https://doi.org/10.46813/2025-157-113

# DETERMINATION OF MINIMUM DETECTABLE ACTIVITY OF $^{214}$Bi IN URANIUM OXIDE FOR URANIUM AGE DATING USING HIGH-RESOLUTION GAMMA SPECTROMETRY (HRGS)

*D.V. Kutnyi[1], D.D. Burdeinyi[1], S.N. Afanasiev[1]*, S.A. Vanzha[1], O.P. Zhukov[2]*
*[1]NSC "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine;*
*[2]Institute for Nuclear Research, Kyiv, Ukraine;*
**E-mail: afanserg@kipt.kharkov.ua*

This study investigates the detection limits of $^{214}$Bi in uranium oxides and the minimum required mass of $U_3O_8$ for determining uranium age using high-resolution gamma spectrometry. Measurements were conducted with BEGe 3830 (NSC KIPT, Kharkiv) and GC 6020 (INR, Kyiv) HPGe detectors. Background gamma radiation intensities of $^{214}$Bi at 609.312 and 1120.287 keV were determined: (0.0164±0.0003) and (0.0068±0.0003) cps at NSC KIPT, and (0.0058±0.0004) and (0.0029±0.0002) cps at INR, respectively. The minimum detectable activities (MDA) of $^{214}$Bi for gamma radiation at 609.312 and 2204.21 keV were 15 and 10 Bq for BEGe 3830, and 5 and 2 Bq for GC 6020, respectively. The dependence of $^{214}$Bi activity in 1 g of $U_3O_8$ on $^{235}$U content (0.7…90 wt.%) and age (3-60 years) was calculated, showing that the lowest specific activity of $^{214}$Bi is 0.03 Bq per gram of $U_3O_8$ in the investigated range. Minimum required sample masses for uranium age determination using HRGS were estimated. For gamma radiation at 609.312 and 2204.21 keV, the masses should be 500 and 370 g for BEGe 3830, and 160 and 70 g for GC 6020, respectively.

PACS: 29.30. Kv

## INTRODUCTION

Counteracting the illicit trafficking of nuclear and other radioactive materials is a crucial component of international security. Such materials pose risks to global safety and stability [1]. The emerging interdisciplinary field of nuclear forensics [2] enables the determination of characteristics of confiscated radioactive samples through analytical methods. This information can be used to trace the origin and production of nuclear material, aiding in identifying its source.

A key tool in nuclear forensics is radiochronometry [3], which determines the time elapsed since the material's production (chemical separation from daughter nuclides or purification) or enrichment. The radioactive decay of parent isotopes into daughters allows for age determination through the activity ratio of isotope pairs, including uranium.

Numerous techniques exist to determine the age and origin of nuclear materials. Destructive methods, such as mass spectrometry and α-spectrometry, provide precise results but require additional sample preparation, including chemical separation or thin-layer sample creation [4–9].

Non-destructive methods, such as gamma spectrometry, are often preferred when preserving samples is essential for judicial purposes. The activity ratio of $^{214}$Bi/$^{234}$U has been proposed as a gamma spectrometry-based chronometer for uranium dating [10]. This method has demonstrated good agreement with mass spectrometry data, with measurement uncertainties slightly exceeding 10%. Subsequent studies [11–13] extended its application to low-enriched uranium and analyzed $^{232}$U for recycled uranium detection. During the 4th collaborative materials exercise of the Nuclear Forensics International Technical Working Group (ITWG) [5, 14], radiochronometry was applied to date young low-enriched uranium samples with a minimum enrichment of 2%, indicating that ages as low as ten years can be determined using the $^{214}$Bi/$^{234}$U chronometer. However, attempts to use other chronometers, such as $^{223}$Ra/$^{235}$U [15], were unsuccessful for uranium with enrichment below 40% due to low peak intensity of $^{223}$Ra's 269.5 keV gamma line. Research on uranium dating using HRGS remains limited. Existing publications lack data on measurable $^{214}$Bi activities, their dependence on uranium enrichment and age, detection limits, and background effects. Investigating these factors is critical for accurate age determination and planning nuclear forensic analyses. Understanding experimental conditions enables experts to select appropriate analytical methods.

## 1. EXPERIMENTAL METHODOLOGY

Certified reference materials (CRM) of uranium-bearing samples from the CRM 969 series, with $^{235}$U content ranging from 0.32 to 4.46% by weight, were studied. Gamma spectra were acquired using wide-range HPGe detectors: BEGe 3830 (Canberra, USA), with a diameter of 70 mm and thickness of 30 mm, at NSC KIPT (Kharkiv), and GC 6020 (Canberra, USA), with a diameter of 74 mm and thickness of 50 mm, at INR (Kyiv). Optimal gamma-line energies for $^{214}$Bi activity determination were selected based on intensity and potential overlap with $^{238}$U gamma lines.

Table 1 presents characteristics of the most intense gamma lines of $^{214}$Bi and $^{234m}$Pa. From the data presented in the table it is evident that most of the gamma lines of $^{214}$Bi can interfere with the gamma lines of $^{234m}$Pa (daughter isotope of $^{238}$U). Despite the low

intensity of gamma radiation of $^{234m}$Pa, its contribution to the intensity of gamma radiation of $^{214}$Bi must be taken into account due to the fact that its quantity can exceed the quantity of $^{214}$Bi by several orders of magnitude.

Table 1

Gamma radiation characteristics for $^{214}$Bi and $^{234m}$Pa isotopes

| Gamma-ray energy $^{214}$Bi, keV | Number of emitted gamma quants per 100 decays | Gamma-ray energy $^{234m}$Pa, keV | Number of emitted gamma quants per 100 decays |
|---|---|---|---|
| 609.312 | 45.49 | - | - |
| 768.356 | 4.892 | 766.361 | 0.323 |
| 1120.287 | 14.91 | 1120.6 | 0.00173 |
| 1238.111 | 5.831 | 1237.28 | 0.00528 |
| 1764.494 | 15.31 | 1765.44 | 0.0084 |
| 2204.21 | 4.913 | - | - |

## 2. RESULTS AND DISCUSSION

### 2.1. MEASUREMENT OF BACKGROUND GAMMA SPECTRA

Fig. 1 shows the background gamma spectra measured using the BEGe 3830 and GC 6020 detectors. The gamma spectra are shifted along the ordinate axis (OY) for clarity.

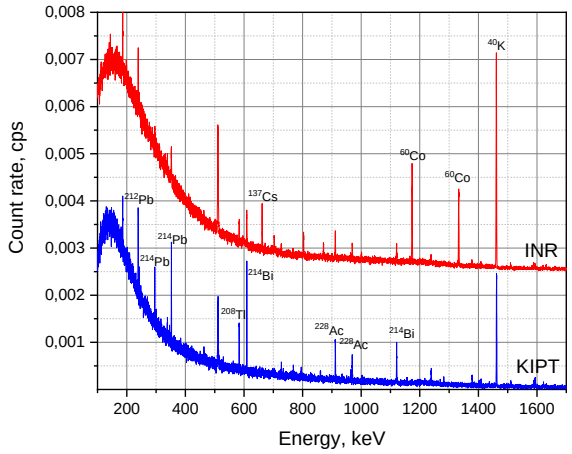



*Fig. 1. Background gamma spectra measured using BEGe 3830 and GC 6020 detectors*

In the background gamma spectrum measured with the coaxial detector GC 6020, there are quite intense peaks from anthropogenic radionuclides $^{60}$Co and $^{137}$Cs. However, the gamma radiation intensity of $^{214}$Bi with an energy of 609.312 keV is significantly lower compared to the gamma spectrum obtained with the BEGe 3830 detector.

To determine the average background gamma radiation intensities of $^{214}$Bi and their fluctuations, measurements of background gamma spectra were carried out in the laboratories of the KIPT and INR over a period of 7 months, and counting rates in the relevant $^{214}$Bi peaks were evaluated. The results of the study are presented in Fig. 2.

The average intensities of the background gamma radiation of $^{214}$Bi measured using the GC 6020 detector are 2–3 times lower than those measured with the BEGe 3830 detector. The uncertainty in the intensity measurements in the KIPT geometry does not exceed 4%, while in the INR geometry it is 7%. Clearly, the conditions for gamma spectrometric measurements at INR allow for the detection of lower activity values of the $^{214}$Bi isotope and, likely, lower uranium ages compared to the measurement conditions at KIPT, with identical values of $^{235}$U enrichment.

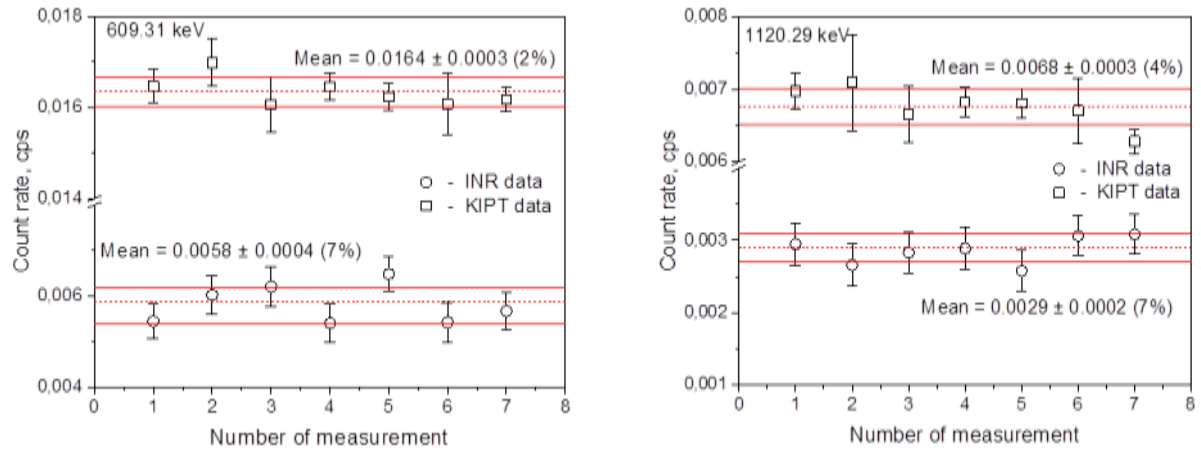



*Fig. 2. Intensities of background gamma radiation from $^{214}$Bi for energies 609.312 and 1120.287 keV measured using BEGe 3830 (KIPT data) and GC 6020 (INR data) detectors, along with their average values and measurement uncertainties*

Fig. 3 shows the photoelectric absorption peaks of $^{214}$Bi with energies of 609.312 and 2204.21 keV, according to literature data [10, 11], as well as those measured using the BEGe 3830 and GC 6020 detectors.

It is evident that the gamma radiation intensity at 2204.21 keV is an order of magnitude lower than the intensity at 609.312 keV, which significantly complicates the processing and analysis of the peaks.

Once again, in support of our previous statement, it is evident that the highest intensity of background gamma radiation from $^{214}$Bi is characteristic of the KIPT measurement geometry using the BEGe 3830 detector. On the other hand, the BEGe 3830 detector has slightly better energy resolution compared to the GC 6020 detector, with values of 1.0 and 1.4 keV, respectively, for the 609.312 keV energy.

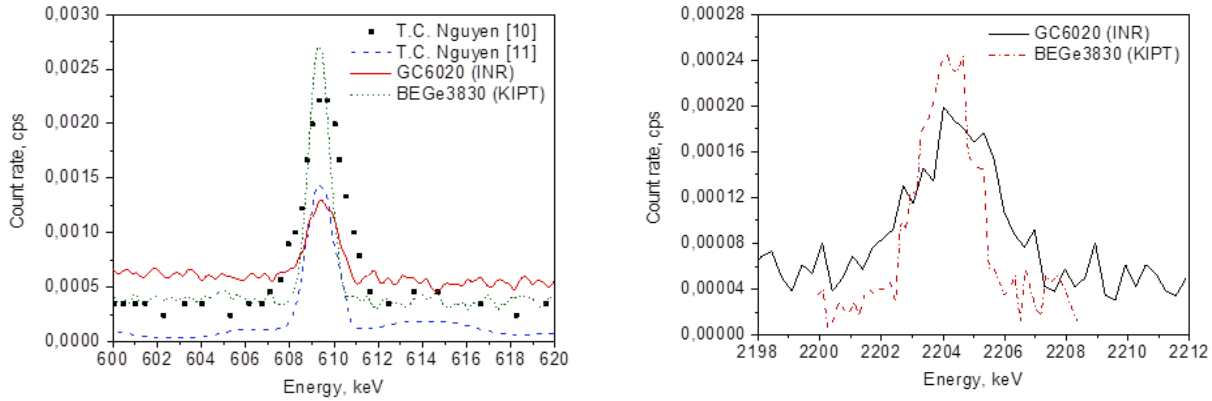



*Fig. 3. Photopeak absorption of $^{214}$Bi at energies 609.312 and 2204.21 keV measured using BEGe 3830 and GC 6020 detectors, as well as data from [10, 11]*

### 2.2. DETERMINATION OF THE MINIMUM DETECTABLE ACTIVITY (MDA) OF $^{214}$Bi

Next, using certified standard samples of uranium-containing materials from the CRM 969 set, the minimum detectable activity (MDA) of $^{214}$Bi was measured with the BEGe 3830 and GC 6020 detectors. The MDA calculations were performed using the expression provided below:

$$MDA = \frac{k^2 + 2k\sqrt{2 \cdot B}}{\varepsilon \cdot i \cdot t},$$

where $k$ is the confidence level, equal to 1.96 for a 95% confidence probability; $B$ – is the background; $\varepsilon$ – is the absolute detection efficiency of the detector; $i$ – is the probability of gamma quantum emission at the given energy; $t$ – is the gamma spectrum acquisition time (72 h).

Table 2 presents the results of the calculations of the minimum detectable activity (MDA) of $^{214}$Bi when registering its gamma radiation with energies of 609.312 and 2204.21 keV using the BEGe 3830 and GC 6020 gamma detectors.

For all the studied LEU samples (with $^{235}$U isotope content ranging from 0.71 to 4.46 mass.%), the minimum detectable activity of $^{214}$Bi when registering its gamma radiation with energies of 609.312 and 2204.21 keV was 15 and 10 Bq, respectively, using the BEGe 3830 gamma detector, and 5 and 2 Bq, respectively, using the GC 6020 gamma detector.

Table 2

Minimum detectable activities of $^{214}$Bi for gamma radiation at energies 609.312 and 2204.21 keV as registered by BEGe 3830 and GC 6020 gamma detectors

| Sample number/type | Uranium isotope content $^{235}$U, mass.% | MDA, Bq (BEGe 3830) | | MDA, Bq (GC 6020) | |
|---|---|---|---|---|---|
| | | 609.312 keV | 2204.21 keV | 609.312 keV | 2204.21 keV |
| CRM071 | 0.71 | 15.03 | 9.44 | 5.16 | 2.18 |
| CRM194 | 1.94 | 16.16 | 8.52 | 5.86 | 2.52 |
| CRM295 | 2.95 | 15.35 | 10.21 | 4.56 | 2.32 |
| CRM446 | 4.46 | 16.02 | 11.38 | 4.90 | 2.40 |
| **The average value of MDA:** | | **15.64** | **9.89** | **5.12** | **2.36** |

### 2.3. CRITERION FOR THE MINIMUM SAMPLE MASS FOR URANIUM AGE DETERMINATION

Having determined the minimum detectable activities of $^{214}$Bi when registering its gamma radiation with the BEGe 3830 and GC 6020 gamma detectors, the question arises: what activity values might characterize this isotope in uranium of varying enrichment and age?

Fig. 4 presents the dependence (heat map) of the $^{214}$Bi activity value in 1 g of uranium oxide ($U_3O_8$) on the content of the $^{235}$U isotope (0.7…90 mass.%) and age (3–60 years).

We did not consider extreme cases, such as LEU samples with ages less than 5-10 years, since the impossibility of determining their age by HRGS methods is evident.

The lowest values of $^{214}$Bi activity will be associated with uranium oxides containing the minimum amount of the $^{235}$U isotope/minimal age, and this value is 0.03 Bq per 1 g of $U_3O_8$. As the content of the $^{235}$U isotope/age increases, the activity of $^{214}$Bi also increases, reaching 5…6 Bq at the maximum considered values of enrichment/age.

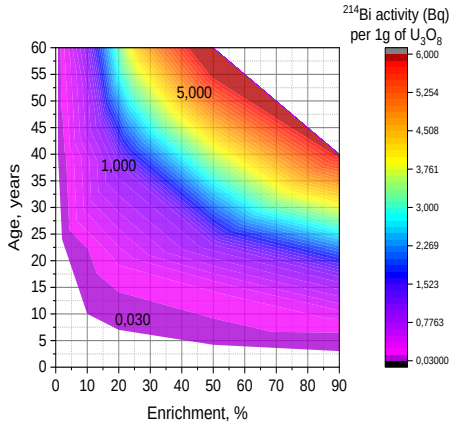



*Fig. 4. Activity dependence of $^{214}$Bi in 1 g of uranium oxide ($U_3O_8$) on its enrichment and age*

Knowing the minimum detectable activities of $^{214}$Bi when registering its gamma radiation with energies of 609.312 and 2204.21 keV using the BEGe 3830 and GC 6020 gamma detectors, as well as the activity values of $^{214}$Bi in 1 g of uranium oxide ($U_3O_8$) with varying content of the $^{235}$U isotope and different ages, one can estimate the sample masses of uranium oxide ($U_3O_8$) required for the gamma radiation of $^{214}$Bi to be detectable (Fig. 5).

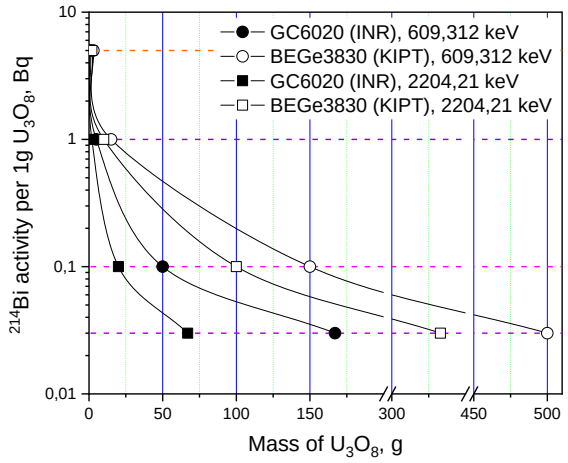



*Fig. 5. Required masses of uranium oxide ($U_3O_8$) samples for detecting specific activities of $^{214}$Bi ranging from 0.03 to 5 Bq when registering its gamma radiation with energies of 609.312 and 2204.21 keV using BEGe 3830 and GC 6020 gamma detectors*

Fig. 5 shows the dependencies illustrating the required mass of uranium oxide with varying specific activity of $^{214}$Bi (from 0.03 to 5 Bq per 1 g $U_3O_8$) for the activity of $^{214}$Bi to exceed the minimum detectable activity of the BEGe 3830 and GC 6020 gamma detectors when registering gamma radiation with energies of 609.312 and 2204.21 keV, i.e., for the gamma radiation of $^{214}$Bi to be detectable in the sample. It can be seen that the mass of samples with low specific activities of $^{214}$Bi (0.03 Bq per 1 g $U_3O_8$, with minimal content of the $^{235}$U isotope/minimal age) should be 500 and 370 g for the possibility of registering gamma radiation with energies of 609.312 and 2204.21 keV using the BEGe 3830 gamma detector. For the GC 6020 detector, these masses are 160 and 70 g, respectively. As the specific activity of $^{214}$Bi increases, the required sample masses decrease, and for an activity of 1 Bq per 1 g $U_3O_8$, they do not exceed 25 g for both gamma detectors.

## CONCLUSIONS

In this work, the limits of detection of $^{214}$Bi for determining the age of uranium using high-resolution gamma-ray spectrometry are investigated.

The intensities of the background gamma radiation of $^{214}$Bi with energies of 609.312 and 1120.287 keV, measured using the BEGe 3830 detector at the National Science Centre "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine, and the GC 6020 detector at the Institute of Nuclear Research, National Academy of Sciences of Ukraine, Kyiv, Ukraine, were determined. It was shown that the average intensities of the background gamma radiation of $^{214}$Bi measured with the GC 6020 detector are 2-3 times lower than those measured with the BEGe 3830 detector.

The minimum detectable activities of $^{214}$Bi using the BEGe 3830 and GC 6020 detectors were analyzed. For all the studied low-enriched uranium (LEU) samples (with $^{235}$U isotope content ranging from 0.71 to 4.46 mass.%), the minimum detectable activity of $^{214}$Bi when registering its gamma radiation with energies of 609.312 and 2204.21 keV was 15 and 10 Bq, respectively, using the BEGe 3830 gamma detector, and 5 and 2 Bq, respectively, using the GC 6020 gamma detector.

The dependence of the $^{214}$Bi activity value in 1 g of uranium oxide ($U_3O_8$) on the content of the $^{235}$U isotope (0.7…90 mass.%) and age (3-60 years) was calculated. It was shown that the lowest specific activity values of $^{214}$Bi (0.03 Bq per 1 g $U_3O_8$) are associated with uranium oxides with the minimum content of the $^{235}$U isotope/minimal age.

The minimum sample masses of uranium oxide ($U_3O_8$) required for determining the uranium age using high-resolution gamma spectrometry methods were estimated. For samples with low specific activities of $^{214}$Bi (0.03 Bq per 1 g $U_3O_8$, with minimal content of the $^{235}$U isotope/minimal age), the sample masses must be 500 and 370 g to allow registration of gamma radiation with energies of 609.312 and 2204.21 keV using the BEGe 3830 gamma detector. For the GC 6020 detector, these masses are 160 and 70 g, respectively.

## REFERENCES

1. M.J. Kristo, S.J. Tumey. The state of nuclear forensics // *Nucl. Instrum. Methods Phys. Res. B*. 2013, v. 294, p. 656-661. https://doi.org/10.1016/j.nimb.2012.07.047

2. K. Mayer, M. Wallenius, T. Fanghannel. Nuclear Forensic Science – from Cradle to Maturity // *Journal of Alloys and Compounds*. 2007, v. 444, p. 50-56. https://doi.org/10.1016/j.jallcom.2007.01.164

3. M. Wallenius, A. Morgenstern, C. Apostolidis, K. Mayer. Determination of the age of highly enriched uranium // *Anal. Bioanal. Chem.* 2002, v. 374, p. 379–384. https://doi.org/10.1007/s00216-002-1555-9

4. Z. Varga, A. Nicholl, E. Hrnecek, M. Wallenius, K. Mayer. Measurement of the 231Pa/235U ratio for the

age determination of uranium materials // *J. Radioanal. Nucl. Chem.* 2018, v. 318, p. 1565-1571. https://doi.org/10.1007/s10967-018-6247-9
5. M. Kristo, R. Williams, A. Gaffney, et al. The application of radiochronometry during the 4th collaborative materials exercise of the nuclear forensics international technical working group (ITWG) // *J. Radioanal. Nucl. Chem.* 2018, v. 315, p. 425-434. https://doi.org/10.1007/s10967-017-5680-5
6. K. Mayer, M. Wallenius, K. Lützenkirchen, et al. Nuclear Forensics: A Methodology Applicable to Nuclear Security and to Non-Proliferation // *Journal of Physics: Conference Series*. 2011, v. 312, p. 062003. https://doi:10.1088/1742-6596/312/6/062003
7. R. Williams, I. Hutcheon, M. Kristo, et al. Radiochronometry by mass spectrometry: Improving the precision and accuracy of age dating for nuclear forensics // *Proceedings of the Conference on Advances in Nuclear Forensics*. 2014, Vienna, Austria. IAEA-CN-218/014.
8. A. Hubert, M. Mendes, J. Aupiais, F. Pointurier. Advances in nuclear forensics analysis at CEA/DIF: Radiochronology studies // *Proceedings of the Conference on Advances in Nuclear Forensics*. 2014, Vienna, Austria. IAEA-CN-218/078.
9. R.W. Willams, A.M. Gaffney. $^{230}$Th-$^{234}$U model ages of some uranium standard reference materials // *Proc. Radiochim. Acta*. 2011, v. 1, p. 31-35. https://doi.org/10.1524/rcpr.2011.0005
10. C.T. Nguyen. Age-dating of highly enriched uranium by gamma-spectrometry // *Nucl. Instrum. Methods Phys. Res. B*. 2005, v. 229, p. 103-110. https://doi.org/10.1016/j.nimb.2004.10.089
11. C.T. Nguyen, J. Zsigrai. Gamma-spectrometric uranium age-dating using intrinsic efficiency calibration // *Nucl. Instr. Meth. B*. 2006, v. 243, p. 187–192. https://doi.org/10.1016/j.nimb.2005.07.205
12. C.T. Nguyen, J. Zsigrai, L. Lakosi. Characterization of uranium-bearing material by passive non-destructive gamma spectrometry // *Proceedings of the Conference on Nuclear and Particle Physics. NUPPAC*, 2009, Sharm El-Sheikh, Egypt. p. 413-424.
13. J. Zsigrai, T.C. Nguyen, A. Berlizov. Gamma-spectrometric determination of $^{232}$U in uranium-bearing materials // *Nucl. Instr. Meth. B*. 2015, v. 359, p. 137-144. https://doi.org/10.1016/j.nimb.2015.07.047
14. L. Lakosi, J. Zsigrai, A. Kocsonya, et al. Gamma spectrometry in the ITWG CMX-4 exercise // *J. Radioanal. Nucl. Chem.* 2018, v. 315, p. 409-416. https://doi.org/10.1007/s10967-017-5667-2
15. H.-D. Choi, J. Kim. Basic characterization of uranium by high-resolution gamma spectroscopy // *Nucl. Eng. Technol.* 2018, v. 50, p. 929-936. https://doi.org/10.1016/j.net.2018.04.008

*Article received 14.04.2025*

## ВИЗНАЧЕННЯ МІНІМАЛЬНОЇ ДЕТЕКТОВАНОЇ АКТИВНОСТІ $^{214}$Bi В ОКСИДІ УРАНУ ДЛЯ ЙОГО РАДІОХРОНОМЕТРІЇ МЕТОДАМИ ГАММА-СПЕКТРОМЕТРІЇ ВИСОКОЇ РОЗДІЛЬНОЇ ЗДАТНОСТІ (HRGS)

***Д.В. Кутній, Д.Д. Бурдейний, С.М. Афанасьєв, С.О. Ванжа, О.П. Жуков***

Досліджено межі детектування $^{214}$Bi в оксидах урану та критерії мінімальної маси $U_3O_8$ для визначення віку урану методами гамма-спектрометрії високої роздільної здатності із використанням гамма-детекторів на основі германію високої чистоти (HPGe) типу BEGe 3830 у ННЦ ХФТІ НАН України (м. Харків) та GC 6020 в ІЯД НАН України (м. Київ). Визначено інтенсивності фонового гамма-випромінювання $^{214}$Bi з енергіями 609,312 та 1120,287 кеВ, виміряні в ХФТІ – (0,0164±0.0003) та (0,0068±0,0003) імп./с та в ІЯД – (0,0058±0.0004) та (0,0029±0,0002) імп./с відповідно. Мінімальні детектовані активності $^{214}$Bi при реєстрації його гамма-випромінювання з енергіями 609,312 та 2204,21 кеВ гамма-детектором BEGe 3830 склали15 та 10 Бк, а детектором GC 6020 – 5 та 2 Бк відповідно. Розраховано залежність активності $^{214}$Bi у 1 г оксиду урану ($U_3O_8$) від вмісту ізотопу $^{235}$U (0,7…90 мас.%) та віку (3–60 років). Показано, що найменше значення питомої активності $^{214}$Bi у розглянутому діапазоні збагачень і віків становить ~0,03 Бк у 1 г $U_3O_8$. Оцінено мінімальні маси зразків оксиду урану, необхідні для визначення віку урану методами гамма-спектрометрії високої роздільної здатності. Ці маси складають ~500 та ~370 г для можливості реєстрації гамма-випромінювання з енергіями 609,312 та 2204,21 кеВ гамма-детектором BEGe 3830. Для детектора GC 6020 ці маси становлять ~160 та ~70 г відповідно.