instruments at different count rates and settings, as well as their time-stability and noise-sensitivity. The resolution was found to be worse than with the analogue system, when used over the large energy range of PGAA. The noise-related FWHM component increased almost linearly as the gain was lowered [1], but the slope was different for each model. The XIA Polaris and the DSP-2060 were found to be the best in these tests.

When settings for best resolution was used, the FWHMs were almost count-rate independent in the range of 10 000–40 000 cps with Polaris, but where increased by 1 keV with DSPs of Canberra. The spectral peak shapes were close to the ideal Gaussian, unlike peaks recorded by the present analogue system. The better throughput makes it possible to measure more active samples, reduce the necessary beam time and increase the throughput of the lab. Thanks to the accurate dead-time correction in MCA mode, absolute measurements can also be performed.

The gain showed daily periodicity in long measurements that could be related to the fluctuation of the ambient temperature. The shift of the peak positions were only about 20 ppm, and therefore can be neglected in practice [1]. The digital systems were unexpectedly sensitive to both external electronic and mechanical noise.

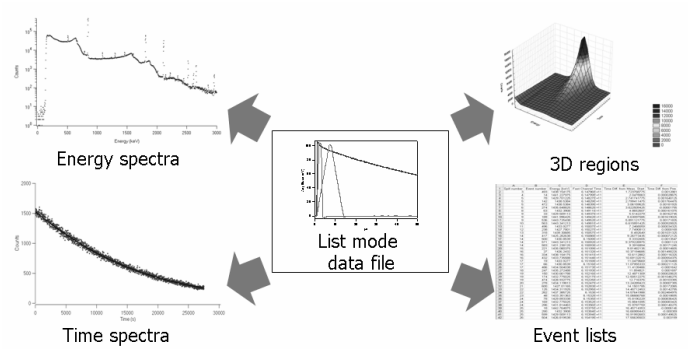
Many of the advantages offered by the digital technology (flexibility, stability, peak shape, PC control) were already implemented in the systems we tested. Problems with the resolution, noise sensitivity and the incompatibility with older detectors are still persistent when applied in PGAA.

2. I worked out the time-resolved gamma-spectrometry. I proved that sophisticated data analysis can be done on the list-mode data

Some spectral interferences between elements can be resolved in PGAA by considering energy and time information simultaneously. The flexibility of conventional time-dependent measuring systems (e.g. Multichannel Scaler, MCS) is limited and multiple measurements may be required to completely characterize the sample. A more sophisticated approach is proposed, based on the so-called list-mode feature of the XIA Polaris digital signal processor.

During the data acquisition, the energy and the detection time of each event are recorded and the data are later analyzed off-line. This separation of acquisition and evaluation minimizes the information-loss during the measurement, while offering greater flexibility. I created a data analysis program that reads in the records from the event stream, and classifies them according to predefined criteria. Energy spectra of 64k channels, time spectra for each peak, and energy-time-intensity matrices can be generated simultaneously. A time-dependent background-correction was performed for the peaks, using the counts in the neighboring regions (decay-curve method for singe energy-region) [4]. I derived multivariate functions to fit the above mentioned 3D data matrices [6].

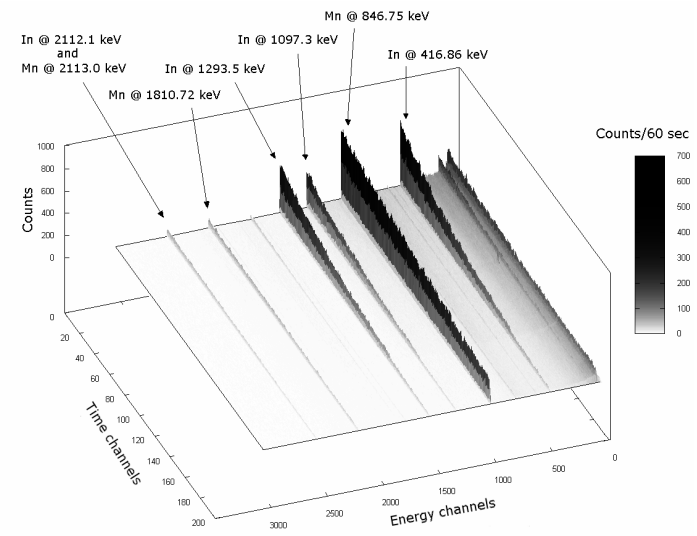
Due to significant changes in the incoming count rate during the measurement, accurate dead-time correction is necessary. The Polaris did not offer this possibility in list-mode; hence it was done as part of the off-line analysis. Among many possibilities examined, a semi-empirical formula was found to be the most useful, based on the known behavior of the instrument's subsystems. This has been experimentally validated at both constant and varying count rates [3, 4].



The outputs of the data processing

Demonstration measurements were done with short- and medium-lived radionuclides (^{28}Al, ^{52}V, ^{20}F, ^{128}I, ^{116m}In, ^{56}Mn, ^{64}Cu, ^{24}Na), where the list-mode approach was found to be applicable. Half-lives were determined from the decay curves with nonlinear least-square fits. The results were in good agreement with the literature [4]. The uncertainties of the decay-curve method and the 3D fitting were compared with that from the well-known MCS method on the same dataset. It was found that the new procedure can improve the precision by a factor of 2–6 over the results of the MCS method. The half-life uncertainties were about 10% lower for the 3D fit than using the decay curve evaluation. The former was especially advantageous in case of low statistics [6].

I proved that peaks overlapping in the energy spectrum can be quantitatively decomposed by also considering their half-lives [4, 6]. This was demonstrated on a sample containing In and Mn, where the interference between peaks at 2112.1 keV and 2113.0 keV was successfully resolved.



The energy-time-intensity histogram of a list-mode data file.

3. I derived formulas for chopped-beam PGAA.

The decay peaks of radionuclides produced during the irradiation are also used in the quantitative analysis. However, the numerous prompt peaks increase the possibility of spectral interference, while the high baseline, due to the Compton-plateaus from higher-energy prompt peaks, raises the detection limits of the decay peaks well above the values calculated from the peak areas alone. Therefore the separation of the decay events from the prompt events is useful, and is accomplished by taking advantage of their different time-behavior. The use of a beam chopper offers this possibility. When the beam is open, the usual prompt-gamma spectrum is collected, while, when no neutrons are present, only the decay-gamma radiation is detected with a substantially lower background.

I simplified the formulas of cyclic neutron activation analysis for use in chopped-beam PGAA. I calculated the in-beam saturation factor (B) for branching activation (Type IV. nuclides) [8, 9].

4. The partial gamma-ray production cross-sections and k_0-factors for 16 short- and medium-lived radionuclides were determined with chopped beam PGAA. I identified the elements for which detection limits may be lowered this way.

Recently a redesigned beam chopper was installed at the PGAA facility. I set up electronics to concurrently acquire two spectra, one in the open and the other in the closed phase of the chopper cycle [8].

I measured the partial gamma-ray production cross-sections (σ_γ) and k_0-factors for 16 short- and medium-lived radionuclides, using stoichiometric compounds. Internal standardization was applied to calculate the σ_γ or k_0 for the peak of interest: its intensity is directly compared to that of another peak with accurately known σ_γ value and good counting statistics. Such comparator lines were the 2223-keV peak of hydrogen, the 1951-keV line of chlorine, the 1884-keV line of nitrogen, the 841-keV line of sulphur, and the 4945-keV line of carbon.

1–3-gram portions of the powder samples or 1–2 ml of liquids were used as targets. The neutron beam was collimated to a small spot to approximate a point source geometry, and to keep the count-rate and consequently the dead-time low. Whenever it was possible, the sample chamber was evacuated to further reduce the background.

At the present stage of the work, the emphasis was on determining the data of most intense peaks of each investigated radionuclide with a

typical accuracy of 2 %. Therefore, for their weaker peaks the uncertainties are often higher, about 3–7 %. The general agreement with the k_0-values available in the literature is good; the Z-scores are mostly within the ±2 band [9]. For the nuclides ^{24}Na, ^{28}Al and ^{128}I, slight deviations were found from the k_0-NAA recommendations, while other references seem to confirm our values. Special care was taken to quantify the sources of uncertainties, following the ISO guidelines.

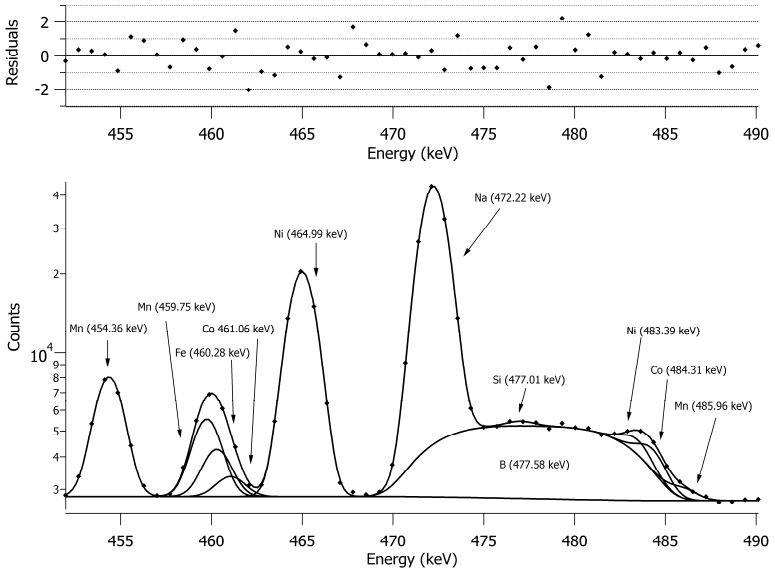
The chopped-beam PGAA makes it possible to lower the detection limits for the following elements: F, Na, Al, Sc, V, Mn, Se, Br, Rb, Ag, In, I, Hf, Au, Er, Yb. For about 20 more nuclides the decay lines are weak and therefore improvement can be achieved only in the presence of a very intense matrix spectrum. I proposed a decision criterion based on the Peak-to-baseline ratio to decide whether to use chopped-beam or conventional PGAA method.

5. A procedure was worked out and experimentally validated to fit the boron peak and resolve interferences.

The spectrum region with the broadened peak of boron can be evaluated only with special methods. The two solutions proposed in the literature are the reference peak method and fitting with semiempirical functions. In the first case, the net counts of the boron peak region (including the interferences) are summed up, and other peaks of the interfering elements are used to subtract the contribution of overlapping lines. Alternatively, the counts in the region can be fitted with a model function, that includes terms for the background, the boron- and other gamma peaks as well. None of the existing peak fitting methods proved to

be appropriate for our spectra, hence improvements were necessary. A detailed response function, more sophisticated background terms and the effect of the energy-dependent efficiency were included. A computer program was prepared to perform the fit efficiently.

Validation experiments were done with test samples and with six different setups. The results of peak fitting and the reference peak method were compared in case of the Boron-Sodium interference. Good statistical agreement was found. The matrix-dependence of the peak shape was investigated on many real samples. Finally the procedure was successfully applied in the analysis of geological and dosimetrical samples [5, 7].



The 450–490-keV spectrum region of the Dhrumsala meteorite

APPLICATION PERSPECTIVES

We intend to integrate the results of this work into the daily procedures of our laboratory, further improving the accuracy of the analytical results.

We have already utilized the decay peaks to lower the detection limit of Th in a series of measurements on industrial samples. Following the prompt-measurement, decay spectra were recorded at close-in geometry. The complete analysis could be done only by combining the results from the two spectra.

In our opinion, the advantages of the list-mode are not restricted to the PGAA. Wherever γ-radiation with changing activity has to be measured, the approach presented here might also be useful. (e.g. short-time NAA). Similarly, it seems to be quite applicable for scanning objects (γ-imaging, medical diagnostics), if there is a strict relation between time and position. Some practical problems are still to be solved to extend the available count-rate domain and to make it practical in detecting faster time-dynamics.

The chopped-beam PGAA, besides its capabilities in complementing the routine measurements, can be an important methodological link between PGAA and reactor-NAA. The two methods determine the same quantities with completely different techniques. Comparing results can help in harmonizing nuclear data by revealing possible biases.

LIST OF PUBLICATIONS

Research papers:

1. **L. Szentmiklósi**, T. Belgya , Zs. Révay, G.L. Molnár: Digital signal processing in prompt-gamma activation analysis, *J. Radioanal. Nucl. Chem.* **264** (1) (2005) 229-234
2. Zs. Révay, T. Belgya, **L. Szentmiklósi**, G.L. Molnár: Prompt gamma activation analysis using a chopped neutron beam, *J. Radioanal. Nucl. Chem.* **264** (2) (2005) 277-281
3. G. L. Molnár**,** Zs. Révay, **L. Szentmiklósi**: New perspectives for very short-lived neutron activation analysis, *J. Radioanal. Nucl. Chem.* **262** (1) (2004) 157-163
4. **L. Szentmiklósi**, T. Belgya, G.L. Molnár, Zs. Révay: Time resolved gamma-ray spectrometry. (*J. Radioanal. Nucl. Chem.* **270** (2), in press)
5. **L. Szentmiklósi**, K. Gméling, Zs. Révay: Fitting the boron peak and resolving interferences in the 450-490 keV region of PGAA spectra. *J. Radioanal. Nucl. Chem.* **270** (2), in press)
6. **L. Szentmiklósi**, Zs. Révay, G.L. Molnár: Three-dimensional data processing for the time resolved gamma-ray spectrometry, *J. Radioanal. Nucl. Chem.* **265** (2) (2005) 213-219.
7. **L. Szentmiklósi**, Zs. Révay, R. Chobola, P. Mell, S. Szakács, I. Kása: Characterization of $CaSO_4$-based dosimeter materials with PGAA and thermoluminescent methods, *J. Radioanal. Nucl. Chem.* **267** (2) (2006) 415-420
8. **L. Szentmiklósi**, Zs. Révay, T. Belgya: An improved beam chopper setup at the Budapest PGAA facility (submitted, *Nucl. Instr. Meth. B* – IRRMA-6 conference proceedings)
9. **L. Szentmiklósi**, Zs. Révay, T. Belgya: Measurement of partial gamma-ray production cross-sections and k_0-factors for short-lived nuclides with chopped-beam PGAA, (in press, *Nucl. Instr. Meth. A* – 4^{th} k_0-Users Workshop Proceedings)

Posters:

10. T. Belgya, Zs. Révay, **L. Szentmiklósi**, M. Lakatos: The application of a digital spectrometer in PGAA (International Topical Meeting on Industrial Radiation and Radioisotope Measurement Applications (IRRMA) 5, 9–14 June 2002, Bologna, Italy)
11. **L. Szentmiklósi**, K. Gméling, Zs. Révay: Fitting the boron peak and resolving interferences in the 450-490 keV region of PGAA spectra. (Modern Trends in Activation Analysis (MTAA) 11, Guildford, UK, 20–25 June 2004)
12. K. Gméling, Zs. Kasztovszky, **L. Szentmiklósi**, Zs. Révay, Sz. Harangi: Geological use of prompt-gamma activation analysis: importance of the boron concentration in volcanic rocks from the Eastern- and Western-Pannonian volcanic fields. (Modern Trends in Activation Analysis (MTAA) 11, Guildford, UK, 20–25 June 2004)

Oral presentations:

13. Digitális méréstechnika a prompt-γ aktivációs analízisben: Conference series "Őszi Radiokémiai Napok" (Gyula, 16–18 October 2002)
14. Prompt-γ aktivációs analízis hideg neutronokkal: Hungarian Chemical Society (MKE) – Kémiai Előadói Napok (Szeged, 28 October – 1 November 2002)
15. First experiences with digital signal processing in Prompt-gamma activation analysis: IAEA Meeting on applications of PGAA (Budapest, 5 December 2002)
16. Digital signal processing in Prompt-gamma activation analysis, Methods and Applications of Radioanalytical Chemistry (MARC) 6, Kailua-Kona, USA, 7–11 April 2003.
17. Digitális méréstechnika a prompt-γ aktivációs analízisben, Scientific symposium of the Chemical Research Center, Hungarian Academy of Sciences, 28–29 May 2003.
18. Időfelbontásos gamma-spektrometria az aktivációs analízisben: Conference series "Őszi Radiokémiai Napok" (Balatonföldvár, 8–11 October 2003)
19. Időfelbontásos gamma-spektrometria, First Conference of PhD students at the Faculty of Chemical Engineering, BUTE, 26 November 2003

20. The time resolved gamma-ray spectrometry in the activation analysis, Modern Trends in Activation Analysis (MTAA) 11, Guildford, UK, 20–25 June 2004.
21. A bór csúcsalak vizsgálata és csúcsinterferenciák feloldása a PGAA spektrumok 450–490 keV-es tartományában, Conference series "Őszi Radiokémiai Napok" (Eger, 13–15 October 2004)
22. A bór csúcsalak vizsgálata és csúcsinterferenciák feloldása a PGAA spektrumok 450–490 keV-es tartományában, Second Conference of PhD students at the Faculty of Chemical Engineering, 24 November 2004
23. Investigation of short-lived nuclides with chopped-beam PGAA, 4th International k_0-Users Workshop, Madeira, Portugal, 11–14 September 2005.
24. A besugárzás során keletkező radionuklidok vizsgálata nyalábszaggatós PGAA módszerrel, Conference series "Őszi Radiokémiai Napok", Mátraháza, 12–14 October 2005