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Prompt gamma activation analysis of samples in thick containers

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Two methods are presented for the prompt gamma activation analysis (PGAA) of samples in relatively thick containers. In the "invisible container" method, the prompt gamma-radiation from the activated parts of the container can be suppressed in the spectrum. The target can be analyzed simultaneously with the shielding material, when the target signal in the spectrum is stronger. Uranium containing compounds were analyzed in lead capsules.

Introduction

In prompt gamma activation analysis (PGAA) the sample is irradiated in a neutron beam and the emitted prompt gamma-radiation is collected in the form of an energy spectrum from which the elemental and isotopic composition of the sample can be determined. Both neutrons and high-energy gamma-rays penetrate through the material easily and thus PGAA is not sensitive to the form or to other physical conditions of the target. In most cases it yields the average composition of the irradiated volume.[1]

In most PGAA laboratories the neutron beam is collimated, and the gamma-detector, placed perpendicular to the beam, is also surrounded by a heavy shielding, transmitting to the detector only the gamma-radiation emitted at the sample position.[2] This double collimation is of great importance in this technique, as it keeps the direct neutron activation of the detector at minimum level.

This beam geometry defines an active volume in the cross-point of the beam and the direction of detection, where the sample has to be located.[3] Anything outside this active volume will not generate a significant signal in the collected spectrum. That is how a relatively low background level can also be achieved in spite of the massive structural materials in the vicinity of the sample.[4,5]

Two methods were developed and investigated for the chemical analysis of samples in containers. The first of them can be used for sample geometries where the container is outside the active volume. The second method is based on the fact that PGAA provides the average composition of the active volume of any inhomogeneous samples. A special emphasis is laid on thick containers, i.e., for containers with wall thicknesses not transparent to other instrumental analytical techniques, which cause a significant attenuation of incident neutron intensity and of the emitted gamma-radiation.

Experimental

The measurements were performed at the Budapest PGAA facility. The cold neutron beam has a thermal equivalent flux of $3 \cdot 10^7$ n·cm^{-2}·s^{-1} at the sample position, and its cross section is 2×2 cm^2. The sample chamber is made of aluminum, and is lined with ^{6}Li containing plastic to absorb scattered neutrons. It is capable of accommodating a sample of about 7×7×7 cm^3. The high-purity germanium detector, pointed toward the sample, is surrounded by an active and a passive shielding: a BGO scintillator, which serves as a Compton suppressor, and a further 10-cm thick lead shielding that covers the whole detector system. The diameter of the gamma-collimator is 2.4 cm. The sample-to-detector distance is 23 cm.[2,6] Within a 1.2-cm diameter circle around the center point of the sample holder the illumination of the detector is constant; while the detected intensity is gradually decreasing outside of it due to the partial illumination of the detector. The 2×2 cm^2 neutron beam cuts out of this region the so-called active volume, which is approximately 30 cm^3 in our case, and its effective volume (where the parts with partial illumination are taken into account with lower weight) is about 20 cm^3. The volume with full neutron and gamma-illumination is about 9 cm^3. Further details can be found in Reference 3.

Method of "invisible container"

Figure 1 shows the geometric arrangement of the "invisible container" method. The neutrons are transported inside an evacuated aluminum tube lined also with ^{6}Li containing plastic (^{6}Li-poly). In the middle of the sample chamber a cylindrical container is located. As can be seen, the container walls, activated by the neutrons, are outside both the full illumination zone (parallel beam marked with the symbol γ) and the partial illumination zone (within the dotted lines), while the wall sections directly in front of the detector are not activated by the direct neutron beam.

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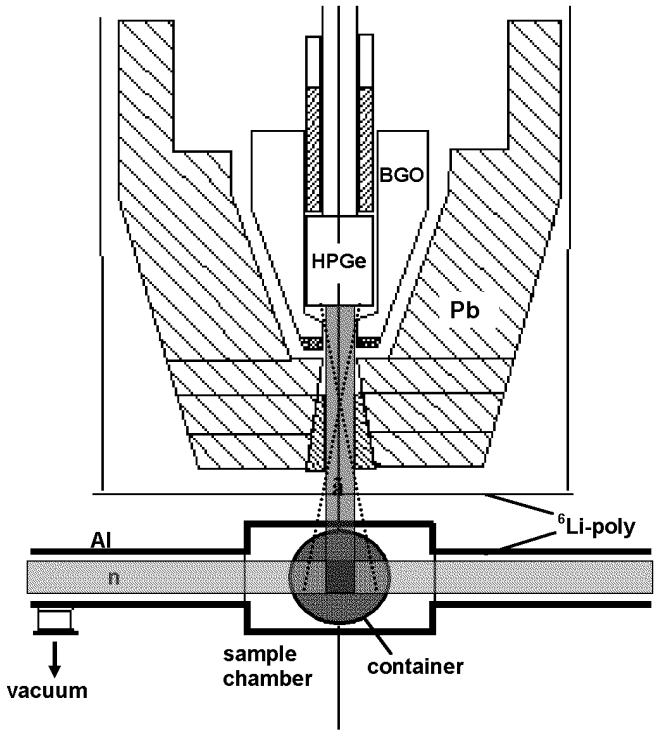

Fig. 1. Arrangement of the "invisible container" method

This technique is ideal for the PGAA measurement of gases pressurized into cylinders. The higher cross section ones can also be measured under atmospheric conditions. They can be measured in their original cylinder. This method was used during the acquisition of the elemental spectra of three noble gases (Ne, Ar and Kr) for the determination of the relative intensities of their prompt gamma-lines.[4] Ne and Kr were stored at 12-bar pressure in 1-liter aluminum cans with a wall thickness of 0.5 mm and diameter of 70 mm, while Ar was in atmospheric Teflon balloon of the approximate diameter of 10 cm. This method must be used in any case when the cross-section of the target material is much smaller than that of the container.

Simultaneous measurement of sample and container

When the sample geometry makes the suppression of the signals from the container impossible, one has to perform measurements similar to that of any inhomogeneous sample. For homogeneous samples the neutron self-shielding and the gamma self-absorption affect the count rates of each component to the same extent, thus in many cases (at least when determining mass ratios) these effects can be neglected. This assumption cannot be made for inhomogeneous samples. Targets inside of containers, however, form a special case of inhomogeneous sample, as the transmissions of activating neutrons and of gamma-rays through the wall of the container can be separated, and the attenuations, caused by the individual processes, can partly be calculated.

Certainly the target components can be measured well, if their signal is stronger at least in one region of the spectrum. This happens, if one or more of the following criteria is met: (1) when the mass of the sample is larger than that of the container (assuming similar cross sections); (2) when the average cross section in the sample is higher than that in the container (assuming similar masses); (3) when the maximum energy appearing in the spectrum is higher from the sample than from the container; and (4) when highly radioactive nuclides are formed in the sample, while they are not in the container, and the decay gammas are collected in a separate spectrum. This special case is discussed here because of the similarity with the in-beam activation techniques.

The combination of Cases (1) and (2) is the most common in the daily routine of PGAA, since we use thin, low cross section foils (typically Teflon or FEP) as packing materials. The binding energy of the neutron is energy dependent. That is the basis of Case 3. We can say as a general rule that light elements have their highest-energy peaks in the PGAA spectrum above 8 MeV (e.g., N: 10830 keV, Mg: 11092 keV, Cl: 8578 keV, Fe: 9296 keV, Ni: 8999 keV, etc.), while for

the heavy elements it is below 8 MeV (e.g., Pb: 7367 keV, Bi: 4604 keV). That is why many light elements can be detected in the presence of more massive heavy elements, because above the maximum-energy peak of the container the counts may originate only from the sample. Figure 2 illustrates the detection of N in a Ni container. In fact, the sample was a homogeneous Ni metal, which contained 4 weight% N, but the spectrum for the inhomogeneous composition or for the gas container would certainly be the same.

Performing a decay counting after the activation makes possible the measurement of elements like Na, Al, Cu, Ag, Au or U etc., e.g., in Fe, Zr or Pb. When measuring short-lived nuclides, the chopped-beam technique can be used.[7]

Detection of uranium in lead containers

Figure 3 shows the attenuation of gamma-rays through different materials all having the thickness of 1 cm. Mass absorption coefficients were taken from X-mudat code.[8] It can be seen that at higher energies the transmission values are almost constant: above 2 MeV they remain constant within 10% for any material. That makes possible a special application of PGAA that is based on the detection of high-energy gamma-rays. If we confine ourselves to determining the composition with a lower precision, we may simply use only the lines above 2 MeV corrected with the normal efficiency function. When analyzing bulk samples made of heavy metals, this practice is often followed in our laboratory, and it proved to be sufficient in most practical cases.

A method was developed for the detection of uranium in lead containers. It summarizes in a way all the above mentioned cases. The test materials were 1 g of uranyl acetate $[UO_2(CH_3COO)_2{\cdot}2H_2O]$ containing uranium in natural isotopic composition, and 0.1 g of U_3O_8 of highly-enriched uranium. The samples were sealed in a 25 μm thick Teflon foil, and irradiated in the cold-neutron beam. Then they were also measured in 0.5 and 1.5 cm thick lead containers.

To attain higher accuracy, the counting efficiencies for the given arrangements have been determined using our standard procedure.[9] Calibrated radioactive sources (^{152}Eu and ^{226}Ra) were put into the lead containers and then counted with our detector system. The high-energy part of the efficiency was determined using the Cl prompt gamma-lines[10] by activating a 1-g NaCl sample in lead containers. 8th-order polynomials were fitted to measured values with a simultaneous normalization of the chlorine and ^{226}Ra intensities to the most accurate ^{152}Eu values, as is described in Reference 9. The fitted functions for 0.5 and 1.5 cm lead containers are plotted in Fig. 4 together with the normal (unshielded) one being used in our routine analysis. As expected, the efficiency functions on a log-log scale run almost parallel above 2 MeV.

The curves of the shielded sources show lower values due to the attenuation of the gamma-rays in the shielding material. This decrease, however, does not include the attenuation of the neutron beam, as the data were normalized to a radioactive source, not to a sample activated in beam. Though lead has a relatively low capture cross section (0.154 barn), its scattering cross-section is relatively high (11.1 barn).[11] That is why a significant decrease in the count rates from the NaCl sample, activated in beam, was observed, as shown in Fig. 5. The local neutron flux inside the lead container can only be calculated by taking the multiple scattering into account. Since the actual neutron flux at sample position is unknown, only a relative measurement can be performed, i.e., the mass ratios of the visible components, or, when assuming that all components of the sample appear in the spectrum, its composition can be determined. The estimation of the total mass of sample inside the container needs further investigations.

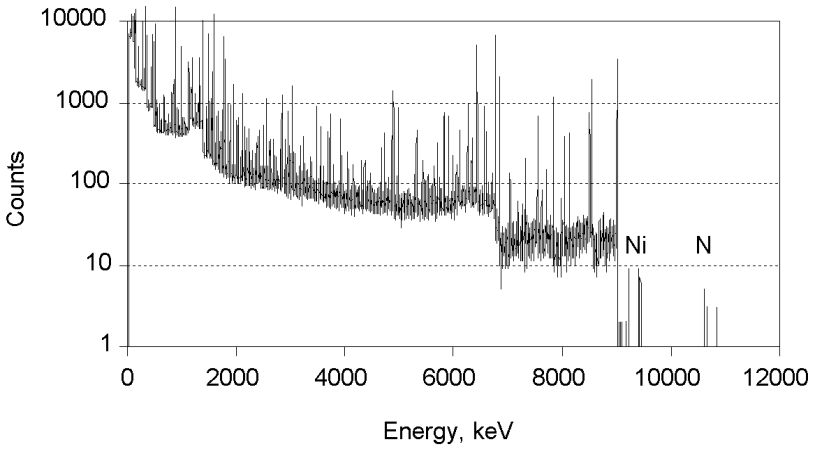

Fig. 2. PGAA spectrum of Ni metal sample containing 4 wt% of N

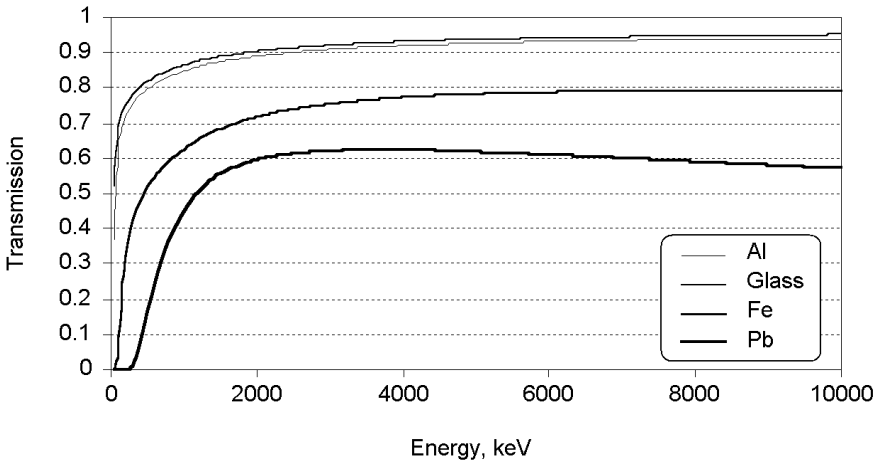

Fig. 3. Transmission of gamma-radiation as a function of energy through different materials with the thickness of 1 cm

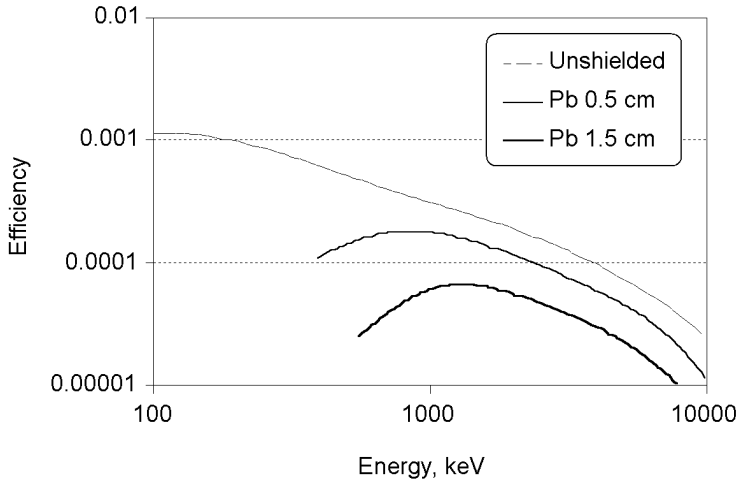

Fig. 4. Fitted efficiency functions for the Budapest PGAA system under normal conditions, and for samples inside a 0.5- or a 1.5-cm thick lead container

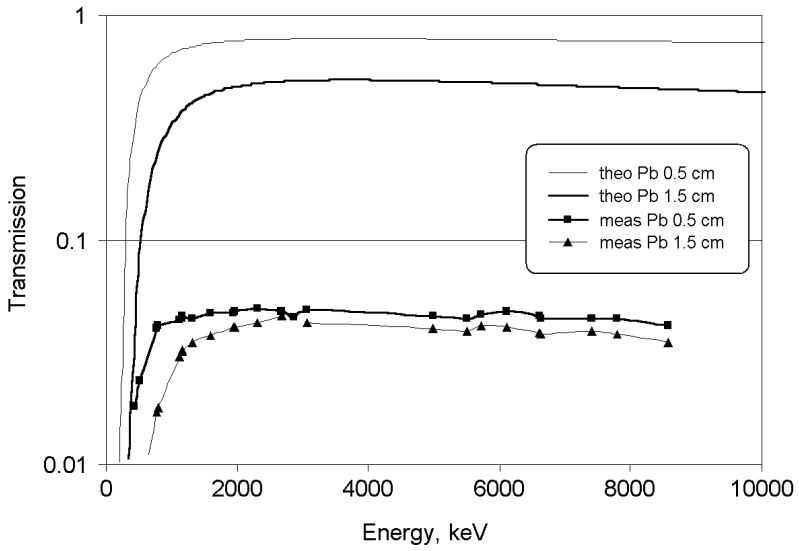

Fig. 5. Theoretical transmissions and measured peak intensities for chlorine placed in 0.5- and 1.5-cm thick lead container

Results and discussion

Using the "invisible container" method a complete series of measurements was performed using the 12-bar aluminum cans for all four measurable noble gases (Ne, Ar, Kr and Xe). The performance of the technique can be best characterized with the measurement of Ne, whose neutron capture cross section is only 0.039 barn, and its density in the can was 0.01 g·cm^{-3}, while the cross section of Al is 0.231 barn and its density 2.7 g·cm^{-3}. This results in a reaction rate of about 3 orders of magnitude lower for Ne, though the detected peak areas were similar.

Table 1 shows the count rates from the Al 1779-keV peak in the noble gas measurements and the beam background, as well as for an Al plate for comparison. It can be seen that the suppression of the Al peak from the container was always very good for the "invisible container" arrangement. When irradiating the atmospheric Ar in the Teflon balloon, the Al background was similar to the background measurement. For the measurements of the pressurized gases in cans, the suppression of the aluminum peaks proved to be different, but it was at least a factor of 25 (for Ne), but it was about 80 for Kr. The reason for these differences might have been partly due to improper positioning. The Al peaks in the spectra most likely originate from the activation of the container walls in front of the detector by the scattered neutrons. This effect is the highest for gases with low capture, but with relatively high scattering cross sections. The attenuation of the lines of interest was always lower than 2% (as calculated by XMuDat)[8] and they were corrected for.

Table 2 summarizes count rates for the most important detectable peaks from the uranyl acetate and the oxide of highly-enriched uranium. In the first case the prompt gamma-lines from hydrogen, ^{238}U and the strongest decay line from a fission product (^{90}Rb, half-life 4.3 min) are listed, while in the second case the 6395-keV prompt gamma-line and the same fission-product decay line are tabulated. As can be seen, the count rate ratios agree reasonably well. That means that one can estimate the mass ratios of the detected components and the enrichment of the uranium content of the sample in a container.

The presence of fissile material can be recognized in the lead container based on the characteristic shape of the spectrum, too. Figure 6 shows the spectra of the empty lead container, of the uranyl acetate sample (divided by ten to compensate the effect of the neutron scattering) and the spectrum of the sample in the container. The lower-energy part of the spectrum from uranium in lead follows the steep decrease typical for fissile material. This behavior appears after a few minutes of irradiation. A longer measurement then can help to decide the composition and the enrichment of the material hidden inside the shielding.

Table 1. Count rates of the Al peak at 1779 keV in the case of the beam background, of an Al plate, of the noble gas measurements

Sample	Count rate of Al peaks, cps
Beam background	0.015
1 mm Al	32
12 bar Ne	1.2
Atmospheric Ar	0.017
12 bar Ar	0.5
12 bar Kr	0.4
12 bar Xe	0.2

Table 2. Peak count rates for the most important peaks from uranyl acetate and highly-enriched uranium oxide samples without shielding and in 0.5-cm thick lead container

Sample	Energy, keV	Count rate, cps	Count rate in 0.5 cm Pb, cps	Ratio
$UO_2(CH_3COO)_2{\cdot}2H_2O$	2223 (H)	32.0 (3)	0.70 (4)	0.0220 (13)
	4060 (^{238}U)	0.99 (3)	0.020 (2)	0.020 (2)
	4135 (^{90}Rb)	0.076 (3)	0.0014 (4)	0.018 (6)
U_3O_8 (~95% ^{235}U)	4135 (^{90}Rb)	0.200 (10)	0.130 (10)	0.65 (5)
	6395 (^{235}U)	0.0362 (10)	0.022 (3)	0.61 (8)

Due to the high count rate, the highly enriched uranium sample was measured using a neutron collimator, while it was not used in the case of the same sample in container, so the count rate ratios, listed in the fourth column, are different from the case of uranyl acetate, where the same beam cross sections were used.

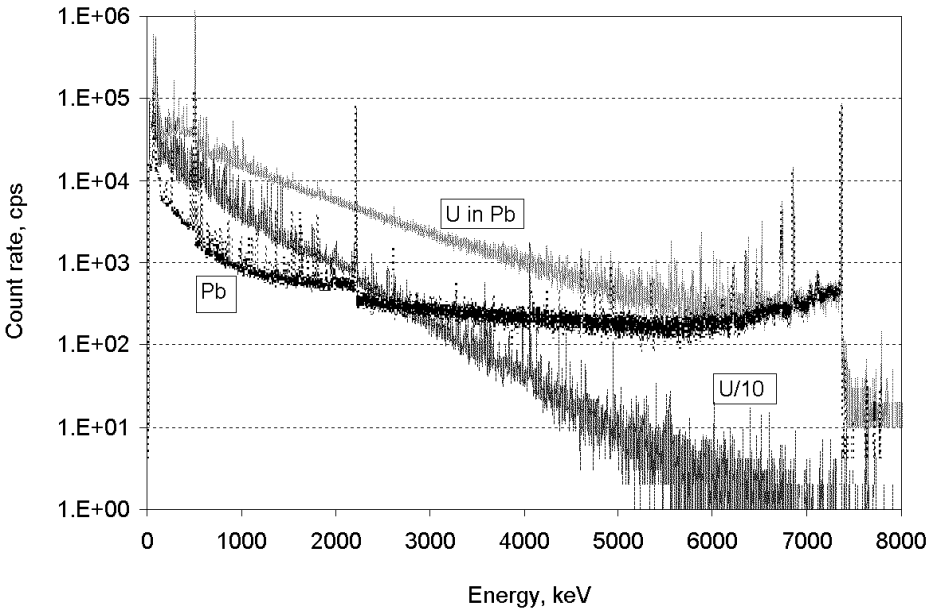

Fig. 6. Prompt gamma-spectra of lead (dotted line), uranium (gray line, intensity divided by 10) and uranium in a lead container (light gray line)

Conclusions

Methods were developed and investigated for PGAA measurements of samples in containers. The "invisible container" method proved to be especially useful for the measurement of pressurized gases and was used for the acquisition of elemental spectra of noble gases stored in aluminum cans. Uranyl acetate with natural isotopic abundance and the oxide of highly-enriched uranium were irradiated in 0.5- and 1.5-cm thick lead containers. The prompt and decay gamma-lines above 2 MeV were found to show similar relative intensities to those without the container. After determining the counting efficiencies with radioactive and (n,γ)-sources for the shielded setup, the composition of the test sample could be determined with a fair accuracy. The spectrum of a uranium containing material in a lead container shows the characteristics of the bare uranium at the low-energy half of the spectrum, so the fissile material can be detected in the thick shielding.

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