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Isotopic composition analysis and age dating of uranium samples by high resolution gamma ray spectrometry

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ABSTRACT

Non-destructive methods were applied to determine the isotopic composition and the time elapsed since last chemical purification of nine uranium samples. The applied methods are based on measuring gamma and X radiations of uranium samples by high resolution low energy gamma spectrometric system with planar high purity germanium detector and low background gamma spectrometric system with coaxial high purity germanium detector. The "Multigroup γ-ray Analysis Method for Uranium" (MGAU) code was used for the precise determination of samples' isotopic composition. The age of the samples was determined from the isotopic ratio $^{214}Bi/^{234}U$. This ratio was calculated from the analyzed spectra of each uranium sample, using relative detection efficiency. Special attention is paid to the coincidence summing corrections that have to be taken into account when performing this type of analysis. In addition, an alternative approach for the age determination using full energy peak efficiencies obtained by Monte Carlo simulations with the GESPECOR code is described.

1. Introduction

There were over 630 cases of illicit nuclear trafficking recorded in the Black Sea region only, and this number is constantly increasing [1]. These cases can lead to radiological incidents, the proliferation of nuclear terrorism and may cause a psychological, social and economic impact to the contemporary society. Seized radioactive materials may originate from various sources. Nuclear forensic science is dealing with the investigation of these materials. It determines the sample's signatures (isotopic and elemental compositions, age, microstructure, morphology, geometry etc.) using various analytical techniques like gamma spectrometry, ion beam analysis, secondary electron microscopy, mass spectrometry, etc. [2]. Further, those properties are compared with the data from national nuclear forensic library, which includes information about the radioactive materials stored or produced in the specific country. This procedure can help finding out the analyzed samples' point of loss of last authorized control, reproduce the crime scene and prevent the radiological incidents.

The main objective of this paper was to characterize uranium samples stored for more than 20 years in the facility holding nuclear material of Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH). For these samples, no reference information was available. Another objective was to use high resolution gamma spectrometry and take into account all the corrections that have to be made for our experiment (ex. peak interferences [3], coincidence summing effects, etc.).

The idea behind the age-dating of uranium samples consists of measuring the specific daughter-parent ratios which depend on the time elapsed since their last separation (age of the material). When the uranium material is produced, its isotopic composition is formed mainly of three isotopes: ^{234}U, ^{235}U and ^{238}U. Each of them is radioactive. Assuming that uranium isotopes were separated completely from their daughter products, it is possible to determine their age by measuring parent - daughter ratios, as the daughter is formed after the separation [2]. Of course, the simplest approach to obtain the age would be to measure the ratio between the parent and its first daughter, in order to overcome the uncertainties due to ^{238}U–^{226}Ra series decay corrections that have to be made. This can be done using most of the mass spectrometers able to analyze actinides. However, the age can also be determined using a less expensive, widely available technique, namely gamma-ray spectrometry, by selecting proper isotope pairs with suitable gamma emissions, and applying specific decay corrections [4–6].

The isotopic composition analysis was done with MGAU 4.2 code [7], using measurements performed with a planar high purity

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germanium (HPGe) detector while the age of the samples was determined using the $^{214}Bi/^{234}U$ chronometer. Finally, it should be mentioned that most of the measurements with the coaxial detector were done in the conditions of a high efficiency configuration. Therefore, we have shown that by applying proper coincidence summing corrections the results obtained in these conditions are reliable, extending thus the applicability of the method to small samples and low enrichment.

2. Experimental

2.1. Experimental set-up for gamma spectrometry

Nine metallic samples (pieces of metal) containing uranium (S1–S9) with different enrichments (ranging from depleted to 93%) were analyzed. Each of them weighed around 2 g and had similar, generally non-regular geometries.

The isotopic composition analysis of the samples was performed using a planar high purity germanium (HPGe) detector system with liquid nitrogen, type GL0105P (Ortec). The source to detector distance (SDD) for all the samples was around 1.5 cm. The MGAU 4.2 code was used to perform the spectra analysis (energy range 0–307 keV).

The planar detector's characteristics are presented in Table 1. Its energy resolution is much better than the one required for the proper work of the MGAU. The detector's calibration was performed using the recommendations from [8]. The energy window was set to 4 k channels so that the 185.71 keV peak of ^{235}U matched the 2476-th channel. The sample containing 10% enriched uranium (S5), which had a reasonably good count rate for 185.71 keV peak was used for this purpose. These calibration settings are required for the proper functioning of the MGAU 4.2 code.

The uranium age analysis was based on measurements performed with two spectrometric systems. Complementary to gamma spectrometry with planar detector, the spectra of the investigated samples were collected using a coaxial HPGe detector (GEM-30185, Ortec) placed in the low background laboratory GamaSpec of IFIN-HH [9]. Samples S1–S4 and S6 were measured on the detector's cap, while S5, S7 and S8 were measured at SDD of 2.54 cm. Due to its higher activity, S-9 highly enriched uranium (HEU) sample was measured at SDD of 7.62 cm, the acquisition dead time being lower than 10%. The counting time for all nine samples (S1–S9) varied between 15 and 62 h (19.1, 23.3, 46.2, 61.6, 43.1, 22.2, 25.3, 15.0, and 15.9 h, respectively). In order to find the best statistical uncertainty for 609 keV peak of ^{214}Bi, the samples were measured several times and the optimal geometrical configuration, counting conditions and background level was chosen.

The coaxial detector's physical characteristics are presented in Table 2. Detector shielding consisted of 10 cm thickness cylindrical lead screen (inner diameter 29 cm, height 42 cm) coated with 1 mm Sn and 1.5 mm Cu foils.

2.2. Uranium age-dating by gamma spectrometry

One of the isotopic ratios used for gamma spectrometric assay of uranium age is $^{214}Bi/^{234}U$. ^{214}Bi is a daughter product of ^{234}U, which decays through long-lived ^{230}Th and ^{226}Ra and short-lived ^{222}Rn, ^{218}Po and ^{214}Pb isotopes. For the analyzed samples, ^{226}Ra and ^{214}Bi were considered to be in the secular equilibrium (^{222}Rn emanation from the uranium sample is low; the samples were kept tightly closed in the measuring boxes for about 1 month before the measurement), so that Eq. (1) can be used for the age determination [4,5]:

$$\frac{A(^{214}_{83}Bi)}{A(^{234}_{92}U)} = \frac{1}{2}\lambda_2\lambda_3 T^2 \quad (1)$$

where, λ_2 and λ_3 are the decay constants of ^{230}Th and ^{226}Ra, respectively, A is the radionuclides' activity, and T is age of the uranium sample. The Eq. (1) was obtained using the assumption that the half-lives of ^{234}U, ^{230}Th, ^{226}Ra are much larger than the age of the samples, while the half-lives of ^{222}Rn, ^{218}Po and ^{214}Pb are much smaller.

In order to overcome the uncertainties associated with incomplete separation of the daughter products, another chronometer may be applied to check the results. $^{227}Th/^{235}U$ activity ratio can be useful for this purpose [6]. This method only works for very highly enriched uranium as the ^{227}Th peaks in low enriched uranium are too weak to be seen.

In nuclear forensic analysis by gamma spectrometry, the full energy peak efficiency calibration becomes an issue. The samples seized in illicit trafficking are usually samples with hard to define geometry. Therefore, experimental calibration with standards traceable to metrology institutes is seldom possible, whereas efficiency calibration using e.g. Monte Carlo simulation may have uncertainties difficult to estimate. That is why the approach described in [4] (where no full energy peak efficiency calibration of the detector is needed) is very convenient. The idea of the approach is to evaluate activity ratios of two nuclides using gamma energies belonging to a common range (E_1, E_2), chosen such that the energy dependence of the efficiency in this range can be reliably estimated (even if the absolute efficiency is not known). This can be done for the pairs $^{214}Bi/^{238}U$, $^{235}U/^{238}U$ and $^{234}U/^{235}U$. Using this idea and simple algebra, it is possible to define the $^{214}Bi/^{234}U$ activity ratio as a product of other isotopes' activity ratios as follows:

$$\frac{A(^{214}_{83}Bi)}{A(^{234}_{92}U)} = \frac{A(^{214}_{83}Bi)}{A(^{238}_{92}U)} \cdot \left(\frac{A(^{235}_{92}U)}{A(^{238}_{92}U)} \cdot \frac{A(^{234}_{92}U)}{A(^{235}_{92}U)}\right)^{-1} \quad (2)$$

Generally, this method was applied for measurements in which the sample was placed at several centimeters distance from the detector, corresponding to a rather low efficiency. In this measurement configuration, the assessment of small samples and of samples with low enrichment is difficult. In order to improve the detection limit and reduce the acquisition time for such samples, a higher efficiency measurement configuration would be advantageous. But in this case, appropriate procedures to correct for the inherent coincidence summing effects should be applied.

Table 1
GL0105 Canberra planar detector's characteristics.

Active diameter	11.3 mm
Active area	100 mm^2
Thickness	5 mm
Distance from window (outside)	5 mm
Window thickness	2 mm
Window material	Be
Energy resolution at the ^{57}Co energy of 122 keV	479 eV
Energy resolution at the ^{55}Fe energy of 5.9 keV	136 eV

Table 2
GEM-30185 Ortec coaxial detector's characteristics.

Crystal diameter	58.4 mm
Crystal length	58.9 mm
End cap to crystal distance	3 mm
Relative efficiency	30%
Energy resolution at the ^{57}Co energy of 122 keV	980 eV
Energy resolution at the ^{60}Co energy of 1.33 MeV	2.2 keV