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DETERMINATION OF URANIUM ISOTOPIC RATIOS BY HRGS USING VARIOUS EFFICIENCY CALIBRATION APPROACHES[†]

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The effect of various efficiency calibration approaches on the value and source of the HRGS measurement uncertainty of $^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$ isotopic ratios for the purposes of technological control, nuclear forensics, and environmental monitoring has been studied. The Canberra Broad Energy Germanium detector BEGe3830 and five samples of uranium certified reference materials CRM 969 and CRM 146 with a content of $^{235}U/U$ ranging from 0.7 to 20.0 wt. % have been used. To calculate the uranium isotope ratios, the acquired gamma spectra were processed using: commercial MGAU (LLNL), FRAM (LANL), ISOCS software (Canberra/Mirion Technologies), based on intrinsic and absolute efficiency calibration approaches. It has been found that maximum relative biases, for the $^{234}U\,/\,^{238}U$ and $^{234}U\,/\,^{235}U$ isotopic ratios determined using the MGAU \ FRAM \ ISOCS software, are ~ 25 % \ ~ 10 % \ ~ 10 %, and the random uncertainty is varied within ± [18-25 % \ 2-15 % \ ≤ 3 %], respectively. In the case of $^{235}U\,/\,^{238}U$ isotopic ratio determination using the MGAU \ FRAM \ ISOCS software, maximum relative biases come to ~ 3 % \ ~ 4 % \ ~ 1 %, and the random uncertainty values decrease to ± [1 % \ 1 % \ 1 %], respectively. In the present paper we propose a combined intrinsic efficiency calibration approach with the use of the polynomial functions for analytical description of the relation $\varepsilon_{rel.i}(E_i)$. In this approach a maximum relative biases, in the determination of the $^{234}U\,/\,^{238}U$ and $^{234}U\,/\,^{235}U$ isotopic ratios is 2.7 % at a random uncertainty of ≤ 1 %, and in the case of the $^{235}U\,/\,^{238}U$ ratio a maximum relative deviation is 0.5 % at a random uncertainty of ≤ 0.7 %.

Keywords: high resolution gamma spectrometry, uranium isotope ratios, efficiency calibration, measurement uncertainty, uranium ore, MGAU, FRAM, ISOCS
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Natural uranium is a mixture of three isotopes: ^{238}U (isotopic abundance $^{238}U/U = 99.2745$ %, half-life $T_{1/2} = 4.468\cdot10^9$ years), ^{235}U ($^{235}U/U = 0.7200$ %, $T_{1/2} = 7.04\cdot10^8$ years) and ^{234}U ($^{234}U/U = 0.0055$ %, $T_{1/2} = 2.455\cdot10^5$ years) [1]. In some stages of the fuel nuclear cycle, and due to the radionuclide migration in the geosphere, the uranium isotopic composition can vary, therefore, there is a need to measure the uranium isotopic ratio in the view of economic and technologic strategy for the purposes of nuclear safety and environmental monitoring.

The values of the isotopic abundances ($^{234}U/U$, $^{235}U/U$, $^{238}U/U$) are a subject of technological control in the uranium material production. They are regulated by the international ASTM standards, e.g. C 787 and C 996. The standard test method for uranium isotopic abundance analysis using the inductively coupled plasma mass spectrometry (ICP-MS), described in the ASTM C 1477 standard, is applied in the destructive analysis (DA) of feed raw material in order to fabricate the nuclear fuel with a relative content of $^{235}U/U \le 5.0$ % for power reactors. Using this destructive method it is possible to reach the measurement uncertainty for $^{235}U/U$ at a level of ≤ 0.1 % and for $^{234}U/U$ at a level ≤ 1.0 %, i.e. even minor variations in the isotopic composition can be quantified. A quantitative identification of uranium isotopes is also required in the complex of scientific methods known as nuclear forensics. As defined by the IAEA the nuclear forensics is a field of applied nuclear physics directed at the analysis of nuclear and radioactive materials, seized from the illicit trafficking, to obtain analytical data needed to reconstruct the history of the origin of these materials. In this field the uranium isotopic ratios ($^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$) are of particular interest compared to their isotopic abundances [2, 3].

The information on the geographic region of the material deposit plays a substantial role in tracking its deposit. The values of the uranium isotopic ratios in the complex may be used for establishing the origin of uranium ores (UO) and uranium ore concentrates (UOC).

Moreover, the $^{234}U\,/\,^{238}U$ isotopic ratio is used in the hydroindication studies as a high-precision indicator of the source of groundwater flow formation. The values of the $^{234}U\,/\,^{238}U$ ratios give important information for estimation of the groundwater recovery and flow separation, for determining mixing proportions of several sources and studying the dynamics of interaction in the water-ore system.

The $^{235}U\,/\,^{238}U$ isotopic ratio in natural uranium has been widely accepted as 7.25×10^{-3} for many years and until recently has been invariant [4]. In 1972 the uranium ores from the Oklo deposit (Gabon, Western Africa) revealed a

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significant deviation in the $^{235}U\,/\,^{238}U$ isotopic ratio [5]. It has been found that the $^{235}U\,/\,U$ isotopic abundance in the deposit ores is depleted nearly 2.5 times apparently due to the uranium “burn-up” as a result of a spontaneous chain nuclear reaction. Subsequent research has shown that variations of the $^{235}U\,/\,^{238}U$ isotopic ratio in natural uranium usually do not exceed 1.3 % for different deposits and most often are caused by the physical-chemical factors [6].

The $^{234}U\,/\,^{238}U$ ratio for natural uranium accepted as 5.5×10^{-5}, on the other hand, has been found to vary considerably due to the natural cause in many water, soil, sediments and uranium ores of different geographical origin [7]. The mechanism of such variation is a preferential leaching of ^{234}U compared with ^{238}U from the solid phase, caused by radiation damage of the crystal lattice upon the alpha decay of ^{238}U, oxidation of insoluble tetravalent ^{234}U to soluble hexavalent ^{234}U during decay, and alpha recoil of ^{234}Th (and its daughter ^{234}U) into solution phase [8]. The $^{234}U\,/\,^{238}U$ ratio in water reportedly varies from 2.8×10^{-5} to 2.2×10^{-3} (variation quantified as a mean absolute deviation of about 100 %), that in soil typically ranges from 2.8×10^{-5} to 6.6×10^{-5} (variation of about 40 %), while that in uranium ores ranges from 5.2×10^{-5} to 8.4×10^{-5} (variation of about 20 %) [9].

The natural $^{234}U\,/\,^{235}U$ isotopic ratio can also appreciably vary for different uranium deposits [10]. The $^{234}U\,/\,^{235}U$ ratios of the high-temperature and non-redox deposits appear to lie close to the secular equilibrium value 7.6×10^{-3}, whereas the $^{234}U\,/\,^{235}U$ ratios of the low-temperature deposits show a significant scatter. This difference is likely related to the nature of the deposits themselves as open or closed systems. Low-temperature deposits primarily consist of sandstone deposits that form below the water table. The relatively high porosity of the host sandstone allows for greater open system behavior than does the more compacted lithology of the host rocks of high-temperature and non-redox deposits. Whenever large amounts of groundwater interact with a deposit, the deposit is expected to contain either excesses of ^{234}U, if the deposition is still occurring or depletions in ^{234}U if the deposition has stopped. In the first case the $^{234}U\,/\,^{235}U$ ratio can reach ~ 1.3×10^{-2}, in the second case it is 6.3×10^{-3}, and the ratio variation is of about 30 %.

Furthermore, slight differences in the $^{234}U\,/\,^{235}U$ ratio may point to the different enrichment processes at the enrichment stage of the nuclear fuel cycle [11]. Hence, when using the gas centrifugation process for uranium enrichment to the $^{235}U\,/\,U$ abundance ~ 93 %, a typical $^{234}U\,/\,U$ abundance increases to 0.89 %, the gaseous diffusion enrichment process under the same conditions increases the $^{234}U\,/\,U$ abundance to 0.93 % [12]. Thus, using different enrichment technologies the variations in the $^{234}U\,/\,^{235}U$ isotopic ratio can be about 2 %.

A comparison of $^{235}U\,/\,U$ measurement uncertainty results obtained in [13] by destructive (ICP-MS) and non-destructive (high resolution gamma spectrometry – HRGS) methods show that in the range of $^{235}U\,/\,U$ abundance from 1.0 to 20.0% the international target values for measurement uncertainties of DA methods are 0.14 % and these of non-destructive (NDA) methods are 3.6 %.

In this paper we have studied the effect of various efficiency calibration approaches on the magnitude and sources of the HRGS measurements uncertainty of $^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$ isotopic ratios for the purposes of technological control, nuclear forensics, and environmental monitoring.

MATERIALS AND METHODS

The Canberra Broad Energy Germanium detector BEGe3830 with active area of 3800 mm^2 and thickness of 30 mm has been used for the spectra acquisition. The detector is equipped with a carbon composite input window of 0.6 mm thickness. The energy resolution (FWHM) of the detector is 720 eV at 122 keV.

Five samples of uranium certified reference materials CRM 969 and CRM 146 from the US National Bureau of Standards with $^{235}U\,/\,U$ abundance from 0.7 to 20.0 wt. % have been used in testing. The calculated reference uranium isotope ratios and their relative uncertainties are shown in Table 1. Reference samples were made of 200 or 230 g of U_3O_8 powder encased with a filling height of 20.8 or 15.8 mm in aluminum cans with bottom wall thickness of about 2 mm and side wall thickness of about 5 mm.

The sample cans were placed in front of the detector in the “bottom configuration” geometry keeping the symmetry of mutual position. The counting time for data acquisition was 2 h. The dead time varied typically from 0.62 to 2.65 %. The 185.7 keV peak of ^{235}U was checked to be at the channel 2476 corresponding to the required detector calibration gain of 0.075 keV per channel.

Table 1. Reference uranium isotopic ratios and relative uncertainties in the materials CRM 969 and CRM 146

Sample ID	$(^{235}U\,/\,U)^{Ref.}$, wt. %	$(^{234}U\,/\,^{238}U)^{Ref.}$ ± Rel. Unc.	$(^{235}U\,/\,^{238}U)^{Ref.}$ ± Rel. Unc.	$(^{234}U\,/\,^{235}U)^{Ref.}$ ± Rel. Unc.
071	0.7119	5.2376×10^{-5} ± 3.85 %	0.00717 ± 0.07 %	7.3044×10^{-3} ± 3.85 %
194	1.9420	1.7442×10^{-4} ± 1.17 %	0.01981 ± 0.07 %	8.8054×10^{-3} ± 1.17 %
295	2.9492	2.8757×10^{-4} ± 1.43 %	0.03039 ± 0.07 %	9.4602×10^{-3} ± 1.43 %
446	4.4623	3.7594×10^{-4} ± 0.84 %	0.04673 ± 0.07 %	8.0452×10^{-3} ± 0.84 %
NBL0013	20.107	1.8682×10^{-3} ± 0.25 %	0.25277 ± 0.09 %	7.3910×10^{-3} ± 0.25 %

In order to calculate the uranium isotopic ratios, the gamma spectra were processed using:

- Commercial software MGAU (Ver. 3.2), developed at the Lawrence Livermore National Laboratory and FRAM (Ver. 5.0), developed at the Los Alamos National Laboratory;
- ISOCS efficiency calibration combined with Geometry Composer (Ver. 4.2.1) software, developed at the Canberra (Mirion Technologies);
- Intrinsic (relative) efficiency calibration approach [14-17].

The commercial software MGAU and FRAM use the «response function» approach for determination of the uranium isotopic composition [18, 19]. According to this approach, the response functions, describing the contribution of each isotope to the fitted energy range, are constructed or, in other words, the true intensities of uranium gamma lines are calculated. At constructing, the available prior information on the energies, peak shapes, energy resolution, branching ratios and relative intensities of gamma and x-rays is utilized.

To determine accurately the areas of the photoelectric absorption peaks, a relative efficiency curve is calculated using the intrinsic efficiency calibration. The efficiency calibration is intrinsic in the sense that it relates to a specific gamma spectrum, i.e. for each sample under study (a set of spectral data) it is necessary to perform its own intrinsic calibration based on the information coming directly from the measured spectrum. Mathematically, the intrinsic efficiency calibration is described in [20, 21]. The observed net count rate in the photopeak corresponding to the radioisotope of interest is expressed as:

$$n_i^R = \lambda^R \cdot N^R \cdot I_i^R \cdot \varepsilon_i \,, \tag{1}$$

where n_i^R is the net count rate in the peak at energy *i* of radioisotope *R*; λ^R – the decay constant for radioisotope *R*; N^R – the number of atoms for the radioisotope *R*; I_i^R – the gamma-ray emission probability at energy *i* from radioisotope *R*; ε_i – absolute detection efficiency at energy *i*.

To express equation given above in the relative terms, we need to introduce the ratio of the radioisotopes considered in the analysis by dividing their corresponding amounts N^T by an amount of a "reference" radioisotope. The reference radioisotope represents the radioisotope relatively to which the remaining radioisotopes considered in the analysis are normalized. In this case the counting efficiency becomes expressed in relative terms:

$$n_i^R = \lambda^R \cdot \left(N^T / N^R\right) \cdot I_i^R \cdot \varepsilon_{rel.i} \,. \tag{2}$$

If ^{238}U is used as the reference radioisotope, then the ratios $^{235}U\,/\,^{238}U$ and $^{234}U\,/\,^{238}U$ can be estimated. After the division by the primary radioisotope the counting efficiency is viewed in the relative term which is the detection efficiency for ^{234}U and ^{235}U gamma-ray peaks with respect to those of ^{238}U.

For a given pair of radioisotopes the atomic ratio is defined as division of the number of atoms N^T by the number of atoms corresponding to the reference radioisotope (in our case ^{238}U), thus for the gamma peaks corresponding to the reference radioisotope (^{238}U) the ratio N^T/N^R is equal to unity (since the atomic ratio $N^{238}/N^{238}=1$), whereas for the gamma peaks of ^{234}U and ^{235}U radioisotopes their values are determined from the fitting routine.

If to analyze the isotope ratio, the $^{235}U\,/\,^{238}U$ gamma-lines with energies of 258.3, 766.4, 1001.3 keV of ^{234m}Pa (daughter of ^{238}U) and 143.8, 163.3, 185.7 keV of ^{235}U are measured, then using the information from all the available gamma-ray signatures, corresponding to the radioisotopes considered in the analysis, a system of simultaneous equations is constructed, as given by the system of equations:

$$\begin{gathered}
n_{258}^{238} = \lambda^{238} \cdot 1 \cdot I_{258}^{238} \cdot \varepsilon_{rel.258} \,, \\
n_{766}^{238} = \lambda^{238} \cdot 1 \cdot I_{766}^{238} \cdot \varepsilon_{rel.766} \,, \\
n_{1001}^{238} = \lambda^{238} \cdot 1 \cdot I_{1001}^{238} \cdot \varepsilon_{rel.1001} \,, \\
n_{143}^{235} = \lambda^{235} \cdot \left(N^{235}/N^{238}\right) \cdot I_{143}^{235} \cdot \varepsilon_{rel.143} \,, \\
n_{163}^{235} = \lambda^{235} \cdot \left(N^{235}/N^{238}\right) \cdot I_{163}^{235} \cdot \varepsilon_{rel.163} \,, \\
n_{186}^{235} = \lambda^{235} \cdot \left(N^{235}/N^{238}\right) \cdot I_{186}^{235} \cdot \varepsilon_{rel.186} \,.
\end{gathered} \tag{3}$$

In such a way the system of *n*-equations is constructed for the available gamma-ray peaks. A minimum number of gamma peaks necessary for the fitting routine is determined as a total number of fitting parameters plus one, for at least one degree of freedom. In such a system of equations the atomic ratios are fitted altogether with the coefficients of the relative counting efficiency model applied to describe the shape of the counting efficiency curve using the data points from both radioisotopes.

If in the graphical representation Equation (1) is written as: $n_i^R / I_i^R = (\lambda^R \cdot N^R) \cdot \varepsilon_i$, then for different gamma-quantum energies *i* of a single radioisotope *R* we obtain $\varepsilon_i \sim n_i^R \big/ I_i^R$. Plotting the $n_i^R \big/ I_i^R$ ratio as a function of gamma-quantum energy E_i and approximating its polynomial functions $f(E)$ we obtain a relative efficiency curve $\varepsilon_{rel.i}(E_i)$ for a radioisotope *R*. For single measurement geometry the curves $\varepsilon_{rel.i}(E_i)$ have the same shape for all the isotopes being analyzed and differ only by the coefficient $\lambda^R \cdot N^R$. The software FRAM uses for approximation the function such as: $\ln \varepsilon_{rel.i} = f(E_i) = c_1 + c_2 \big/ E_i^2 + c_3 \cdot \ln E_i + c_4 \cdot (\ln E_i)^2 + c_5 \cdot (\ln E_i)^3$ where $c_1 ... c_5$ are the coefficients determined by fitting the reference isotope peaks. The type of approximating polynomial function, used in the MGAU software, is not given by the developers.

As a result, the software codes MGAU and FRAM fit normalized responses in the required energy range and then calculate relative abundances as follows, e.g. for $^{238}U / U$:

$$\frac{^{238}U}{U} = \frac{N^{238}}{N^{234} + N^{235} + N^{238}} = \frac{1}{N^{234} \big/ N^{238} + N^{235} \big/ N^{238} + 1}. \tag{4}$$

The MGAU code performs an efficiency calibration in the 89-100 keV energy range, while FRAM code has a choice of the two alternative energy ranges: 60-210 keV and 120-1001 keV.

An ISOCS efficiency calibration software is a mathematical package built for the absolute detector efficiency $\varepsilon_{abs.}$ calculation using a MCNP Monte Carlo modeling code. For the efficiency calibration an accurate model of the sample geometry – position of the sample relative to the detector, distribution of the source in the sample, shape and thickness of the container, density of the original matrix, composition of the container and matrix – was created using a Geometry Composer software. After that, ISOCS effectively integrates the characterization function across the sample volume and, as a result, the absolute efficiency data points are generated which further are used for efficiency calibration of the measured gamma-spectrum. The activity A_i^R of the radioisotope *R* with gamma-line energies *i* is calculated as: $A_i^R = n_i^R \big/ (I_i^R \cdot \varepsilon_{abs.})$. Subsequently, using the specific activity values of the isotopes, their masses and isotope ratios can be calculated.

RESULTS AND DISCUSSIONS

To evaluate the results of uranium isotope ratios analysis by various software, statistical methods were used [22]. A comparison between the calculated values of isotope ratios with reference ones was based on a statistical quantity called the ς-score, which is estimated as:

$$\varsigma = \frac{(x - X)}{\sqrt{(u_x^2 + u_X^2)}}, \tag{5}$$

where x and u_x are the values of the calculated isotope ratio and its uncertainty; X and u_X are the values of the reference isotope ratio and its uncertainty. The results of the analysis are considered to be acceptable if $|\varsigma| \le 2$, i.e. the calculated and reference values are consistent. The value of $|\varsigma|$ from 2 to 3 indicates that the results are of a questionable quality or inconsistent with a medium confidence. If $|\varsigma| > 3$, the analysis was considered to be out of control, i.e. the results are inconsistent with a high confidence. The results of uranium isotope ratios evaluation using the statistical approach are shown in Fig. 1.

The values of $^{234}U / {}^{238}U$ and $^{234}U / {}^{235}U$ isotopic ratios, calculated using the MGAU and FRAM software and the relative efficiency calibration approach satisfy the statistical criterion $|\varsigma| \le 2$, i.e. they are in agreement with reference values. However, the value of ς is negative and $|\varsigma| \to 2$ for the results obtained by the MGAU software, i.e. probably, there occurs a systematic underestimation of the ^{234}U isotope abundance. The ISOCS results do not coincide with the reference values for samples 194, 295, 446. The biases have a diverse character and, probably, they are related with a ^{234}U isotope determination error. In the case of analysis of the $^{235}U / {}^{238}U$ isotopic ratio there was observed a tendency to overestimate by the software MGAU and to underestimate by the software FRAM its value.

The written above is graphically shown in Fig. 2 where the results of $^{234}U / {}^{238}U$, $^{235}U / {}^{238}U$, $^{234}U / {}^{235}U$ isotopic ratio measurement by different software are represented. In addition, there is a reference value of the isotopic ratio determined with measurement uncertainty limits, relative bias (systematic uncertainty) of the measured value from the reference and software measurement uncertainties (random uncertainties).

It is seen that the relative bias of $^{234}U / {}^{238}U$ and $^{234}U / {}^{235}U$ ratio values, measured by the MGAU software, is negative and its absolute value is ~ 25 %. So, really, the MGAU software significantly underestimates the ^{234}U isotope abundance, and the agreement of $^{234}U/^{238}U$ and $^{234}U/^{235}U$ isotopic ratio values with the statistical criterion $|\varsigma| \leq 2$ is explained only by a high value of the random uncertainty u_x (± 18-25 %), being in the denominator of Equation (5). The abundance of the ^{234}U isotope is determined by analysis of its single gamma-line with energy of 120.9 keV. As the software MGAU performs the efficiency calibration in the narrow energy range from 89 to 100 keV, the efficiency curve approximation up to 120.9 keV can introduce a significant error that, likely, is a cause of the ^{234}U isotope abundance underestimation.

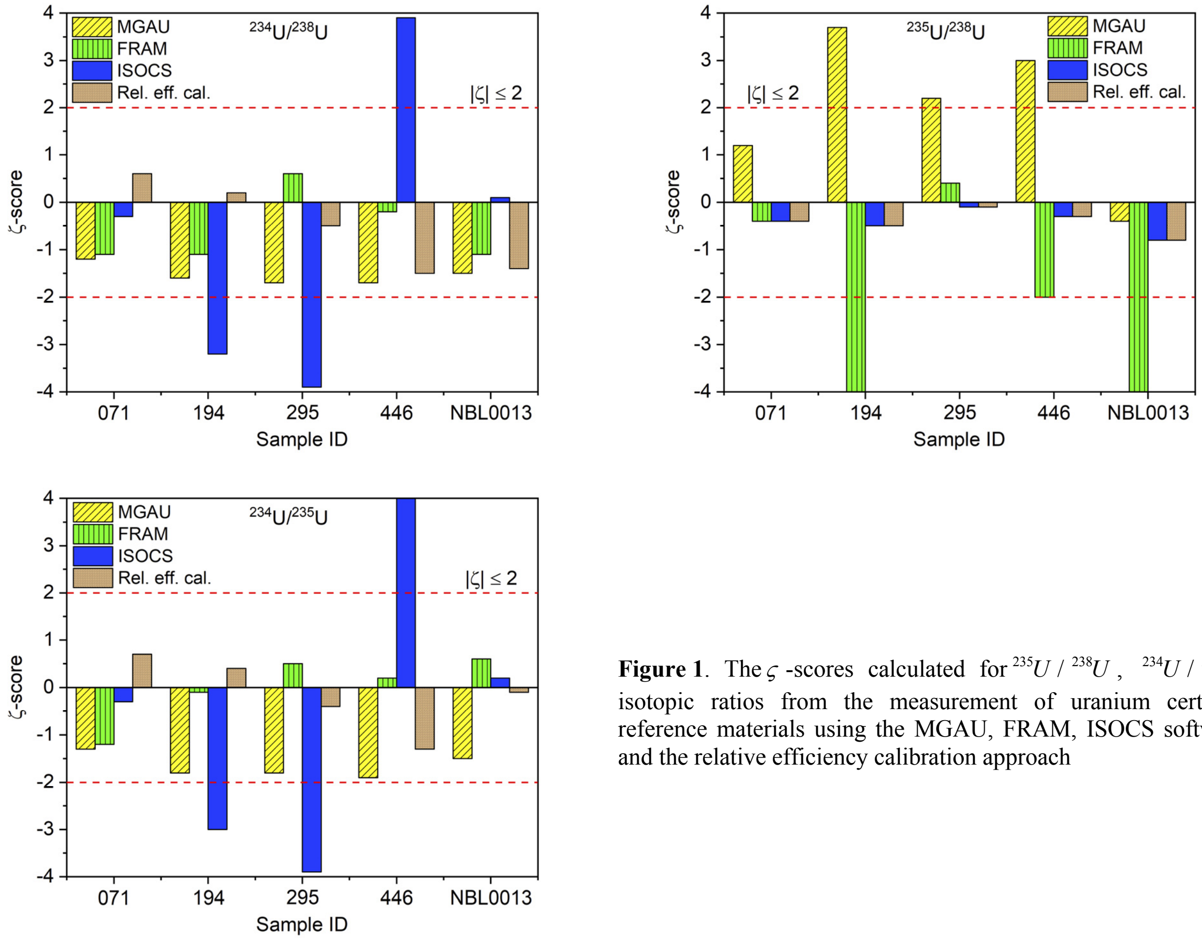

Figure 1. The ς -scores calculated for $^{235}U/^{238}U$, $^{234}U/^{235}U$ isotopic ratios from the measurement of uranium certified reference materials using the MGAU, FRAM, ISOCS software and the relative efficiency calibration approach

In the case of $^{235}U/^{238}U$ isotopic ratios the software MGAU gives, mainly a result overestimated by 1-3%, and the random uncertainty u_x does not exceed 1%. In Ref. [18] such a relative bias is explained by the ^{232}U, ^{233}U, ^{234}U, ^{236}U, ^{238}U contribution into the intensity of ThKα analytical lines (93.35 and 89.96 keV), emitted in the decay process $^{235}U \rightarrow {}^{231}Th$, being the base lines for estimation of the ^{235}U isotopic abundance.

The FRAM software, compared to MGAU, determines the $^{234}U/^{238}U$ and $^{234}U/^{235}U$ isotopic ratios with a lesser systematic uncertainty. Thus, a maximum relative bias of ~ 10 % was obtained for a sample of natural uranium (sample ID: 071). When the ^{235}U abundance and, consequently that of ^{234}U, increases (in the process of uranium enrichment with isotope ^{235}U the material is enriched with isotope ^{234}U more effectively) the systematic and random uncertainties decrease to 2-3 %. This occurs due to the increase in the gamma-line 120.9 keV intensity of ^{234}U and, respectively, due to the decrease in the peak area determination error. Similarly to the case with the MGAU, the occurrence of a relative bias, when determining ^{234}U with the FRAM, can be explained by the shortcomings in the intrinsic efficiency calibration procedure. But FRAM, unlike MGAU, uses a larger energy range (from 143.8 keV to 1001.3 keV) directly for the relative efficiency curve calculating, therefore the curve approximation to 129.9 keV provides a lesser error. By determining the $^{235}U/^{238}U$ isotopic ratio, FRAM, most often, underestimates the ratio by < 5 % in the ^{235}U abundance range being studied, and the random uncertainty u_x does not exceed 1 % that correlates with the data [23].

Despite the fact that the values of the $^{234}U/^{238}U$ and $^{234}U/^{235}U$ isotopic ratios, calculated with the ISOSC software, do not satisfy the statistical criterion $|\varsigma| \leq 2$ for some samples, the values of the relative bias and random uncertainty obtained by such a method are lower than in MGAU and FRAM codes and do not exceed 10 % and 3 %

respectively. The $^{235}U\,/\,^{238}U$ isotopic ratio can be calculated more accurately and in this instance the statistic parameters (relative bias and random uncertainty) do not exceed 1 %. A main disadvantage of the ISOCS efficiency calibration software is that the absolute efficiency can be calculated only from the exact measurement geometry data in order to take correctly into account the effects of absorption and scattering of gamma-quanta in the material under study, container material and other absorbers that is not always possible in the real conditions.

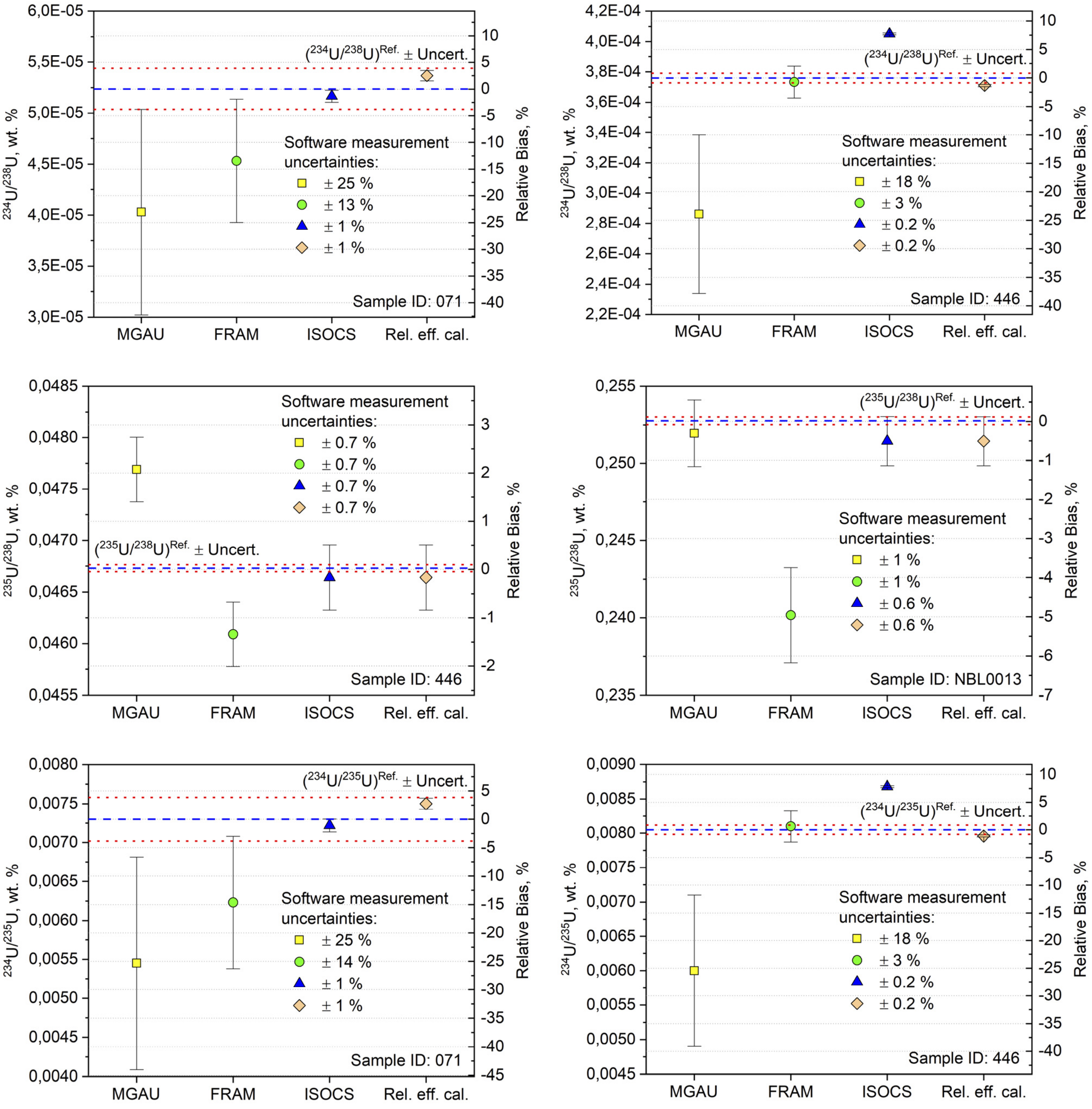

Figure 2. Calculated $^{234}U\,/\,^{238}U$ (1st row), $^{235}U\,/\,^{238}U$ (2nd row), $^{234}U\,/\,^{235}U$ (3rd row) isotope ratios vs reference values, relative biases and measurement uncertainties in the uranium certified reference materials (samples ID: 071, 446 and NBL0013)

The uranium gamma-ray spectrum is essentially divided into two regions below 1 MeV. The low-energy region up to about 200 keV contains major gamma rays from ^{235}U at 143.8, 163.3, 185.7, 202.1, and 205.3 keV. The ^{238}U gamma rays in the high-energy region arise from its ^{234m}Pa daughter with energies of 742.8, 766.4, 786.3, and 1001.3 keV for the most intense lines [24]. This peak plays an important role in the routine intrinsic calibration approach for defining the relative efficiency curve. Data points from ^{235}U usually determines the low-energy portion of the relative efficiency curve. The high-energy portion of the curve is usually determined by a series of gamma rays from ^{234m}Pa with only a single point at 258.3 keV to make the normalization between the high- and low-energy portions of the curve.

We have proposed a combined intrinsic efficiency calibration approach consisting in the following. The $^{235}U\ /\ ^{238}U$ isotopic ratios can be rather correctly calculated using the MGAU, FRAM or ISOCS codes, then, taking into account the specific isotope activity, the relative efficiency curve can be obtained by fitting the data of a single polynomial functions $f(E)$ in the whole gamma-quantum energy range of ^{235}U and ^{234m}Pa, and thus the $^{234}U\ /\ ^{238}U$ and $^{234}U\ /\ ^{235}U$ isotopic ratios can be calculated.

In the present study for the $^{235}U\ /\ ^{238}U$ ratio estimations we have applied the results obtained with the ISOCS code, i.e. the absolute efficiency calibration approach. For experimental data fitting we have used three polynomial functions: $f_1(E_i) = c_1 \cdot E_i^{c_2} \cdot \exp(c_3 \cdot e^{c_4 \cdot E_i})$; $f_2(E_i) = c_1 + c_2 \cdot \ln(E_i) + c_3 \cdot \ln^2(E_i) + c_4 \cdot \ln^3(E_i) + c_5 \cdot \ln^4(E_i) + c_6 \cdot \ln^5(E_i)$; $f_3(E_i) = c_1 \cdot \ln(E_i) + c_2 \cdot \ln^2(E_i) + c_3 \cdot \ln^3(E_i) - c_4 \cdot E_i^{c_5}$ [25-27]. A gamma-quantum energy range was extended to 2 MeV including additional peaks of ^{234m}Pa: 1193.8, 1510.2, 1737.7 and 1831.3 keV. The extension of energy range and finding in it of an analytical function $\varepsilon_{rel.i}(E_i)$ can be fruitful for a tasks of uranium age-dating by means of a $^{214}Bi\ /\ ^{234}U$ chronometer in which the high-energy lines of ^{214}Bi: 609.3, 1120.3, 1764.5 keV are used.

Fig. 3 shows the results of fitting the relative efficiency vs. gamma-rays energy of ^{235}U and ^{234m}Pa by the $f_1(E)$, $f_2(E)$, $f_3(E)$ functions and residuals in the whole range of energies and in its low-energy portion. It can be seen that all the three proposed functions fit the experimental data in the range of gamma-ray energies up to 2 MeV with residuals of no more than ± 2, and in the low-energy portion, no more than ± 1. For purposes of determining $^{234}U\ /\ ^{238}U$ and $^{234}U\ /\ ^{235}U$ ratios, the accuracy of the low-energy fitting is critical, since this is where the relative efficiency for the 120.9 keV of ^{234}U line is calculated.

When the uranium isotope ratios was calculated by applying the combined intrinsic efficiency calibration approach, a minimum relative bias in most cases, has been obtained using a fitting function $f_3(E)$, for which the residuals in the low-energy region were minimum and did not exceed ± 0.5. In some cases, the most reasonable results for uranium isotope ratios have been obtained using a fitting function $f_1(E)$.

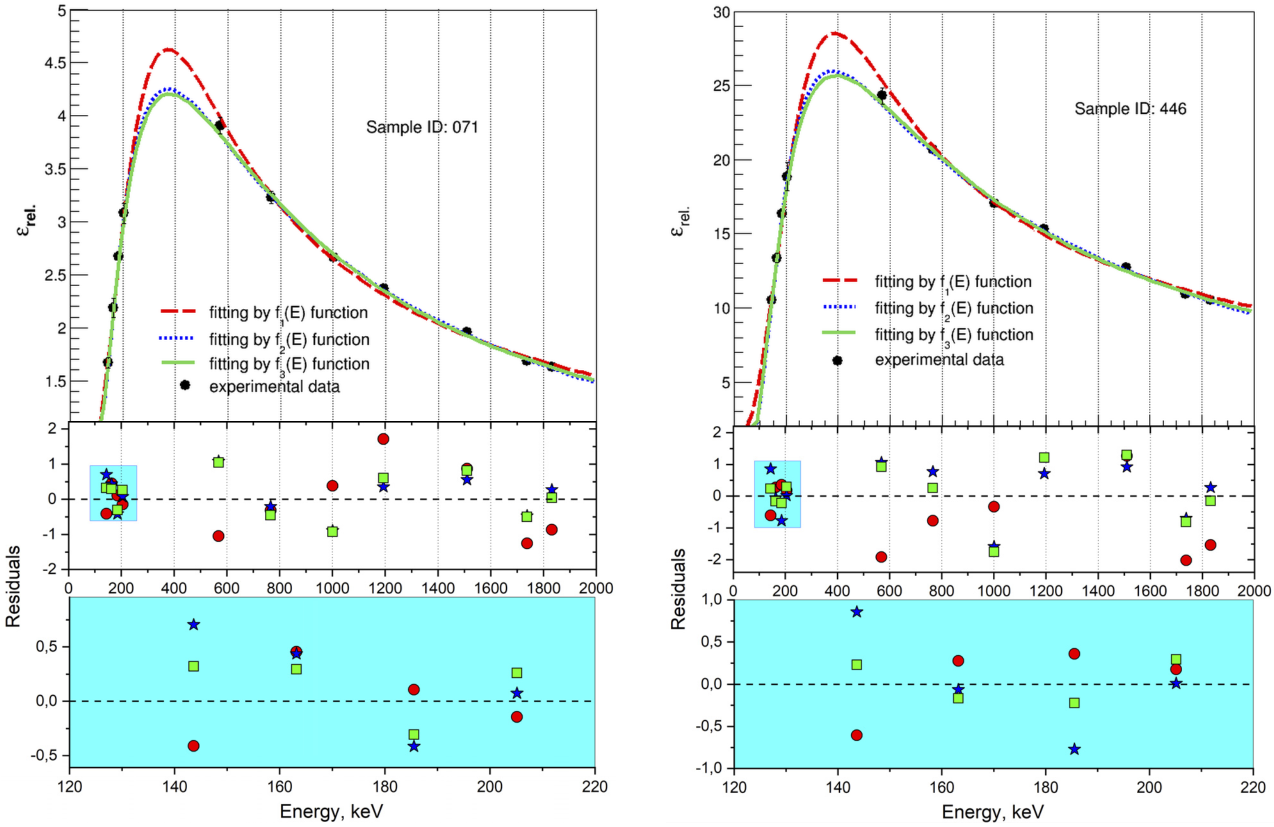

Figure 3. Fitting the relative efficiency vs. gamma-rays energy of ^{235}U and ^{234m}Pa using the $f_1(E)$, $f_2(E)$, $f_3(E)$ functions and residuals (● – residuals of $f_1(E)$ function; ★ – residuals of $f_2(E)$ function; 🟩 – residuals of $f_3(E)$ function)

A maximum relative bias in the $^{234}U\ /\ ^{238}U$, $^{235}U\ /\ ^{238}U$, $^{234}U\ /\ ^{235}U$ isotopic ratio calculation after the best fit was 2.7 % in the natural uranium (sample ID: 071), in the other samples the relative bias did not exceed 1 % at a random uncertainty of ≤ 1 %.

CONCLUSIONS

The effect of various efficiency calibration approaches on the value and sources of the HRGS measurement uncertainty of $^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$ isotopic ratios for the purposes of technological control, nuclear forensics, and environmental monitoring was studied.

The calculations of uranium isotopic ratios were performed in the $^{235}U\,/\,U$ abundance range from 0.7 to 20.0 wt. % using commercial MGAU, FRAM and ISOCS software based on the intrinsic and absolute efficiency calibration approaches. It is shown that the values of maximum relative bias in the $^{234}U\,/\,^{238}U$ and $^{234}U\,/\,^{235}U$ ratio estimations using MGAU \ FRAM \ ISOCS software are ~ 25 % \ ~ 10 % \ ~ 10 % and the random uncertainty is varied within the ± [18-25 % \ 2-15 % \ ≤ 3 %], respectively. The estimation of the $^{235}U\,/\,^{238}U$ isotopic ratios using MGAU \ FRAM \ ISOCS software maximum relative bias are ~ 3 % \ ~ 4 % \ ~ 1 % and the random uncertainty values decrease to ± [1 % \ 1 % \ 1 %], respectively.

For determining the $^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$ isotopic ratios a combined intrinsic efficiency calibration approach has been proposed in which the range of measured gamma-quantum energies was extended up to 2 MeV by including the additional peaks of ^{234m}Pa: 1193.8, 1510.2, 1737.7 and 1831.3 keV, and for analytical description of the relation $\varepsilon_{rel.i}(E_i)$ there were used functions: $f_1(E_i) = c_1 \cdot E_i^{c_2} \cdot \exp(c_3 \cdot e^{c_4 \cdot E_i})$; $f_2(E_i) = c_1 + c_2 \cdot \ln(E_i) + c_3 \cdot \ln^2(E_i) + c_4 \cdot \ln^3(E_i) + c_5 \cdot \ln^4(E_i) + c_6 \cdot \ln^5(E_i)$; $f_3(E_i) = c_1 \cdot \ln(E_i) + c_2 \cdot \ln^2(E_i) + c_3 \cdot \ln^3(E_i) - c_4 \cdot E_i^{c_5}$. In the present approach a maximum relative bias in the determination of $^{234}U\,/\,^{238}U$ and $^{234}U\,/\,^{235}U$ isotopic ratios is 2.7 % at a random uncertainty of ≤ 1 %, and in the determination of $^{235}U\,/\,^{238}U$ ratio a maximum relative deviation is 0.5% at a random uncertainty of ≤ 0.7 %.

It is clear that in the case of $^{235}U\,/\,^{238}U$ isotopic ratio measurement, in order to identify its natural variation as well as to control the uranium material fabrication process, the HRGS method cannot compete with a destructive method of mass-spectrometry. Nevertheless, the gamma-spectrometric measurement of ^{235}U isotope is widely applied in the problems of nuclear material safeguards and nuclear forensics for fast in-field categorization of radiological or nuclear material in order to identify the safety risk to first responders and to the public. Application of the absolute efficiency calibration approach makes it possible to decrease the measurement uncertainty to ~ 1 % compared to the international target values of 3.6 % used for measurement uncertainties of NDA methods.

The commercial FRAM and ISOCS software can be used for environmental monitoring to determine the natural variations of the $^{234}U\,/\,^{238}U$ isotopic ratio in water, soil and sediments, while a proposed combined intrinsic efficiency calibration approach permits to expand the list of investigations with uranium ores for the purpose of determining their geographical origin. A similar situation takes place when determining the $^{234}U\,/\,^{235}U$ ratio variations in the different uranium deposits, limiting values of which can be ~ 30 %. Establishing uranium enrichment process characteristics using $^{234}U\,/\,^{235}U$ variation is probably not feasible for HRGS.

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ГАММА-СПЕКТРОМЕТРИЧНЕ (HRGS) ВИЗНАЧЕННЯ ІЗОТОПНИХ СПІВВІДНОШЕНЬ УРАНУ З ВИКОРИСТАННЯМ РІЗНИХ ПІДХОДІВ КАЛІБРУВАННЯ ПО ЕФЕКТИВНОСТІ

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Досліджувався вплив різних підходів калібрування по ефективності на величину і джерела невизначеності гамма-спектрометричних вимірювань ізотопних співвідношень урану $^{234}U\,/\,^{238}U$, $^{235}U\,/\,^{238}U$, $^{234}U\,/\,^{235}U$ для цілей технологічного контролю, ядерної криміналістики і екологічного моніторингу. Напівпровідниковий детектор на основі HPGe (Canberra Broad Energy Germanium detector BEGe3830) і п'ять еталонних сертифікованих уранових зразків CRM 969 і CRM 146 із вмістом $^{235}U\,/\,U$ від 0.7 до 20.0 мас. % використовувалися при проведенні досліджень. Розрахунок ізотопних співвідношень урану виконували шляхом обробки експериментальних гамма-спектрів комерційними програмними продуктами: MGAU (LLNL), FRAM (LANL), ISOCS (Canberra/Mirion Technologies), які основані на підходах калібрування за абсолютною і відносною ефективністю. Показано, що величини максимальних відносних відхилень результатів при визначенні ізотопних співвідношень $^{234}U\,/\,^{238}U$ і $^{234}U\,/\,^{235}U$ програмним забезпеченням MGAU \ FRAM \ ISOCS складають ~ 25 % \ ~ 10 % \ ~ 10 % при цьому випадкові невизначеності варіюються в інтервалі ± [18-25 % \ 2-15 % \ ≤ 3 %], відповідно. При визначенні ізотопних співвідношень $^{235}U\,/\,^{238}U$ програмним забезпеченням MGAU \ FRAM \ ISOCS, максимальні відносні відхилення складають ~ 3 % \ ~ 4 % \ ~ 1 % при цьому випадкові невизначеності знижуються до ± [1 % \ 1 % \ 1 %], відповідно. Запропоновано комбінований підхід калібрування по відносній ефективності, в якому для аналітичного опису залежності $\varepsilon_{rel.i}(E_i)$ використані поліноміальні функції. В даному підході максимальне відносне відхилення при визначенні ізотопних співвідношень $^{234}U\,/\,^{238}U$ і $^{234}U\,/\,^{235}U$ складає 2.7 % при випадковій невизначеності ≤ 1 %, а в разі визначення співвідношення $^{235}U\,/\,^{238}U$ максимальне відносне відхилення дорівнює 0.5 % при випадковій невизначеності ≤ 0.7 %.

Ключові слова: гамма-спектрометрії високої роздільної здатності, ізотопні співвідношення урану, калібрування по ефективності, невизначеність вимірювань, уранова руда, MGAU, FRAM, ISOCS