

CHARACTERIZATION OF URANIUM-BEARING MATERIAL BY PASSIVE NON-DESTRUCTIVE GAMMA SPECTROMETRY

Cong Tam Nguyen, József Zsigrai, and László Lakosi

*Institute of Isotopes, Hungarian Academy of Sciences, P.O.BOX 77, 1525
Budapest, Hungary*

Characterization of nuclear materials is equally important in nuclear safeguards (inventory verification) and in nuclear security (revealing illicit trafficking). Analysis of materials is a key issue in both fields. Natural (NU), depleted (DU), low-enriched (LEU), and high-enriched uranium (HEU) samples were analysed by high resolution gamma spectrometry (HRGS). Isotopic composition and total U-content of reactor fuel pellets and powder were determined. A unique HRGS method was developed for the first time for determining the production date of the material of unknown origin. Identifying reprocessed uranium proved to be possible by HRGS as well.

Keywords: *Nuclear safeguards, nuclear security, isotopic composition, uranium content, age determination*

INTRODUCTION

Preventing spread of nuclear materials (NM) is a supreme task both of international safeguards and of state authorities combating illicit trafficking of such materials worldwide.

Nuclear safeguards and nuclear forensics both need analytical information of the material. In charge of prompt identification and analysis of seized NM on the spot (e.g. border checkpoint), and also for maintaining the integrity of forensic evidences, non-destructive assay (NDA) methods are preferred.

A governmental decree issued in 1996 delegated the identification, categorization and characterization of NM to the Institute of Isotopes. It has the expertise and capabilities to perform basic measurements for characterization of seized NM to support criminal investigation. Methods reported here – with emphasis on measurement principles – have been routinely used in the institute for quantitative assay of U-containing NMs.

Most of illicit trafficking incidents in Hungary occurred during the nineties, when both radioactive sources and NM have been confiscated from smugglers. NM consists typically of depleted, natural, and low enriched uranium (DU, NU, LEU) pellets and also rods, originated mainly from RBKM, VVER-1000, and CANDU reactors. The main characteristics for three representative types of the seized fuel pellets are – on average – as follows:

- Diameter 12.2 by 13.4 mm height, mass 16.6 g, ²³⁵U fraction 0.78% (natural), density 10.6, matrix UO₂. This is of CANDU type fuel.
- Diameter 11.4 by 14.7 mm height, mass 15.8 g, enrichment 2.72%, density 10.5,

matrix UO₂. This is of RBMK type.

- Diameter 7.6 by 11.3 mm height, mass 4.66 g, enrichment 4.465%, density 10.5, matrix UO₂. This is of VVER-1000 type.

There are also several other types of seized pellets, whose main parameters vary from 5.8 to 13 mm in diameter, 9.9 to 15 mm in height, 2.7 to 16.6 g in mass, and 0.23 to 4.46 % in ²³⁵U abundance. All these samples along with rod type fuel elements were measured.

Measurements include uranium isotopic abundance determination using the peak ratio method by intrinsic calibration, mass determination of materials in form of pellets and powder, based on a standard uranium calibration set, using attenuation correction. Beside isotopic composition, physical form, chemical impurities, etc., the age (production date) of the material is one of the important pieces of information as well. In the present work we use the term "age" of nuclear material to denote the time which has passed since the date of production of the material. More precisely, the age of a uranium sample is the time passed since it has been chemically separated from its daughter nuclides and, possibly, enriched. Among others, the gamma lines of ²¹⁴Bi could be identified in the low-background gamma spectrum of the sample. Relating the activity of ²¹⁴Bi to the activity of ²³⁴U the age of the sample could be estimated. Based on this, we developed a new method for uranium age dating using gamma-spectrometry.

Uranium age dating is difficult because the relevant isotopes (²³⁴U, ²³⁵U, and ²³⁸U) have very long half-lives, so only small amounts of daughter nuclides grow in. Namely, the age of nuclear materials is, at most, merely a few decades, which is very short compared to the long half-lives of the parent isotopes. Therefore, one would expect that the daughter nuclides could only be quantified after destructive chemical separation, followed by mass-spectrometric or alpha-spectrometric techniques. However, it has been demonstrated that the daughter/parent activity ratio ²¹⁴Bi/²³⁴U can be obtained by directly measuring the count rates of the relevant gamma peaks of ²¹⁴Bi and ²³⁴U by low-background gamma spectrometry. This method is non-destructive and does not require the use of reference materials of known ages [1].

Accordingly, the main steps of the analysis are as follows:

Determination of

- the isotopic composition, including the control of the radioactive equilibrium between parent and daughter isotopes;
- the amount of U-isotopes;
- the total U-content (based on the two previous measurements);
- age (production date) of the material.

The performance of the first 3 of the above methods was also tested under field conditions, using portable instrumentation.

DETERMINATION OF THE ISOTOPIC COMPOSITION

The isotopic composition has been determined on the basis of the peak-ratio technique using HRGS. Allowing the enrichment to be determined without use of standards or without determination of geometry-dependent calibration constants, the so-called relative efficiency calibration or intrinsic calibration method [2] is based on the use of a relative efficiency curve as a function of energy. As relying on peak ratios, there is no need to know absolute detection efficiencies. Relative efficiency curve is determined from the same spectrum as the measured activity ratios. Accordingly, the isotopic ratio in the sample material can be obtained from the measured intensity ratio, the relative efficiencies taken at the corresponding energies and from the values of the decay constants and emission probabilities taken from the literature. It means that one determines several gamma

intensities from individual U-isotopes, and normalizes the data to a common (relative) efficiency curve which, at the same time, accounts for the attenuation of different energy gamma rays in the absorbers and in the sample as well. This method is more accurate than the „enrichment meter” concept, which is being limited to „infinitely thick” (for the ^{235}U γ -energies) sample and „calibrated” geometries [3].

The $^{235}\text{U}/^{238}\text{U}$ isotopic ratio was calculated using the intensity ratio of the 84.2 keV line (from ^{231}Th , daughter of ^{235}U) to the sum of the 92.4 and 92.8 keV lines (from ^{234}Th , daughter of ^{238}U) [4]. The existence of secular equilibrium between the ^{238}U and its daughters was verified by repeated measurements. The $^{234}\text{U}/^{235}\text{U}$ ratio was determined from the intensity ratio of the 120.9 to the 185.7 keV gamma line from the respective isotopes.

For relative efficiency calibration the 63.3 keV line and the sum of the 92.4 and 92.8 keV lines of ^{234}Th as well as self-induced fluorescent U- K_α lines at 94.7 and 98.4 keV were employed [4]. A logarithmic second order polynomial approximation was used for determining the energy dependence by a least squares fit of the experimental data for intrinsic calibration efficiency values $C(E_i)/\lambda_i B(E_i)$, where $C(E_i)$, λ_i , and $B(E_i)$ are the counting rate, decay constant, and emission rate (branching), respectively, pertaining to a specific γ -energy E_i of the i -th isotope.

The gamma spectra were taken by high purity planar Ge detectors of different sizes and by the advanced Multi-Group Analysis computer code MGA++ [5]. One module of this software, the “U235” analysis code is to be used for determining U isotopic ratios, which provides reliable results in the range of 0.05 to 95 % ^{235}U abundances, while analyzing gamma and x-rays below 300 keV. Measuring times of about 15 to 60 min were used. Enrichments were determined within 1.5 – 10% uncertainties [6].

It is to be noted that if ^{232}U is present, the result for the enrichment should be taken with some precaution. The effect of the presence of possible ^{232}U peaks on the enrichment evaluation provided by the “U235” software will be treated below.

DETERMINATION OF THE AMOUNT OF THE URANIUM ISOTOPES AND TOTAL U-CONTENT

Unlike the enrichment measurements, which can be considered a more or less routine task, determination of total U mass always requires a specific approach. The reason for this is that the attenuation correction, needed for calculating total mass, depends on the matrix, the cladding, and the geometry as well. A necessary requirement is that the sample be not infinitely thick with respect to the assay gamma energy. Thus, in our case one cannot use low-energy lines, since their intensity gets saturated due to the self-absorption even within the dimension of a single pellet, i.e. the intensity would be practically independent of the size and the U-content of the sample. For this reason, the 1001 keV line of $^{234\text{m}}\text{Pa}$ (daughter of ^{238}U) was used for the U-mass determination, for which our samples were transparent enough.

Applying a relative method, the ^{238}U mass M_{238} was found from the count rate C in the 1001 keV peak, using calibration standards [6]. If the sample is homogeneous in its composition and density, one can write

$$M_{238} = K \frac{C}{F}, \quad (1)$$

where F is the attenuation correction factor, characteristic of the sample material and geometry, while K depends on the detection efficiency and the gamma-yield. In the case of

relative measurements, however, K is a calibration constant, determined by using five certified reference sources (EC Nuclear Reference Material Set 171). The sources are encased in diam. 7 cm cans, each containing 200 g U_3O_8 powder in 2 cm thickness, of enrichment ranging from 0.32 to 4.46%. In the assay geometry, the cylindrical detector viewed a similar sample, the two cylinders having a common axis of symmetry. If the radii of both the detector and the sample are much smaller than the source-to-detector distance, then the deviation of the detected gamma-rays from the direction parallel to the system axis is negligible. In this case the setup can be approximated with a one-dimensional model. Then the attenuation correction factor can be approximated as

$$F = \frac{(s + P_E)^2}{L} \int_0^L \frac{e^{-\mu x}}{(s + P_E + x)^2} dx, \quad (2)$$

where L is the length of the sample, s is the distance from the sample to the detector, P_E is the effective penetration depth of the observed gamma-line in the detector material [7], x is the distance a gamma-ray travels within the sample, and μ is the linear attenuation coefficient of the examined material for the energy E . The effective penetration depth for 1001 keV gamma rays in the detector material was calculated to be 2.41 cm.

Only a certain amount of individual materials was selected for measurements. Pellets to be measured were chosen randomly from each material as a representative set and were arranged, next to each other, into a hexagonal lattice. Samples of unidentified chemicals available in powder form were also examined. Both types of samples were placed into the same type of container as the one of the standard sources. For instance, the batches composed from the first two types of the pellets mentioned above comprised 19 pellets each. The pellets were aligned to the direction of the detector with their longitudinal axes, forming flat cylindrical (or rather hexagonal) disks of diameter 5.7 cm.

AGE DETERMINATION

1. The $^{214}\text{Bi}/^{234}\text{U}$ daughter/parent relation in uranium

The gamma-spectrometric age determination of uranium samples is based on measuring the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ by HRGS in low background [1]. ^{214}Bi is a daughter of ^{234}U , which decays through ^{230}Th to ^{226}Ra , which in turn decays to ^{214}Bi through three short-lived nuclides. The time needed for secular equilibrium between ^{226}Ra and ^{214}Bi to be achieved is about 2 weeks. Once such a time period being elapsed, the activities of ^{226}Ra and ^{214}Bi are equal. Therefore, using the law of radioactive decay, the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ at time T after purification/enrichment of the material may be calculated as

$$\begin{aligned} \frac{A_{Bi214}(T)}{A_{U234}(T)} &= \frac{A_{Bi214}(T)}{A_{U234}(0)} = \frac{A_{Ra226}(T)}{A_{U234}(0)} = \\ &= \lambda_2 \lambda_3 \left[\frac{\exp(-\lambda_1 T)}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} + \frac{\exp(-\lambda_2 T)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} + \frac{\exp(-\lambda_3 T)}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \right] \end{aligned} \quad (3)$$

where $A_{U234}(0)$ denotes the activity of ^{234}U at time $T=0$, while λ_1 , λ_2 , and λ_3 are the decay constants of ^{234}U , ^{230}Th , and ^{226}Ra , respectively. Because $\lambda_1 T$, $\lambda_2 T$, $\lambda_3 T \ll 1$, formula (3) can be approximated as

$$\frac{A_{Bi^{214}}(T)}{A_{U^{234}}(T)} = \frac{1}{2} \lambda_2 \lambda_3 T^2 . \quad (4)$$

This equation can be used for calculating the age, T , of uranium samples after the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ has been determined by gamma spectrometry.

The activity ratio $^{214}\text{Bi}/^{234}\text{U}$ can be determined in several ways from the gamma spectra of the investigated sample. The approach presented here does not require any reference materials but uses the absolute efficiency of the detector determined by “point-like” standard sources. That is, the activities of ^{214}Bi and ^{234}U in the sample were measured in an efficiency-calibrated geometry. In another approach merely a relative efficiency calibration was used to determine the activity ratio $^{214}\text{Bi}/^{234}\text{U}$, without the use of any reference materials [8].

In the present report the two approaches are described on particular measurement examples of determining the age of uranium samples enriched to 90 and 36 %. The age of the 36%-enriched material was determined by both methods. The results of the different methods agree with each other within the error limits, confirming the reliability of the methods.

2. Age dating using efficiency-calibrated measurement geometry

In 90% enriched uranium the amounts of ^{234}U and ^{214}Bi are relatively high, so their activity was easily measured. The results were confirmed in a Round Robin interlaboratory comparison organized by the International Technical Working Group on Combating Illicit Trafficking of Nuclear Materials (ITWG) in 2001 [9]. Namely, the value for the age of the investigated material obtained by gamma-spectrometry was in agreement with the values obtained by other laboratories using mass-spectrometry, applying the method of atom ratio of ^{230}Th to ^{234}U . Our method is novel and unique, and it is applicable whenever the sample can be approximated to be “point-like” or if it has a well defined geometrical shape, for which an efficiency-calibrated geometry can be constructed and for which self-attenuation can also be accounted for.

An amount of 0.981 g of the material received within the above exercise was placed in a thin, closed polyethylene cylinder of 2.9 cm inner diameter. The gamma-spectrum of the sample was taken by the coaxial 150 cm³ Ge detector, placed in a low-background iron chamber, with wall thickness of 20 cm and 120x60x120 cm (height x width x length) inner dimensions.

The activity A of ^{214}Bi in unit mass of the measured sample was calculated from the count rate per unit mass I (cps/g) by the formula $A=I/B\varepsilon$, where $B=0.46\%$ is the decay branching ratio and ε is the detector efficiency measured by standard reference sources. Because the examined amount of the HEU-containing powder formed a very thin layer on the bottom of the polyethylene cylinder, there was no need for correction due to self-absorption, nor for the possible effect of the movement of the ^{222}Rn gas within the sample. The activity of ^{214}Bi per unit mass of the sample was found to be 1.9 ± 0.1 Bq/g.

The agreement of ^{214}Bi activities calculated from the 609.3, 1120.3 and 1764.5 keV gamma-peaks proves that these gamma-rays originate, indeed, from ^{214}Bi present in the assayed material. However, because of small branching ratios and because detector efficiency decreases with energy, the statistical error for the counts was significant (15%) even for long (3 days) counting times. In addition, these peaks have to be de-convoluted from the peaks of ^{238}U at 1120.6 and 1765.5 keV, which also decreases the reliability of the results obtained for the counts at these energies. Therefore, the ^{214}Bi peaks at 1120.3 and 1764.5 keV were merely used for monitoring the origin of the gamma rays, and the 609.3

keV line for calculating the activity of ^{214}Bi which was later used for calculating the age of the sample.

In order to verify that no ^{222}Rn -gas has escaped from the sample while pouring the sample into the container, monitoring the equilibrium between ^{226}Ra and ^{222}Rn was carried out during the measurement by observing the constancy of the count rate of the 609.3 keV line.

The spectra of ^{234}U were taken using a 2000 mm² planar Ge detector. The detector was standing in a vertical position and the different amounts of the assayed material were placed, one after another, above the detector at a fixed distance of 10.8 cm in the same type of polyethylene container as in the previous measurement. Spectra were being recorded until the statistical error of the 121 keV line dropped below 1%.

For these measurements there was no need for using the low-background chamber. The values of the count rates of the 121 keV peak of ^{234}U were standardized in unit mass as the ratio, $K(m)$, of the count rate to the total used mass of the sample. Fig.1 shows the standardized count rates versus total mass. The data were fitted with the function

$$K(m) = K_0 \frac{1 - \exp(-am)}{am}, \quad (5)$$

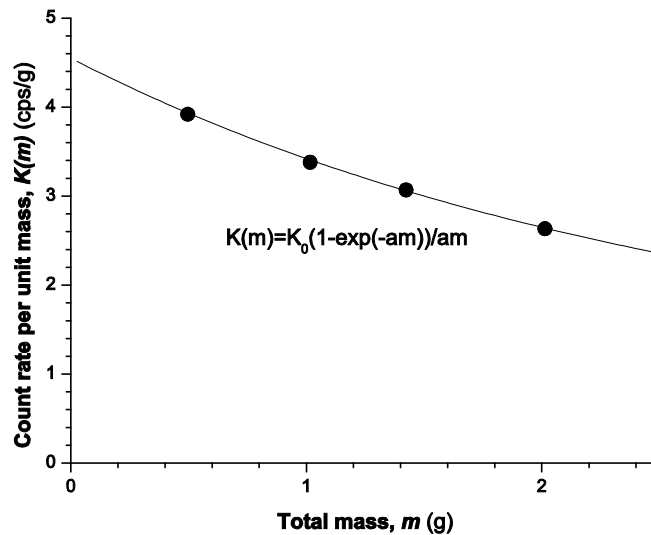


Figure 1: Count rate per unit mass of the sample, $K(m)$, as a function of the mass of the sample.

Modeling the law of self-absorption within the sample. The parameter K_0 is the value where the curve crosses the vertical axis and physically it represents the net count rate of 1 g of the sample corrected for self-absorption. The parameter a provides information about the matrix of the sample and its density. A non-linear least-squares fit yields the values $K_0 \approx 4.60$ cps/g and $a \approx 0.65$ g⁻¹. The activity of ^{234}U in 1 g (specific activity) of the sample can be calculated from formula $A = I/B\varepsilon$, inserting $I = K_0$. Using the appropriate decay branching ratio, $B = 0.0342$ %, and detector efficiency, 0.730 ± 0.015 , at 121 keV, the ^{234}U specific activity of the sample was obtained as $(1.84 \pm 0.06) \times 10^6$ Bq/g. In this way the ^{234}U activity was estimated without using any information about the matrix and the isotopic composition of the sample. Note that ^{234}U is a long-lived isotope, with half-life of 2.46×10^5 years, so one may safely assume that its activity at the time of the measurement is the same as its initial activity at the time of production of the assayed material.

Having obtained the specific activities of ^{214}Bi and ^{234}U of the assayed material, the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ was calculated. Then the age of the material received in the Round Robin exercise was found to be 23 ± 3 years. After the exercise was completed, the results obtained by mass spectrometry for age dating (see Table 1), reported by other laboratories participating in the exercise, were received. Our result was in good agreement with these results.

Table 1: Age values of the material received in the Round Robin exercise, measured by different laboratories using mass spectrometry and our result obtained by gamma-spectrometry.

Laboratory nickname	Age of the sample, y
Azores	22.2 – 22.6
Mindanao	22.4±1.2
Trinidad	23.5±0.5
Tobago(Gamma spectrometry)	23±3

The applicability of the method for uranium age dating was tested by applying it for determining the age of a reference material. The reference material was U_3O_8 powder with 90% of ^{235}U . Unfortunately, the exact date of production was not known, but it is documented that the material was transported to Hungary in 1960. The measurement was carried out in 2001, so the material was at least 41 years old at the time of the measurement. Measurements similar to those in the case of the Round Robin material were carried out on this material as well.

An amount of 1.015 g of the reference material was placed into the same type of polyethylene container as the Round Robin material, and the ^{214}Bi activity was assayed in the described low-background setup. Furthermore, a series of measurements with a varying amount of 0.5 to 2 g of the material was performed using the planar Ge-detector mentioned above for estimating the activity of ^{234}U . The Compton-background in the spectrum of the Round Robin material is higher. This is due to the Compton-tail of the gamma-peaks of ^{208}Tl , coming from the decay of ^{232}U , which was present in the Round-Robin material. The enrichment of the two samples was roughly the same, but the reference material was about two times older, so the count rates of the 609.3, 1120.3 and 1764.5 keV peaks of ^{214}Bi were about four times higher in the reference material.

The values of the ^{214}Bi activity calculated from the count rates of the three ^{214}Bi peaks agree well with each other, which shows again that these gamma-rays originate from the decay of ^{214}Bi . Because of higher count rates, the relative statistical errors are lower than in the case of the Round Robin material. Therefore, the activity of ^{214}Bi was calculated as a weighted average of the activities obtained from the three different gamma peaks and it was found to be 7.06 ± 0.15 Bq/g. The ^{234}U activity was $(1.9 \pm 0.06) \times 10^6$ Bq/g. The age of the reference material was calculated from formula (4) as 43 ± 2 years. This value was to be expected from the date of arrival of the material to Hungary. Although no certified reference material of a known age was available, this test gave a good indication of the applicability of the method.

3. Age dating using relative efficiency calibration

A 36% enriched U_3O_8 powder was used for the measurements. The aim of using a relative efficiency calibration was to develop a method appropriate for age-dating of homogeneous uranium samples of any physical form and shape. The idea is to determine first the activity ratios $^{214}\text{Bi}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ using intrinsic calibration, then to calculate the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ from these results. When measuring the activity ratio $^{214}\text{Bi}/^{238}\text{U}$,

the peaks of ^{234m}Pa are used to construct a relative efficiency curve. The activity of ^{234}U is determined first relative to ^{235}U , and if the activity ratio $^{235}\text{U}/^{238}\text{U}$ is also known, one can calculate the activity ratio $^{234}\text{U}/^{238}\text{U}$ as well.

Gamma spectra of the samples were taken in the 0-2 MeV region in low background and in the 0-300 keV region under standard laboratory conditions. From each spectrum a relative efficiency curve was constructed, using the peaks of ^{234m}Pa and those of ^{235}U , respectively.

The intensity of ^{234m}Pa peaks can be accurately measured within a reasonable time for material of less than approximately 90% enrichment, provided that a sufficient amount of the investigated material is available. It should be noted that for lower enrichments the amount of ^{234}U (and therefore of ^{214}Bi) is lower as well, so the corresponding activity is more difficult to measure and the uncertainty caused by the variation of the natural background becomes more expressed. In addition, a Compton background caused by the peaks of ^{238}U daughters is also present in the spectrum, disturbing the evaluation of the ^{214}Bi peaks. Therefore there exists a lower limit on the enrichment of the material whose age can be determined by gamma-spectrometry, depending, of course, on the amount and the age of the material, detector efficiency, and background level.

For determining the activity ratio $^{234}\text{U}/^{238}\text{U}$, the spectra of the assayed material were taken by a planar Ge detector, whereas the activity ratio $^{214}\text{Bi}/^{238}\text{U}$ was measured by a coaxial Ge detector in the low-background chamber. The latter ratio was calculated from the 609.3 keV peak of ^{214}Bi using the relative efficiency curve obtained using the peaks of ^{234m}Pa , which is assumed to be in equilibrium with its parent ^{238}U , so its activity is equal to the activity of ^{238}U . Therefore, the activity ratio $^{214}\text{Bi}/^{238}\text{U}$ may be calculated as

$$\frac{A_{\text{Bi}214}}{A_{\text{U}238}} = \frac{I_{609.3} / B_{609.3}}{F(609.3\text{keV})}, \quad (6)$$

where $A_{\text{Bi}214}$ and $A_{\text{U}238}$ denote the corresponding activities, respectively, $I_{609.3}$ is the intensity of the 609.3 keV line of ^{214}Bi , $B_{609.3}$ is its emission probability, while $F(609.3\text{keV})$ is the value of the relative efficiency function of the detector at 609.3 keV. The function $F(E)$ is obtained by fitting a second order polynomial to the relative efficiencies at the 569.3, 766.4, 1001.0, 1193.7, 1510.2, 1737.7, and 1831.4 keV peaks of ^{234m}Pa .

For measuring the activity ratio $^{234}\text{U}/^{235}\text{U}$, the gamma peak of ^{234}U at 120.9 keV was observed and the spectrum acquisition lasted until the statistical error dropped below 2 %. If the sample is not “thin”, the activity ratio $^{234}\text{U}/^{235}\text{U}$ of the material can be reliably determined using the “U235” [10] or the “MGAU” [11] code. For thin samples, such as the samples used in this research, however, the results of the “U235” and the older versions of the “MGAU” code before version 4.0 contain large systematic errors (see e.g. [12]).

Using relative efficiency calibration the activity ratio $^{234}\text{U}/^{235}\text{U}$ was determined by an equation analogous to Eq. (6) from the intensity of the 120.9 keV ^{234}U line with $F(120.9\text{keV})$, the value of the relative efficiency function of the detector at 120.9 keV. The function $F(E)$ is obtained by fitting a second order polynomial to the relative efficiencies at the 143.8, 163.3, 185.7 and 205.3 keV peaks of ^{235}U .

The enrichment of the material was determined from the spectra taken by the small planar detector, using the commercial “U235” code, which is part of ORTEC software package “MGA++”. The values obtained for the enrichment of the sample did not depend on the thickness of the sample. Therefore the enrichment was calculated as the weighted average of the values obtained by measuring the enrichment of 3 samples of different masses.

When the enrichment (and therefore also the activity ratio $^{235}\text{U}/^{238}\text{U}$) is known, the activity ratio $^{234}\text{U}/^{238}\text{U}$ can simply be calculated as

$$\frac{A_{U234}}{A_{U238}} = \left(\frac{A_{U235}}{A_{U238}} \right) \times \left(\frac{A_{U234}}{A_{U235}} \right). \quad (7)$$

The new version 4.0 of MGAU code determines more accurately the ^{234}U content for thin samples as well. The values for ^{234}U obtained by MGAU v4.0 from the spectra taken with the small detector agree well with the values obtained from the above equations.

In order to calculate the age of the sample, one needs the activity ratio $^{214}\text{Bi}/^{234}\text{U}$. It is calculated from the results of the previously described measurements as

$$\frac{A_{Bi214}}{A_{U234}} = \frac{(A_{Bi214} / A_{U238})}{(A_{U234} / A_{U238})}. \quad (8)$$

The age of the material was calculated from Eq. (4) for each sample separately. The values $T_{1/2}(^{230}\text{Th}) = 7.538 \times 10^4$ y and $T_{1/2}(^{226}\text{Ra}) = 1600$ y were used in the calculations.

The results obtained using different amounts of the investigated material were 43(6), 43(5), and 42(4) y, agreeing well with each other. For comparison, the age of the investigated material was also calculated by using the absolute efficiency of the detector as described earlier. In order to account for the self-absorption of the 120.9 keV line within the sample, the procedure described there was applied. In the case of the 10 g sample the count rate is the highest, so in this case the relative uncertainty produced by the fluctuation of the background level is the lowest. Therefore, only the results of the measurements with the largest (10 g) sample were used for calculating the activity of ^{214}Bi in this comparison. The age obtained using the absolute efficiency of the detector is 45 ± 4 years, which, within the error limits, agrees with the value obtained above using the relative efficiency calibration.

IDENTIFYING REPROCESSED URANIUM

Identifying reprocessed uranium is an important clue in the characterization of nuclear material, especially of unknown origin. In order to find out whether a uranium sample was made of material that has already been used in a nuclear reactor and then reprocessed, one should look for traces of fission or activation products. One of the nuclides frequently used for this purpose is ^{236}U , which can easily be quantified using mass spectrometry. With gamma spectrometry ^{236}U can only be detected in very highly enriched (weapon grade) uranium, with a large uncertainty. Another nuclide which can only be present in uranium if it has already been used in a nuclear reactor is ^{232}U . This nuclide can easily be quantified by low-background gamma spectrometry, regardless of the ^{235}U enrichment

The activity of ^{232}U is calculated from the activity of its gamma-emitting daughters, ^{212}Bi and ^{208}Tl by solving Eq (9) for A_{U232} :

$$A_{Bi212} = \frac{A_{Tl208}}{B} = A_{U232} \left[\frac{1 - \exp((\lambda_{U232} - \lambda_{Th228})t)}{1 - \lambda_{U232} / \lambda_{Th228}} \right], \quad (9)$$

where λ_{U232} and λ_{Th228} are the corresponding decay constants, while t is the age of the sample, $B = 35.9\%$ is the decay branching probability of the $^{212}\text{Bi} \rightarrow ^{208}\text{Tl}$ decay. Using the

measured activities of ^{212}Bi and ^{208}Tl and the measured or estimated age of the sample as well as the known half-lives, the activity of ^{232}U is obtained. The age for some of the samples was determined by low-background gamma spectrometry, or alpha-spectrometry, or it was estimated from the available sample documentation. If the samples are older than 1-2 years, then the uncertainty of the age of the sample does not influence noticeably the results for the ^{232}U activity (the half-life of ^{232}U is 68.9 y).

In the present work the activities of ^{212}Bi and ^{208}Tl were determined relative to ^{238}U , using the peaks of ^{238}U to construct a relative efficiency curve. The activity ratio $^{232}\text{U}/^{238}\text{U}$ was measured in the low-background iron chamber using 150 cm³ coaxial Ge detector. The detector was standing in vertical position and the samples were placed, one after another, either below the detector or by the side of the detector [13].

For the study a set of certified reference materials and several other uranium samples were used, with ^{235}U enrichments in the range of 0.23 – 90 %.

For each sample an intrinsic efficiency calibration curve was constructed, using the peaks of ^{234}Pa and $^{234\text{m}}\text{Pa}$ which are short lived daughters of ^{238}U . Using this intrinsic efficiency curve and the count rates of the 727.3, 583.0 860.3 and 2614.3 keV gamma lines of ^{212}Bi and ^{208}Tl , the activity ratio $^{232}\text{U}/^{238}\text{U}$ was calculated for each assayed sample.

The results of the measurements are shown in Fig. 2. For two of the investigated samples the count rates of the relevant peaks of ^{212}Bi and ^{208}Tl were about 100 times larger than for other samples with similar ^{235}U enrichment and about 1000 times larger than the background, clearly indicating that there is much more ^{232}U in them than in the other samples. It is interesting to note that in all samples, except in those with natural isotopic composition, there is some ^{232}U , although it is not a naturally occurring isotope. This is probably due to the ^{232}U contamination in the enrichments facilities, because sometimes they enrich uranium from reprocessed irradiated materials. Fig. 2 presents the ratio of ^{232}U to the total mass of U in the investigated samples as a function of ^{235}U enrichment, indicating that two of the samples have been probably produced from reprocessed uranium. For one of them (the highly enriched one) this conclusion is also supported by the fact that the 49.4 keV gamma peak of ^{236}U could also be evaluated in its gamma spectrum.

For the certified reference materials and for 4 other samples results of mass spectrometric uranium isotope ratio measurements were also available. The mass spectrometric results showed that in those two samples in which a higher amount of ^{232}U was found, there is also much more ^{236}U than in the other ones, confirming that these samples, indeed, contain reprocessed uranium.

It can be concluded that low-background gamma-spectrometry can be successfully used to show whether or not a material of unknown origin was made of reprocessed uranium, by measuring the amount of ^{232}U in the sample. Although a small amount of ^{232}U was found in enriched and depleted uranium samples even if they were not produced from reprocessed material, the samples made of irradiated uranium contain at least 100 times more ^{232}U than those in which ^{232}U occurs merely because of the contamination of the enrichment facilities, making it possible to distinguish between reprocessed and not reprocessed materials.

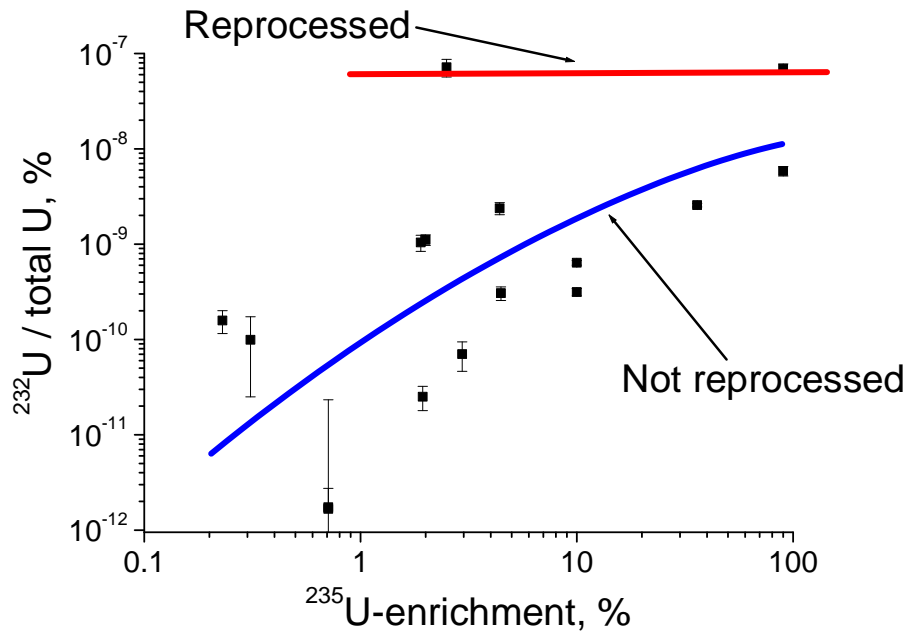


Figure 2: ^{232}U content as a function of ^{235}U enrichment.

CONCLUSIONS

HRGS seems to be an adequate tool for passive quantitative assay of isotopic composition of LEU samples of unknown origin. For determining the enrichment to a few percent accuracies, 15 - 60 min acquisition times are needed, and the method is suitable for in-field analysis. As a laboratory method, the total U-content can be determined by the usage of standard sources, and the results of the measurements are independent of the detector efficiency and γ -yields, so the uncertainties, which are usually involved in determining these quantities, are avoided. The convenient geometrical setup makes possible the simple measurement of the linear attenuation coefficient μ and the precise calculation of the attenuation correction factor F . This way a total relative uncertainty of less than 2% could be achieved for the measured value of the total uranium content of the samples. The matrix of the unknown sample can be characterized (if not a mixture) on the basis of the relative U-content $M_{\text{U}}/M_{\text{total}}$.

Two methods for gamma-spectrometric age-dating of uranium samples are described. Both methods use the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ as a “chronometer” for calculating the age of the material. These methods do not require the use of reference materials of known ages. For the first method it is necessary to know the absolute efficiency of the detector, so the measurements can only be performed in an efficiency-calibrated geometry. In contrast, the second method, using merely a relative efficiency calibration, is appropriate for age dating of uranium samples in arbitrary measurement geometry. The accuracy of these methods is close to the accuracy of mass-spectrometric age dating. The “difficult” samples are the same as in the case of mass spectrometry: low-enriched and/or “young” uranium. Using the coaxial Ge detector and the low-background iron chamber, the lower bound for age determination of 90 % enriched HEU was estimated to be around 5 years. The sensitivity and the range of applicability of the methods may be improved by using a detector with a higher efficiency, by further lowering the background level and by minimizing the background fluctuations. If a well-type Ge detector could be used, the sensitivity of the method could be improved, so that the lower bound for the applicability of the method

would be approximately 1 year for 90% enriched uranium and 20 years for natural uranium, under the present background conditions.

It can be concluded that gamma-spectrometric age dating of uranium is, within the described limits, a reliable tool for determining the age of uranium samples encountered in combating illicit trafficking of nuclear materials and in nuclear safeguards.

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