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DETERMINATION OF THE ^{234}U ISOTOPE CONTENT IN URANIUM-BEARING MATERIALS USING HIGH-RESOLUTION GAMMA SPECTROMETRY

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The paper presents an overview of the research into the available non-destructive methods of determining the ^{234}U isotope content in uranium-bearing materials. An alternative approach to a problem of detector calibration by the characteristic “intrinsic” efficiency is proposed. Certified reference uranium-bearing materials CRM 969 and CRM 146 (a range of ^{235}U enrichments studied was 0.3…93%) were used as test samples, measurements were carried out with a wide-range energy detector based on the high-purity BeGe 3830 germanium (Canberra, USA) with 38 cm^2 area and 3 cm thickness. An approach used for the “intrinsic” efficiency calibration for the ^{234}U analysis permits to decrease the measurement error to 7.5% in the whole range of ^{235}U enrichment (from 0.3 to 93%) and ^{234}U concentrations (20 to 9800 μg/g). The proposed method does not demand standard samples for equipment calibration and does not depend on the physical (chemical) form of the investigated material and measurement geometry.

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INTRODUCTION

Natural uranium is a mixture of three isotopes: ^{238}U (the content in natural mixture 99.280 wt. %), ^{235}U (0.714 wt. %), and ^{234}U (0.006 wt. %) [1]. A ^{234}U isotope is radiogenic, not a primary one, it is a part of the radioactive series of ^{238}U. Despite an utterly low content of ^{234}U, its activity in natural uranium is almost equal to the ^{238}U activity, as these isotopes are in balance. Thus, ^{234}U and ^{238}U contribute each more than 49% to the total activity of natural uranium.

When making fuel for nuclear plants, natural uranium is enriched in order to increase the ^{235}U isotope content. At the same time, the content of ^{234}U isotope, as even lighter, also increases. Although in the nuclear fuel the content of ^{234}U remains at the level of hundredths of a percent its activity becomes predominant. That is why, from a sanitary point of view, ^{234}U carries the greatest radiological hazard to the staff health that indicates an urgency of determining even its small contents.

Furthermore, in conformity with the nuclear fuel cycle (NFC) processes, the ^{234}U content limit in the raw material of natural and enriched uranium hexafluoride (UF_6) is regulated by ASTM C 787 and ASTM C 996 standards at 60 and 11 μg/g of U, respectively. Consequently, the quantitative identification of ^{234}U is urgent both for the radiation safety and for the implementation of analytical quality control of NFC products.

Currently the destructive methods of analysis (inductively coupled plasma mass spectrometry, alpha spectrometry) of the isotopic composition of uranium-bearing materials are well developed [2 - 5]. One of the disadvantages of destructive methods is complex and time-consuming sample preparation: for example, for alpha spectrometry it is necessary to separate completely the analyte from the matrix and to transfer the sample into the thin-disk mold using electrodeposition, evaporation, co-precipitation [6]. Therefore, the non-destructive methods with a simplified sample preparation are quickly developing. In addition, the use of such methods decreases the time of direct contact with the sample that is especially important when working with radioactive materials and does not lead to the formation of radioactive waste, which subsequently should be disposed.

Gamma-ray spectrometry, as a non-destructive method of analysis of the isotopic composition of uranium-bearing materials, began to be used in the 1970s [7, 8]. To date, available are the Canberra's commercial software for uranium isotope analysis: MGAU (Multi-Group Analysis for Uranium) and FRAM (Fixed-energy Response-function Analysis with Multiple Efficiency) developed in U.S. national laboratories (LLNL, LANL) [9, 10].

As a result of processing the gamma spectrometric data the software calculates the content of isotopes ^{238}U, ^{235}U, ^{234}U (and in some cases ^{236}U). As these software codes were developed primarily to determine the enrichment of uranium-bearing materials, the metrological characteristics of ^{235}U, ^{238}U measurements were thoroughly investigated and determined [11 - 13], in contrast with the ^{234}U isotope. The paper [14] shows that the error of determining the ^{234}U content using MGAU code can range from 20 to 50%. So, the purpose of this study was to analyze the available non-destructive methods and to develop an alternative approach for determining the isotope ^{234}U content in uranium-bearing materials as well as to substantiate the choice of the best method for providing the radiation safety and analytical quality control of NFC products.

EXPERIMENTAL TECHNIQUE

Investigations were carried out using certified reference uranium-bearing materials (CRM 969: level of enrichment from 0.3 to 4 wt. % and CRM 146: level of enrichment from 20 to 93 wt. %) manufactured by the New Brunswick Laboratory of USA. The characteristics of the samples are given in Table 1.

Table 1

Interferences of the main analytic lines of K and L series elements with uranium lines of L and M series

Sample ID	^{235}U, wt.%	^{238}U, wt.%	^{234}U, wt.%
031	0.3166 ±0.0002	99.6668 ±0.0004	0.002 ±0.0002
071	0.7119 ±0.0005	99.2828 ±0.0004	0.0052 ±0.0002
194	1.9420 ±0.0014	98.0404 ±0.0018	0.0171 ±0.0002
295	2.9492 ±0.0021	97.0196 ±0.0029	0.0279 ±0.0004
446	4.4623 ±0.0032	95.4950 ±0.0032	0.0359 ±0.0003
NBL0013	20.1070 ±0.0200	79.5470 ±0.0200	0.1486 ±0.0004
NBL0014	52.4880 ±0.0420	46.8760 ±0.0430	0.3718 ±0.0010
NBL0015	93.1703 ±0.0052	5.5559 ±0.0053	0.9800 ±0.0029

The gamma-ray spectra of the samples investigated were acquired using a broad-energy detector based on the high-purity germanium of BeGe 3830 type (Canberra, USA) with a 38 cm^2 area and 3 cm thickness having the energy resolution of 0.468 at 5.9 keV; 0.572 at 122 keV, and 1.51 at 1.332 keV.

Experimental spectrometric data were processed using the commercial program packages MGAU and FRAM. Besides, the ^{234}U isotope content evaluation was performed using an empirical equation from [15], $C(^{234}U) = 0.0015 + 0.0058\cdot C(^{235}U) + 0.000054\cdot C^2(^{235}U)$, where $C(^{234}U)$ is the ^{234}U content; $C(^{235}U)$ is the ^{235}U content (enrichment).

An alternative approach for the ^{234}U content determination was based on the approach of "intrinsic" efficiency calibration proposed in the studies of the age-dating of uranium-bearing materials [16]. 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. A desired content can be derived from the activity ratio of isotopes ^{234}U and ^{235}U.

The isotope activity in the sample is written as $A = P/\varepsilon_{abs}\cdot I$, where P is the detector counting rate at the selected peak of photoelectric absorption; ε_{abs} is the detector absolute efficiency and I is the emission intensity of gamma-ray of a given energy. The main problem in determining the absolute values of the isotope activity is to find ε_{abs} which depends on many factors (gamma-ray energy, detector and sample characteristics, distance, absorbers, etc.). This problem can be avoided with the use of isotope activity ratio. In the region of gamma-ray energies from 120 to 210 keV (Fig. 1) there are lines of ^{234}U isotope (120.90 keV, $I = 0.0342\%$) and of ^{235}U isotope (143.76 keV, $I = 10.96\%$; 163.33 keV, $I = 5.08\%$; 185.72 keV, $I = 57.20\%$, and 205.31 keV, $I = 5.01\%$). By rewriting the activity equation as $A\cdot\varepsilon_{abs} = P/I$, plotting the ratio P/I versus ^{235}U gamma-ray energy (E) and extrapolating the resulting dependence by the linear or quadratic function into the 120 keV energy range, we obtain the value of $P^{U-235}_{120.90}/I^{U-235}_{120.90}$ equal to the detection "intrinsic" efficiency of the conventional ^{235}U gamma-quanta with 120.90 keV energy at a fixed activity value ($A^{U-235}\cdot\varepsilon^{120.90}_{abs}$).

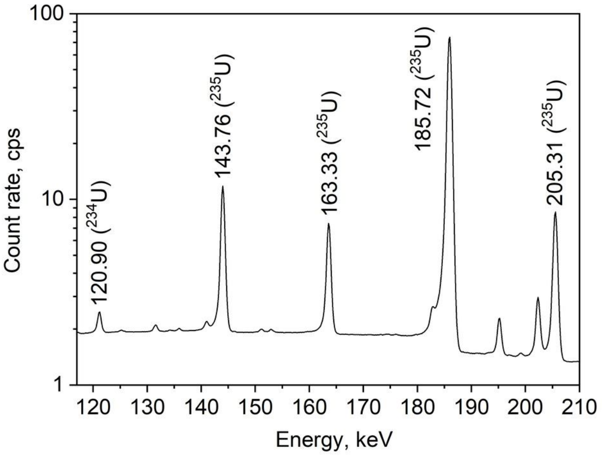

Fig. 1. Gamma-spectrum of the certified reference uranium-bearing material ID No 194 in the energy range from 120 to 210 keV

Then the activity ratio ^{234}U/^{235}U can be written as:

$$\frac{A^{U-234}\cdot\varepsilon^{120.90}_{abs}}{A^{U-235}\cdot\varepsilon^{120.90}_{abs}} = \frac{P^{U-234}_{120.90}/I^{U-234}_{120.90}}{P^{U-235}_{120.90}/I^{U-235}_{120.90}}.$$

By canceling the values of absolute efficiency $\varepsilon^{120.90}_{abs}$ finally we get:

$$\frac{A^{U-234}}{A^{U-235}} = \frac{P^{U-234}_{120.90}/I^{U-234}_{120.90}}{P^{U-235}_{120.90}/I^{U-235}_{120.90}}.$$

Having the resulting ratio of the ^{234}U and ^{235}U isotope activities and determining the content of ^{235}U in the sample by the software codes MGAU or FRAM, and taking into account the values of their specific activities 2.30×10^8 and 7.98×10^4 Bk/g it is possible to calculate the ^{234}U isotope content. The proposed method eliminates the need of standard samples for an equipment calibration, does not depend on the physical (chemical) form of materials under study and geometry of measurements.

RESULTS AND DISCUSSION

Fig. 2 shows the uranium isotope activity contributions into the total activity of the certified reference samples with various enrichments (uranium mass ~ 169 g in the samples CRM 969 and ~ 194 g in the samples CRM 146). It is seen that, indeed, starting with the contents of ^{235}U more than 0.7 wt. %, the ^{234}U isotope activity becomes predominant and reaches ~ 90% of the total activity for highly enriched uranium.

Table 2 gives the results of determining the ^{234}U isotope content using the software codes MGAU and FRAM, as well as the empirical equation described above.

In the Table, besides the ^{234}U content values, the standard deviations and relative measurement errors (σ and δ) are given. The research results show that the available methods of ^{234}U analysis are, most likely quantitative, especially for the samples with natural (0.7 wt. %) and depleted (0.3 wt. %) ^{235}U contents.

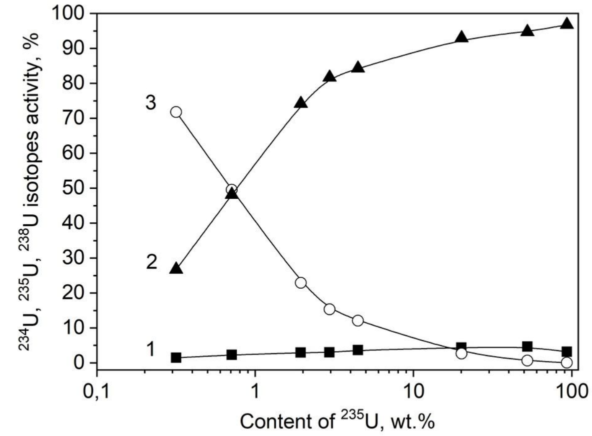

Fig. 2. Contribution of uranium isotope activities into the total activity of uranium-bearing materials versus their enrichment: 1 – activity of ^{235}U; 2 – activity of ^{234}U; 3 – activity of ^{238}U

The results of the MGAU code application leads to the underestimation of the ^{234}U content in the entire range of material enrichments, while the error by formula [15] is of a diverse character. There is observed a tendency to the measurement error decrease with enrichment increasing, so the FRAM code application for analysis of low-enriched samples allows determining the ^{234}U content with an error margin less than ± 10%. Standard deviations (σ) of measurement results, depending mainly on the 120.90 keV line statistic and spectral data processing algorithm, are maximum for ID samples No 031 and No 071 (50 and 67% for MGAU code and 64 and 26% for FRAM code), and they monotonically decrease to 20 and 3%, respectively, with enrichment increasing.

To develop an alternative method for determination of the ^{234}U content based on the "intrinsic" efficiency calibration, the *P/I* ratios were plotted, as a function of ^{235}U gamma-ray energy (143.76; 163.33; 185.72, and 205.31 keV), and then approximated by a quadratic or linear function (Fig. 3). Thus, the coefficients *A1*, *B1*, *B2*, the correlation coefficients *R2* and the mean-square deviation (standard uncertainty) were found. The selection of the approximation function was based on an evaluation of the correlation coefficient and mean-square deviation (MSD), the maximum value of the latter did not exceed 0.9%.

Table 2

Results of determining the ^{234}U isotope content using the software codes MGAU and FRAM, as well as the empirical formula [15]

Sample ID	MGAU		FRAM		By equation [15]	
	$C(^{234}U) \pm \sigma$, wt. %	δ, %	$C(^{234}U) \pm \sigma$, wt. %	δ, %	$C(^{234}U) \pm \sigma$, wt. %	δ, %
031	0.0040±0.0020	+100.00	0.0028±0.0018	+40.00	0.0033	+67.10
071	0.0030±0. 0020	-42.31	0.0070±0.0018	+34.62	0.0057	+8.77
194	0.0110±0.0030	-35.67	0.0169±0.0018	-1.17	0.0129	-24.17
295	0.0200±0.0040	-28.32	0.0254±0.0019	-8.96	0.0191	-31.63
446	0.0250±0.0050	-30.36	0,0377±0.0021	+5.01	0.0285	-20.73
NBL0013	0.1140±0.0230	-23,29	0.1474±0.0090	-0,81	0.1399	-5.83
NBL0014	0.2730±0.0550	-26.57	0.2366±0.0067	-36.36	0.4547	+22.30
NBL0015	0.7270±0.1460	-25.82	0.8930±0.0254	-8.88	1.0106	+3.13

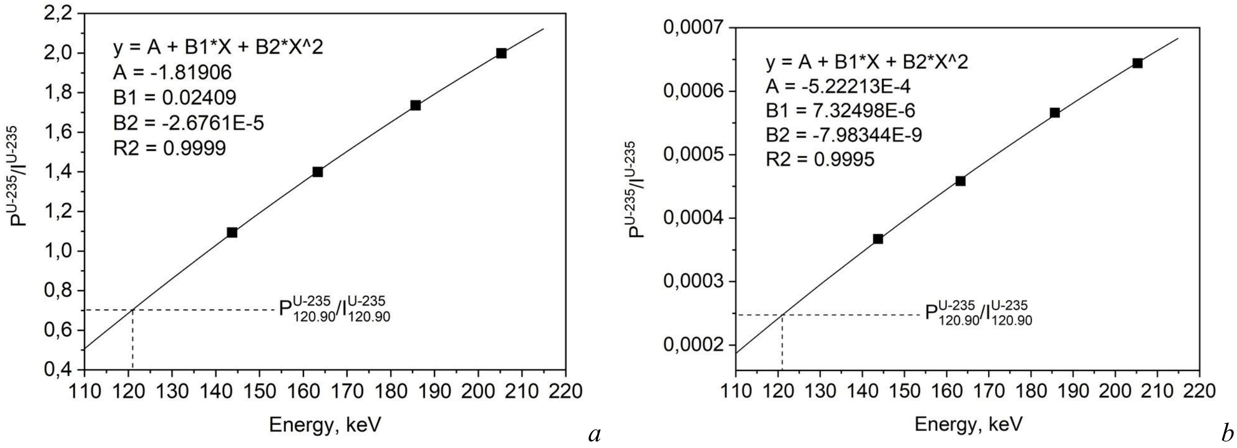

Fig. 3. Results of the approximation of the P/I ratio versus ^{235}U gamma-ray energy and its extrapolation into the 120 keV energy range: a – sample ID No 031; b – sample ID No NBL0015

The resulting functions were used to find the ratio $P^{U-235}_{120.90}/I^{U-235}_{120.90}$ and further, determining $P^{U-234}_{120.90}/I^{U-234}_{120.90}$ by processing the 120.90 keV peak from the obtained spectral data, the ratio of activities A^{U-234}/A^{U-235} was calculated and, as a consequence, the ^{234}U isotope content was determined. The calculation results are given in Table 3.

The maximum standard deviation values (σ) are 28 and 5% for depleted and natural uranium. This is explained by the low ^{234}U peak statistic (120.90 keV) in these samples (0.000136 and 0.0082 counts/s) and, as a consequence, by a significant uncertainty in the analysis of its area. For all other enriched samples, the standard deviation value ranges from 1.0 to 2.5%. The measurement error monotonically decreases with enrichment increasing that is also explained by the increase of the ^{234}U, ^{235}U peak intensities and by the volume of their statistics.

Table 3

Results of the ^{234}U isotope content determination using the method of "intrinsic" efficiency calibration

Sample ID	Certified $C(^{234}U)$, wt. %	Measured $C(^{234}U)$, wt. %	σ, %	δ, %
031	0.0020	0.001854 ±0.000527	28.41	-7.30
071	0.0052	0.005574 ±0.000280	5.02	+7.20
194	0.0171	0.018327 ±0.000394	2.15	+7.18
295	0.0279	0.029392 ±0.000355	1.21	+5.35
446	0.0359	0.037466 ±0.000480	1.28	+4.36
NBL0013	0.1486	0.154782 ±0.002870	1.85	+4.15
NBL0014	0.3718	0.382856 ±0.009655	2.52	+2.97
NBL0015	0.9800	1.007102 ±0.025198	2.50	+2.77

The relative measurement error (δ) behaves similarly to the standard deviation for the same reasons. An insignificant systematic overestimation of the ^{234}U content value is associated with the error of experimental data approximation by a quadratic function, and probably this problem can be solved by selection of an alternative function.

To apply the "intrinsic" efficiency method for detector calibration, in order to determine the ratio of isotopes activities, the presence of their sufficiently intense lines with close energies in the spectrum is required. For ^{234}U and ^{235}U isotopes this condition is optimally satisfied, mechanisms and effects of the interaction between gamma-ray and materials of the sample, detector and container are identical for the specified geometry of measurements in a narrow range of energies. Consequently, the isotope activity ratio under consideration can be reliably derived by approximation of the normalized counting rates in the photoelectric absorption peaks of ^{235}U followed by extrapolation of this dependence into the energy range of ^{234}U gamma-ray.

The lower detection limit of values $C(^{234}U)$ – 0.0020 wt. % (20 μg/g) is consistent, by the value order, with the maximum allowable contents of ^{234}U in the raw material of natural and enriched UF_6 that indicates the possibility of applying the proposed method for the analytical quality control of NFC products. It should be noted that the approaches described in this paper suggest a uniform distribution of uranium isotopes in the matrix and the absence of a significant gamma-ray absorption. For example, the characterization of radioactive waste may require further research to set the sensitivity limits of the proposed method.

CONCLUSIONS

The available methods of non-destructive determination of ^{234}U isotope content in uranium-bearing materials have been analyzed, and an alternative approach of "intrinsic" efficiency calibration of the detector is proposed.

It is shown that the use of up-to-day commercial software products for isotopic uranium analysis does not allow to reliably evaluate the content of ^{234}U isotope in depleted and natural samples due to a significant measurement error (from 35 to 100%). In the case of enriched uranium analysis, the MGAU software code systematically underestimates the ^{234}U content by 20…30%, and the FRAM code can be used in the range of ^{235}U enrichments from 2 to 20%.

Features of the interaction between the gamma-ray and materials of the sample and detector in the energy range of the most intense lines of ^{234}U and ^{235}U (120…210 keV) provide an opportunity to implement the approach of "intrinsic" efficiency calibration for ^{234}U content analysis. As a result, the error of the ^{234}U content analysis did not exceed 7.5% in the entire range of ^{235}U (0.3…93%) enrichment and ^{234}U concentrations (20…9800 μg/g).

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ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ ИЗОТОПА ^{234}U В УРАНСОДЕРЖАЩИХ МАТЕРИАЛАХ МЕТОДОМ ГАММА-СПЕКТРОМЕТРИИ ВЫСОКОГО РАЗРЕШЕНИЯ

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Проанализированы существующие методы неразрушающего определения количественного содержания изотопа ^{234}U в урансодержащих материалах, а также предложен альтернативный метод, основанный на подходе калибровки детектора по «характерной» эффективности. В качестве исследуемых образцов использовали сертифицированные стандартные образцы урансодержащих материалов CRM 969 и CRM 146 (интервал исследуемых обогащений по ^{235}U (0,3…93%), измерения проводили с помощью широкодиапазонного детектора на основе германия высокой чистоты типа BeGe 3830 (Canberra, США) площадью 38 см^2 и толщиной 3 см. Использование подхода калибровки детектора по «характерной» эффективности для анализа ^{234}U приводит к снижению погрешности измерений до 7,5% во всем диапазоне обогащений по ^{235}U (0,3…93%) и исследуемых концентраций ^{234}U (20…9800 μг/г). Предлагаемый метод не требует наличия стандартных образцов для калибровки оборудования, не зависит от физической (химической) формы исследуемых материалов и геометрии измерений.

ВИЗНАЧЕННЯ ВМІСТУ ІЗОТОПУ ^{234}U В УРАНВМІЩУЮЧИХ МАТЕРІАЛАХ МЕТОДОМ ГАММА-СПЕКТРОМЕТРІЇ ВИСОКОГО РОЗПОДІЛЕННЯ

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Проаналізовано існуючі методи неруйнівного визначення кількісного вмісту ізотопу ^{234}U в уранвміщуючих матеріалах, а також запропоновано альтернативний метод, заснований на підході калібрування детектора за «характерною» ефективністю. В якості досліджуваних зразків використовували сертифіковані стандартні зразки уранвміщуючих матеріалів CRM 969 і CRM 146 (інтервал збагачень по ^{235}U (0,3...93%), вимірювання проводили за допомогою широкодіапазонного детектора на основі германію високої чистоти типу BeGe 3830 (Canberra, США) площею 38 см^2 і товщиною 3 см. Використання підходу калібрування детектора за «характерною» ефективністю для аналізу ^{234}U призводить до зниження похибки вимірювань до 7,5% у всьому діапазоні збагачень по ^{235}U (0,3...93%) і концентрацій ^{234}U (20...9800 μг/г). Запропонований метод не вимагає наявності стандартних зразків для калібрування обладнання, не залежить від фізичної (хімічної) форми досліджуваних матеріалів і геометрії вимірювань.