

PHD DISSERTATION THESISES

„DECREASING MATRIX EFFECT IN PGAA”

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1. Scientific background

Prompt-gamma activation analysis (PGAA) is a nuclear elemental analysis method, which makes e.g. inactive tracing possible.

Neutrons have no charge and therefore can penetrate any nucleus without interacting with its Coulomb field, and cause different reactions. The nucleus (with a probability characterized by its neutron absorption cross section) can absorb neutrons. The resulting highly excited compound nuclei has a very short life time (usually $<10^{-16}$ s) and decays by emitting a cascade of gamma photons. (**prompt-gamma photons**). In a number of cases the resulting nucleus is still instable and decays (usually with β -decay) with a longer life time while emitting more gamma photons. These decays continue till the nucleus reaches its stable state. Due to the individual level structure of every nucleus, the energy of the emitted gamma photons are characteristic of the nucleus, while their number is relative to the number of atoms in the sample. If a complex sample is irradiated with a neutron beam, this fingerprint allows the determination of its elemental composition from the measured spectra.

The main difference between prompt gamma activation analysis (PGAA) and the conventional neutron activation analysis (NAA) is the stage where gamma photons are detected.

In the case of **NAA** the sample is irradiated very close to the active zone of the reactor for a given period of time. The measurement takes place in a low background laboratory after some cooling time. This method can not detect the prompt gamma photons, so it can not be used if the resulting nucleus is stable or decays too fast. For selected elements the sensitivity can be increased by optimizing the irradiation and cooling time. NAA is widely

used for trace element detection. Due to its accuracy and ease of use, NAA stations can be found at almost all research reactors around the world.

In the case of **PGAA** the irradiation and the measurement is simultaneous, so this method can also detect prompt gamma photons. Because of this, PGAA spectra for real samples are much more complex and contain more peaks than the NAA spectra of the same sample, making the analysis more difficult.

PGAA transforms only a negligible amount of the sample, thus it is considered nondestructive. All elements except helium produce measurable prompt gamma radiation, so PGAA can detect practically all elements of the periodic table. In most cases neutrons penetrate the sample deeply, so PGAA provides the average elemental composition of the irradiated volume of the sample. PGAA requires minimal sample preparation, can produce instant results, and its precision increases with time. The detection limit (just like in the case of NAA) depends on the neutron capture cross section of the target element and the elemental composition of the sample. In several cases, even concentrations under 1 ppm can be measured, but in the presence of certain elements, the detection limit of other elements decreases substantially. This is called **matrix effect**. The most important elements causing matrix effect are Boron and Hydrogen.

Boron has a high neutron absorption cross section, so even a low concentration can cause big increase in the spectral background. Next to its Doppler shifted peak at 478 keV, it is common to find its double at 2×478 keV in the spectra. The neutron absorption cross section of Hydrogen is lower than boron's, but in biological samples and water solutions its high concentration causes similar matrix effect.

The first prompt gamma activation analysis facility was constructed in 1969 in Saclay; Grenoble was second in 1973. The most well-known PGAA instruments in the world are operated at KFA Juelich in Germany (23 MW FRJ-2 reactor), NIST in the USA (20 MW NBSR reactor), JAERI Tokai in Japan (20 MW JRR-3M reactor). Also two new ones are under construction: one in Munich, Germany, and one in Korea.

The most widely used detection instrument for PGAA is a Compton suppressed spectrometer, which greatly reduces the size of the continuum and of the escape peaks.

The Compton suppressed spectrometer consists of a high purity germanium (HPGE) detector surrounded by a multisegment BGO scintillator guard detector annulus. The detector assembly is surrounded by thick lead shielding. The gamma radiation emitted by the sample goes through lead disk collimators before hitting the germanium detector. If a gamma photon leaves the HPGE detector after a Compton scattering, the scintillator annulus will most probably detect it. To be sure, that only photo peak events are collected, the electronics must filter those events where both the HPGE detector and any segment of the scintillator annulus is fired at the same time. The back side of this setup is that, the sensitive volume of the detector is relative far from the sample (~20 cm).

A possibility that can theoretically compete with the traditional Compton suppression detection technique is the use of the γ - γ coincidence technique. In which case the sample is measured with two (or more) detectors, and only those events are counted, when the detectors are fired within a preset time limit. By choosing an appropriate time limit, we can suppose, that the signals are mostly from the same gamma-cascade.

2. Research goals

The decay scheme of Boron and Hydrogen contains no cascades, only one gamma line, so these elements may appear in a coincidence spectrum only by random coincidence. According to this the coincidence method is expected to decrease their matrix effect. My primary goal was to determine if the applicability of the $\gamma\text{-}\gamma$ coincidence method in those cases when the sensitivity of the Compton suppression detection technique decreases because of the matrix effect. I plan to use two high purity Germanium (HPGe) detectors.

I planned to create a $\gamma\text{-}\gamma$ coincidence PGAA setup, and the software required for its proper usage.

I planned to determine if the new setup is applicable for analytical purposes, and to find special cases where it can compete with the existing traditional method. I expected that, the closer geometry of the $\gamma\text{-}\gamma$ coincidence method can balance the lower efficiency of coincidence.

3. Experimental devices and methods

The PGAA studies at the Budapest research reactor started in 1993. Two measurement facilities operating parallel are set up on a neutron guide at 35 meters from the reactor. The super mirror neutron guides provide high neutron intensity and low background. In 2000 the cold neutron source was installed onto the neutron guide, increasing the neutron flux approximately by a factor of 20 (from $2 \cdot 10^6$ to $5 \cdot 10^7$) at both measurement facilities.

At the first facility we use a Compton suppressed spectrometer. The design of the facility allows the measurement of samples from a few milligrams to

many kilograms. Usually samples with a mass of a few grams can give good statistics spectra. Spectra are evaluated with the Hypermet-PC software developed at our institute. The elements (and isotopes) in the spectra are calculated automatically from the results of the spectrum evaluation with an Excel macro based on the k_0 method.

The second facility (NIPS) was designed according to the results and needs of my experiments. New measurements and methods can be tested and designed here, even with very close detector setups.

4. THESISSES

I. I adopted the g-g coincidence method for PGAA with two HPGe detectors for the first time in the world:

- a. Based on experiments I found an optimal geometry for the $\gamma\text{-}\gamma$ coincidence method: when the detectors are at the closest to the sample (covering maximum solid angle). And the mass of the sample is chosen to cause no substantial pile-up (~10 000 count/second was ideal in the case of the detectors used). The NIPS facility of the institute was designed according to these experiments.
- b. After testing many electronic setups I choose and set up one that provides reproducible measurements, and detects only a small amount of non coincidence events.
- c. I improved the software for the evaluation of the off-line recorded measurement results:
 - to define gates
 - and to create gated spectra

II. I worked out the concept of the regional coincidence:

In the case of peak to peak coincidence, coincidence with a photo peak is required. According to the peak to total ratio in the function of energy, at high energy this method rejects the majority of the events. In the case of regional coincidence, a part of the Compton background is also accepted. This way more events are got (so the peak statistics is better), but also more random coincidence events are counted in, increasing the background below the peak. I obtained the optimal setting (the part of the Compton background accepted) experimentally for every case investigated. And I found that the regional coincidence method substantially increased the efficiency of the γ - γ coincidence method in many cases.

III. I proved that the g-g coincidence method is capable of decreasing the matrix effect, and simplify the PGAA spectra:

- a. I proved with experiments that, by choosing the (regional) coincidence gates correctly the PGAA spectra can be simplified remarkably: background peaks and other irrelevant or disturbing peaks can be completely eliminated. As the processing is off-line; a distinct optimal gate can be defined even on every peak of the spectrum. This solution does not corrupt the comparability of the elements in a series of measurements.
- b. I demonstrated with test samples that peaks of the single-line sources (like Boron and Hydrogen) can be decreased by orders of magnitude or even eliminated completely with γ - γ coincidence method from the spectra even in cases of high concentration. It makes the evaluation of lower intensity peaks (that would otherwise be lost in the statistical fluctuation of the background) possible:

- The Boron double peak at 2×478 keV and its Compton background can be eliminated completely. The Boron peak at 2×478 keV and its Compton background can be decreased by orders of magnitude.
- The Hydrogen peak at 2223 keV and its Compton background can be eliminated completely.
- The back scatter peaks caused by the geometry of the setup can be eliminated completely.

Thus I proved that, the γ - γ coincidence method is capable of decreasing the matrix effect, and simplify the PGAA spectra.

- An industrial inactive tracing method of glass furnaces was developed at our institute recently. Gadolinium tracer is used for measurements of glass samples containing Boron. In this case, matrix effect is a real problem. With the usage of the coincidence method I succeeded to evaluate such Gadolinium peaks, that were neglected in the case of Compton suppression technique, because of the spectral interferences. Thus I demonstrated the usefulness of the method in the case of an industrial application.

IV. I proved that the γ - γ coincidence method can be used for analytical work and its sensitivity can compete with the traditional methods in certain cases :

- I made calibration curves by measuring known concentration sample series. I found that the peak counts are linear with the concentration even in the case of strong matrix effect. The parameters of this linear function are depending on the gates set. I concluded that the γ - γ coincidence method can be used for analytical work. And I found

that (just like in the case of Compton suppression technique) the detection limit differs for each element, and also depends on the matrix.

- b. I compared the $\gamma\gamma$ coincidence method with the Compton suppression technique, and the simple single detector measurement in the cases of different kinds of samples. I found that, in the low energy range ($E < 1\text{MeV}$) it is possible to find a gate setting for most peaks in every sample when the usage of the regional coincidence gives comparable or even better peak-background ratio. With the usage of higher efficiency HPGE detectors, this energy range can be broadened.

5. Possible usage of the results

An advantage of the $\gamma\gamma$ coincidence method is that it does not require special detector system like the Compton suppression unit. Although it requires preprocessing of the data, the final spectra is simplified till the level of automatic evaluation. The method can be used for automating routine measurements.

The method can also be used for portable PGAA measurements with greater efficiency detectors.

Because of the variability of the coincidence gates, an absolute calibration method would be very difficult, so a standard based relative method should be applied for the calculation of the concentrations.

6. Publications

A List of own publications, connected to the subject of the Ph.D. thesis:

- [1] Ember, P.P., Belgya, T., Molnár, G.L., **2002**. Improvement of the capabilities of PGAA by coincidence techniques, Applied Radiation and Isotopes **56**, 535-541. (Thesis-points: II, III, IV, V, VI)
- [2] Ember, P.P., Révay, Zs., Belgya, T., Molnár, G.L., Varga, Zs., **2001**. Inaktív nyomjelzés prompt gamma aktivációs módszerrel, Magyar Kémiai Folyóirat **107**, 438-443.
- [3] Ember, P.P., Belgya, T., Molnár, G.L., **2002**. Coincidence Measurement setup for PGAA and nuclear structure studies, Applied Radiation and Isotopes, **57**, 573-577. (Thesis-points: I, II)
- [4] Ember, P.P., Belgya, T., Weil J.L., Molnár, G.L., **2004**. A practical test of a γ - γ coincidence measurement setup for PGAA, Nuclear Instruments and methods B. 213, 406-409 (Thesis -points: III, V)
- [5] Belgya, T., Révay, Zs., Ember, P.P., Weil, J.L., Molnár, G.L., The cold neutron PGAA- NIPS facility at the Budapest Research Reactor, **2003**. 262-271. Capture Gamma-Ray Spectroscopy and Related Topics, World Scientific Pub Co Inc, Singapore.
- [6] Révay, Zs., Belgya, T., Ember, P.P., Molnár, G.L., **2001**. Recent developments in HYPERMET-PC, Journal of Radioanalytical and Nuclear Chemistry, **248**, 401-405.

- [7] Ember, P.P., Belgya, T., Molnár, G.L., **2000**. Coincidence method for determination of peak to total ratios of HPGe gamma-ray detectors, Budapest Neutron Centre Progress Report 1998- 1999, 114.
- [8] Ember, P.P., Belgya, T., Molnár, G.L., **2000**. Improvement of detection limit and element selectivity by coincidence techniques in PGAA; in Budapest Neutron Centre Progress Report 1998- 1999, 115.

Presentations in the subject of the thesis:

- [9] Ember, P.P., Belgya, T., Molnár, G.L., Csúcs/összes viszony vizsgálata a csúcs energiájának függvényében, Oszi Radiokémiai napok, Kecskemét, **1999**
- [10] Ember, P.P., Belgya, T., Molnár, G.L., A PGAA elemi érzékenységének növelése koincidencia technikával, Központi Kémia Schay Géza emlékülés, **2000**
- [11] Ember, P.P., Belgya, T., Molnár, G.L., A PGAA elemi érzékenységének növelése koincidencia technikával; Oszi Radiokémiai napok, Hévíz, **2000**
- [12] Ember, P.P., Belgya, T., Weil, J.L., Molnár, G.L., A practical test of a γ - γ coincidence measurement setup for PGAA, Poster on IRRMA-V conference in Bologna **2002**
- [13] Belgya, T., Révay, Zs., Ember, P.P., Weil, J.L., Molnár, G.L., The cold neutron PGAA NIPS facility at the Budapest Research Reactor;

Eleventh International Symposium on Capture Gamma-Ray Spectroscopy and Related Topics, Pruhonice near Prague, Czech Republic September 2 - 6, **2002**