Increasing the dynamic range for the analysis of boron in PGAA

Stefan Söllradl · Hanna Lührs · Zsolt Révay ·
Petra Kudejova · Lea Canella · Andreas Türler

Abstract Prompt gamma activation analysis (PGAA) is especially sensitive for elements with high neutron-capture cross sections, like boron, which can be detected down to a level of ng/g. However, if it is a major component, the high count rate from its signal will distort the spectra, making the evaluation difficult. A lead attenuator was introduced in front of the HPGe-detector to reduce low-energy gamma radiation and specifically the boron gamma rays reaching the detector, whose thickness was found to be optimal at 10 mm. Detection efficiencies with and without the lead attenuator were compared, and it was shown that the dynamic range of the PGAA technique was significantly increased. The method was verified with the analyses of stoichiometric compounds: TiB_2, NiB, PVC, Alborex, and Alborite.

Keywords Prompt gamma activation analysis · Boron analysis · High count rate · Gamma-ray attenuation

S. Söllradl (✉) · A. Türler
Laboratory for Radiochemistry and Environmental Chemistry,
Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland
e-mail: stefan.soellradl@frm2.tum.de

S. Söllradl · A. Türler
Department of Chemistry & Biochemistry, University of Berne,
Freiestrasse 3, 3012 Bern, Switzerland

S. Söllradl · Z. Révay · P. Kudejova · L. Canella
Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität
München, Lichtenbergstr. 1, 85748 Garching, Germany

H. Lührs
Fachbereich Geowissenschaften, Universität Bremen,
Klagenfurter Str, 28357 Bremen, Germany

Introduction

Prompt Gamma Activation Analysis (PGAA) is a multi-elemental nuclear analytical technique, allowing the detection of a broad range of elements simultaneously [1]. Due to the deep penetration of neutrons in typical cases, PGAA is a bulk method, i.e. it gives the average composition of the irradiated volume, which is independent of the shape or the physical form of the sample. The possible samples may range from bulky archeological objects down to samples with masses in the region of micrograms. However, for samples with high boron concentrations, this is only true for thin and homogeneous samples due to self-shielding. The analytical sensitivities in PGAA are matrix-independent, as they depend on the neutron-capture cross section, the counting efficiency and the neutron flux, as can be seen from the basic equation of activation in Eq. 1:

$$\frac{A}{\varepsilon t} = \frac{m}{M} N_A \sigma_\gamma \Phi \tag{1}$$

where A is the net peak area, ε is the counting efficiency, t is the live time of the measurement, m is the mass of the emitting nuclide, M is its molar mass, N_A is the Avogadro constant, σ_γ is the partial gamma-ray production cross section, and Φ is the neutron flux, and A/m describes the analytical sensitivity [1, 2].

However, the detection limit of a given element depends on the matrix, though the intensity of the signal is still matrix-independent. The minimum detectable area of a given peak is determined by the dominant ones in the spectrum, thus the area ratios of two close-lying characteristic peaks typically lie in a range of 10^{-3}–10^3. These six orders of magnitude can be regarded as a broad dynamic range. It can also be expressed in the unit of molar ratios (n_1/n_2), when the peak area ratio (A_1/A_2) is divided by the

neutron-capture cross section ratio ($\sigma_{\gamma 1}/\sigma_{\gamma 2}$), and the efficiency ratio ($\varepsilon_1/\varepsilon_2$), as can be seen from Eq. 2, derived from the above equation.

$$\frac{n_1}{n_2} = \frac{A_1}{A_2} \bigg/ \left(\frac{\sigma_{\gamma 1}}{\sigma_{\gamma 2}} \frac{\varepsilon_1}{\varepsilon_2} \right) \qquad (2)$$

Boron analysis is one of the major applications of the PGAA technique. However, due to the above mentioned limitations, boron as a major component is difficult to analyze. Boron has a very high cross section of 716 barn [3], which allows the detection of trace amounts down to ng/g. The activation of samples with relatively high boron concentrations may sometimes even saturate the spectrometer. If the neutron flux in such a case is reduced to lower the overall count rate to a reasonable level, the necessary counting statistics for other elements can be reached only with very long measurements.

Boron emits a single, uniquely broadened prompt gamma ray at 478 keV due the recoil of the α–particle, emitted in the $^{10}B(n,\alpha\gamma)^7Li$ neutron capture reaction. In contrast to this, all the other elements have most of their prompt gamma lines above this energy. If boron becomes a major component in the sample, the counts in the spectrum originating from it dominate not just the first about 500 keV of the spectrum, but, due to the appearance of random-coincidence sum peaks, up to 1,000 keV, or even 1,500 keV, which makes the analysis of the higher-energy peaks rather complicated. To reduce the misbalance between the elevated low-energy part from the boron and the rest of the spectrum, a lowering of the counting efficiency in this energy range can help. This can be achieved by the attenuation of the gamma rays in heavy metals like lead.

Based on the Lambert–Beer law, the gamma-ray transmission through lead sheets with different thicknesses was calculated for different energies (Eq. 3):

$$\frac{I_x}{I_0} = e^{-\left(\frac{\mu(E)}{\rho_{Pb}} \right) \rho_{Pb} l} \qquad (3)$$

where I_x is the intensity the transmitted radiation, I_0 is the initial intensity, ($\mu(E)/\rho_{Pb}$) is the mass absorption coefficient, ρ_{Pb} the density of lead, and l is the thickness of the material. $\mu(E)$ is an energy-dependent coefficient, which involves the three main interactions between gamma radiation and matter: photoelectric effect, Compton effect, and pair production. The values for the mass absorption coefficients of lead at different energies were taken from the XCOM database [4]. Figure 1 shows the transmission values for different thicknesses of lead at different energies.

The goal was to modify the efficiency of the spectrometer in such a way, that the intensity of the boron peak
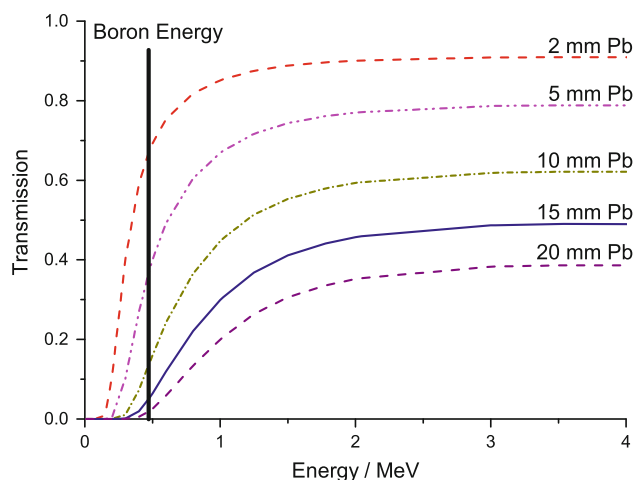

Fig. 1 Transmission of gamma rays through lead sheets with different thicknesses as a function of the energy. The energy of the boron gamma ray at 478 keV is indicated with a *vertical line*

is suppressed by at least a factor of 5 and the suppression at higher energies is less than a factor of 2. A layer thickness of 10 mm lead meets both criteria, as it can be read from the above plots. To test the method, samples with high boron concentrations were measured with and without this attenuator.

Methodology

The experiment took place at the PGAA facility at FRM II [5]. All samples were irradiated in a cold neutron beam with a thermal equivalent flux of 7.2×10^9 n cm^{-2} s^{-1}. A 60 % Ortec (n-type) PopTop HPGe-detector surrounded by a bismuth germanate (BGO) Compton suppressor and an Ortec DSpec-50 digital spectrometer were used to acquire the gamma spectra. An attenuator made of lead sheets with a total thickness of 10 mm was introduced in front of the detector as an addition to the standard PGAA setup [5] as shown in Fig. 2.
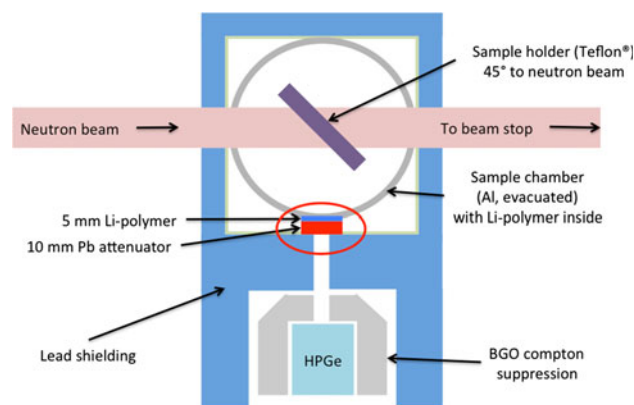

Fig. 2 Schematic view of the PGAA setup with the attenuator

The experiment was then conducted in three parts: first the transmission of the attenuator was determined using a chlorine-containing sample (a PVC foil), then the efficiencies were determined with and without the attenuator, and finally the method was validated with the quantitative analysis of boron containing samples.

Chlorine emits well-distributed gamma rays from 292 to 8578 keV [3] and has a relatively high thermal neutron-capture cross section of 33 barn [3]. To determine the transmission values of the attenuator, the ratios of the peak count-rates with and without the attenuator were determined at different energies (see Fig. 3). For the evaluation of the peaks in the two spectra, the acquisition software Maestro-32 by Ortec was used.

Then, the standard protocol for determining the detection efficiency was followed [2], with and without attenuator. Two radioactive sources (Ba-133 and Eu-152) and two neutron-induced prompt gamma reactions (activation of chlorine in the form of a PVC foil and of nitrogen in the form of a deuterated urea pellet) were used to compile the efficiency over the energy range from 50 keV up to 11 MeV. The spectra were evaluated and the efficiency functions were determined using Hypermet-PC [6].

In the last part of the experiment, boron-containing samples of known compositions were measured. They were all stoichiometric compounds: Alborite ($9Al_2O_3$–$2B_2O_3$, Alborite PF03, Shikoku Chemicals), Alborex ($9Al_2O_3$–$2B_2O_3$, Alborex Y, Shikoku Chemicals), NiB (15.6 wt% boron content, Sigma-Aldrich), and TiB$_2$ (31.1 wt% boron content Sigma-Aldrich) in the form of homogeneous powders. The spectra were evaluated with Hypermet-PC and the peak lists were loaded in the ProSpeRo [2] program, which is used for chemical analysis at the Garching PGAA laboratory. ProSpeRo assigns the fitted peaks to the elements based on the energy match. Then mass values for
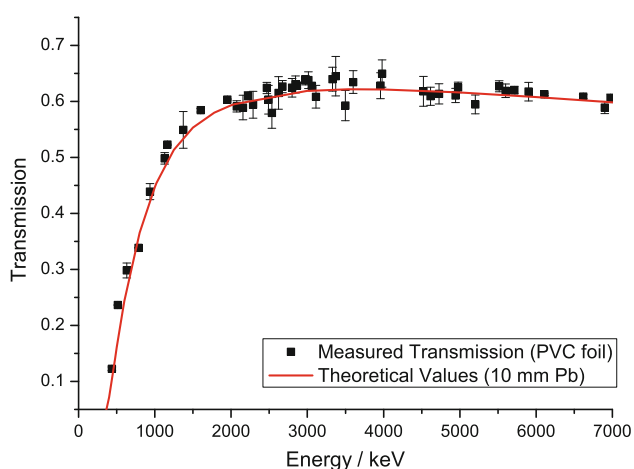
all the assignments are calculated according to Eq. 1. For every identified element, the mass values are then averaged [2] and a composition is calculated. The experimentally determined compositions were finally compared to the nominal compositions.

Results and discussion

Transmission of the attenuator and efficiency

First, the transmission function of the attenuator was determined with the PVC foil. The transmission value at a given energy was calculated as the ratio of the peak count rates from the spectra measured with and without the attenuator. All the peaks with uncertainties less than 3 % were taken into account. Figure 3 shows the experimental values of this measurement in comparison to the theoretical transmission curve (Fig. 1). The theoretical curve calculated for a 10 mm lead attenuator is in very good agreement with the experimental values. In the high-energy range of the gamma spectrum the transmission is about 60 % while at 517 keV a transmission of 24 % was achieved. Its value at 478 keV is slightly lower. Both of these values meet the requirements mentioned.

The efficiency curves determined in the second part of the experiment are shown in Fig. 4. If no attenuator is used, the efficiency reaches its maximum at approximately 100 keV with the value of about 10^{-4} and is somewhat lower in the range of the boron peak. When using the attenuator, the efficiency at a few hundred keV significantly lowers. The efficiency at 500 keV was reduced from
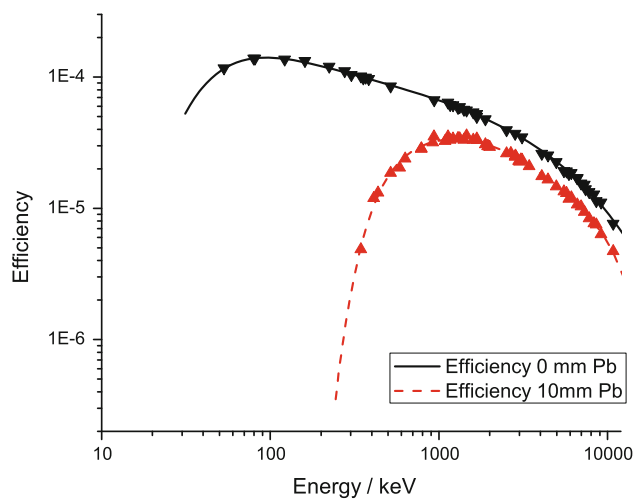
Fig. 4 Efficiencies with and without lead attenuator The *symbols* represent measured values with their uncertainty within *symbol* size. The *lines* show the determined, 6th order polynomial used as efficiency function for quantitative analysis. (Certified radioactive sources: Co-60, Eu-152 PGAA samples: PVC, Urea)

Fig. 3 Theoretical and experimentally determined transmission with a 10 mm lead attenuator in front of the detector. (Sample: PVC foil)

8.8×10^{-5} to 1.7×10^{-5} a reduction of slightly more than a factor of 5. At energies higher than 2 MeV the efficiency is just reduced to 65 % of the values determined without attenuator.

To illustrate the effect of the attenuator, the two spectra of Alborite measured with and without attenuator are shown in Fig. 5. When no attenuator is used, the count rate of the boron peak was 36,500 cps, while the total count rate was as high as 77,100 cps.

If two or even three boron gamma rays hit the detector within the resolution time, they are detected as one peak, having twice or three times the energy of the original peak, in the case of boron at the energies of 956 and 1434 keV. Especially the triple coincidence peak is very unlikely to appear when the count rate is low. The count rates of the double and triple coincidence peaks without the attenuator were 565 cps (1.5 % of boron peak) and 7.6 cps (0.02 % of boron peak), respectively. Thus the boron peak will be reduced significantly more than the other peaks.

If the attenuator is introduced in front of the detector, the count-rate of the boron peak could be reduced from 36,500 to 6,080 cps (i.e. with a factor of 6), resulting in a count rate of only 15.5 cps in the double coincidence peak (i.e. with a factor 36, and its area was just 0.25 % of the single boron peak). In this case, the count rate of the boron peak was already too low for producing a triple coincidence peak. The count rate of the main aluminum peak at 1778 keV in Fig. 5 was reduced from 31 to 18 cps (i.e. 58 % remaining intensity after attenuation).

The attenuator efficiently reduced the overall count rate as well: from 77,100 to 11,600 cps. While the boron peak was reduced by a factor of 6, the baseline around it was lowered by an order of magnitude. Thanks to this, more
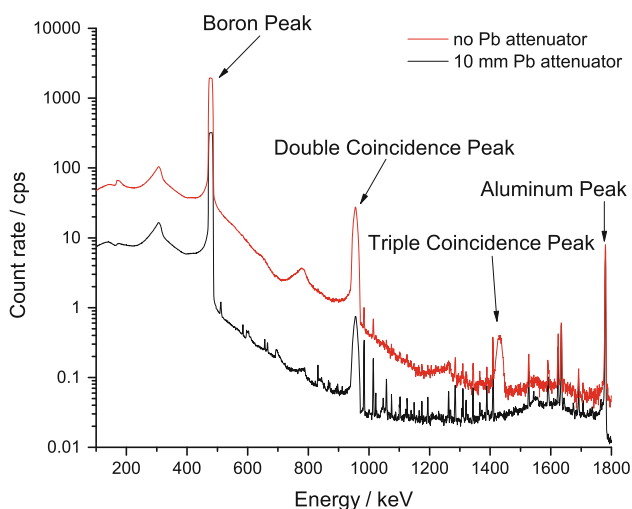
characteristic peaks could be detected, improving the determination of other components.

Analytical results

To verify the method, the compositions of boron containing samples were determined. 600 mg of Alborite and Alborex (both with the nominal compositions of $9Al_2O_3$–$2B_2O_3$) were measured with and without the attenuator under the same conditions as mentioned above. Though PGAA is a multi-elemental technique, oxygen is an element which can be barely detected due to its low neutron-capture cross section. Therefore, the spectra of these two oxides were evaluated based on their Al-to-B molar ratio, the nominal and measured values for Alborite with and without attenuator are given in Table 1.

If the attenuator is used, the determined molar ratio agrees well with the nominal value. However, if no attenuator is used, the ratio is 4.88 ± 0.07 which is significantly higher than expected. A possible reason for the missing counts from the boron peak could be the high count rate.

Theoretical calculations taking into account the double and triple coincidence peaks cannot entirely explain the lost counts. Adding twice the peak area of the double coincidence peak to the peak area at 478 keV yielded an Al/B ratio of 4.72 ± 0.07. The addition of the triple coincidence peak does not contribute significantly to this value, since its area is only 0.02 % that of the boron peak. The rest of the lost counts can be found in the Compton plateau between the double and the triple coincidence peaks, where a significant increase can be observed when no attenuator is used (Fig. 5). A precise quantification of this region is not possible, that is why the determination of boron as a major component without an attenuator cannot be used for reliable analysis.

For further validation of the method, Alborex, NiB, and TiB_2 samples were analyzed using similar masses and

Fig. 5 Spectra of Alborite with (*lower*) and without (*upper*) the attenuator

Table 1 Results of a quantitative measurement of Alborite with both methods and Alborex, NiB and TiB_2 with 10 mm lead attenuator

	Nominal value	Measured, no attenuator	Measured, 10 mm Pb attenuator
Sample: Alborite			
Al/B ratio	4.50	4.88 ± 0.07	4.55 ± 0.07
Sample: Alborex			
Al/B	4.50	–	4.49 ± 0.09
Sample: NiB			
Ni/B	1.00	–	1.00 ± 0.01
Sample: TiB_2			
Ti/B	0.50	–	0.48 ± 0.01

conditions as described above. The results are presented in the lower part of Table 1.

For boron concentrations up to 50 %, the use of an attenuator yielded excellent results. The nominal molar ratios could be confirmed with high precision for Alborex, Alborite, and NiB. In the case of TiB_2, a slight discrepancy was observed, however this cannot be called significant, as it agrees within twice the uncertainty limit. All other results were found to agree with the nominal compositions within the uncertainty limits, and have proven that the method can be applied to samples containing high concentrations of boron.

Conclusion

A method was developed for the measurement of high boron concentrations in PGAA, using a high neutron flux. The lead attenuator with a thickness of 10 mm in front of the HPGe-detector reduced count rates in the boron peaks by a factor of 6 and the count rate of the double coincidence peak by a factor of 36. The baseline was reduced by an order of magnitude. Thanks to this, further peaks could be detected in the low-energy up to energies of 1.5 MeV part of the spectrum, which were not observable when no attenuator was used.

Furthermore, the attenuator reduced the overall count rate leading to lower dead times and thus shorter measurements. The systematic error due to the random coincidence summing at high count rates could also be significantly reduced with this method. The use of an attenuator enables the analyses of samples containing boron as major components, and therefore it increased the dynamic range of the PGAA technique by about an order of magnitude.

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