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DETERMINATION OF $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ ISOTOPE RATIOS IN URANIUM OXIDE BY SECTOR-FIELD ICP-MS

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Influence of mass bias effect, isobaric and polyatomic interferences on the results of $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratio determination in uranium oxide by sector-field ICP-MS was studied. Uranium isotopic standards CRM U100, CRM U200 based on triuranium octoxide (U_3O_8) and single-collector mass spectrometer ICP-SFMS ELEMENT 2 were used for research. It has been demonstrated that the mass bias effect has most influence on the results of uranium isotope ratios determination. To investigate the influence of the mass bias effect on the determinations of uranium isotope ratios, the external standardization calibration was used with three models (linear, power, exponential) describing the behavior of the specific discrimination coefficient β versus the mass of measured isotopes. The mass discrimination factor has been found to vary from 6.00×10^{-3} to 1.20×10^{-2} . The advantage for using the (power/exponential)-law models of the $\beta = F(\Delta m)$ relationship for correcting measured isotope ratios was justified. In case of polyatomic interferences, the efficiency of uranium hydride ion ($^{235}\text{U}^1\text{H}^+$) formation is 3.54×10^{-5} , while the impact of isobaric overlapping due to the contribution of scattered $^{238}\text{U}^+$ ions to the intensities of less abundant ^{236}U and ^{235}U ions reaches 8.17×10^{-6} . The relative measurement error for the $^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ ratios was found to be $< 0.5\%$, and for the $^{235}\text{U}/^{238}\text{U}$ ratio less than 0.1% . The calculated standard uncertainty u of the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurements in the CRM U100 was 0.563 , 0.322 and 0.856% , respectively. These are reasonable estimates in comparison with the uncertainties of certified values of 0.296 , 0.097 and 0.265% .

KEY WORDS: inductively coupled plasma mass spectrometry, uranium oxide, mass bias effect, polyatomic interferences, isobaric overlapping, uranium isotope ratios

The mass-spectrometry methods are intended for isotopic and elemental analysis of materials and applied at atomic industry plants for providing in-process control, as well as quality control and end products certification [1]. The in-process monitoring of nuclear fuel and constructional materials processing is extremely important for predicting the products behavior under irradiation conditions, where even a minor change in the element concentration may lead to a significant property changes [2].

The quality of uranium products (uranium ore concentrate, uranium hexafluoride, uranium dioxide) is regulated by international standards, whereby one of the most important quality characteristics is the isotopic composition of uranium [3]. The analytical methodology of isotope ratio measurements of depleted, enriched, and natural uranium is determined by the ASTM standard (ASTM C 1477-08), which also sets limits on the relative measurement error: less than 0.1% for ^{235}U , and less than 1% for ^{234}U , ^{236}U .

For precise determination of the uranium isotopes abundance, the following types of multi-collector mass spectrometers are mainly used (in accordance with the substance ionization method): the thermal ionization mass spectrometer (TIMS) and the inductively-coupled plasma mass spectrometer (ICP-MS). The presence of several collectors allows simultaneous measurement of a few isotopes at a time, thereby offsetting the influence of signal intensity variations with time, and considerably improving the accuracy of isotope ratio measurements. According to various literature data, the relative measurement error for those mass spectrometers may vary from 0.05 to 0.002% [4,5,6].

The main application of single-collector sector-field ICP-MS is the analysis of extremely low contents of elements (elemental analysis) with the detection limit at level of ppq ($10^{-13}\%$) [7]. This is due to high resolution of such mass spectrometers and their high sensitivity ($\sim 10^6$ cps per 1 ppb ^{115}In). The application of ICP-SFMS in the uranium isotope analysis calls for an additional consideration of the following effects that may affect the measurement results.

The mass bias effect occurs in the interface part of the mass-spectrometer due to the space-charge effect in the skimmer cone region, and promotes a higher heavy-ion transfer efficiency. Thus, two isotopes of the same element in the same concentrations will induce a signal of different intensity.

Isobaric overlapping of the high-intensity peak tail with the mass m on the peak intensities with the masses $(m-1)$, $(m-2)$, $(m-3)$. This effect is associated with ion scattering by the molecules of the residual gas in the vacuum system, and it is referred to as the abundance sensitivity. Its value becomes critical during measuring the extreme isotope ratios (higher than 10^5), uranium isotopes being an example [8, 9].

Polyatomic interferences is caused by the formation of Ar^+ , H^+ , O^+ ions in plasma, which in their transit through the interface part of the mass spectrometer enter into the plasma-chemical reactions with the result that polyatomic ions

are produced. In this case, to estimate the $m = 236$ peak intensity, it is necessary to take into account the contribution of the $^{235}\text{U}^1\text{H}^+$ hydride ions formation [10, 11].

With due regard for the above-mentioned peculiarities in the application of ICP-SFMS for the uranium isotope analysis the following research tasks were formulated:

- to study the influence of ion interaction processes in the ICP SFMS (mass bias effect, isobaric and polyatomic interferences) on the measurement results for the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios in uranium oxide;
- to estimate metrological characteristics of the measured data with regard to the applicability of the ICP-SFMS method for the quality control and certification of uranium products in nuclear power industry.

MATERIALS AND METHODS

Studies were carried out using uranium isotopic standards based on triuranium octoxide (U_3O_8) CRM U100 and CRM U200, made by the U.S. National Bureau of Standards (since 1988 – National Institute of Standards and Technology of the U.S. Department of Commerce). Each standard represents 10 mg of highly purified U_3O_8 powder, certified values of the isotope ratios were obtained using multi-collector TIMS and are given in Table 1.

Table 1. Certified isotope ratio in uranium isotopic standards CRM U100 and CRM U200

$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
CRM U100		
$0.00075359 \pm 0.00000223$	0.11359 ± 0.00011	$0.00042250 \pm 0.00000112$
CRM U200		
$0.00156432 \pm 0.00000378$	0.25126 ± 0.00026	$0.00265659 \pm 0.00000757$

The isotope ratios were measured using single-collector mass spectrometer ICP-SFMS ELEMENT 2 (Thermo Fisher Scientific GmbH, Germany), technical characteristics are given in Table 2.

The mass spectrometer resolution represents the value equal to $M / \Delta M$, where ΔM is the minimum distance (in a.m.u.) between two adjacent peaks at their overlapping at 10 % peak height. For example, the resolution of 1000 means that the peaks with masses of 100.0 a.m.u. and 100.1 a.m.u. are resolved, i.e., not overlapped up to 10 % of their height.

Table 2. Technical characteristics of ICP-SFMS ELEMENT 2

Mass range	from 2 to 264 a.m.u.
Sensitivity	$\sim 10^6$ cps for 1 ppb ^{115}In
Detection limit	1 ppq for non-interfering elements
Dark noise	< 0.2 cps
Dynamic range	$> 10^9$
Mass resolution	low (300), middle (4000), high (10000) at 10 % peak height
Signal stability	better than 1 % for 10 min.

The ions were registered at two modes of mass-spectrometer detecting system operation, namely, in the counting mode with the maximum counting rate of $\leq 10^6$ cps for the measurements of signal intensities from the ^{234}U , ^{235}U , ^{236}U isotopes; and in the analog mode with the maximum counting rate of $\leq 10^9$ cps for the measurements of signal intensities from the ^{235}U , ^{238}U isotopes. The comparison between the analytical signal values, measured in both the counting and analog modes of detector operation, was performed by means of cross-calibration according to the multielement standard ICP-MS-68A.

The aliquots for the analysis were prepared with the use of deionized water (HIGH PURITY STANDARDS, High Purity DI 18 M Ω Water) and nitric acid solutions (HIGH PURITY STANDARDS, Subboiled Distilled Nitric Acid). For preparation of the basis solution with 10 ppm ^{238}U content, 2.4 mg U_3O_8 CRM U100 and 2.8 mg U_3O_8 CRM U200 in powder form were dissolved in 15 % HNO_3 under heated in a boiling-water bath. The final aliquots with the 50 ppb ^{238}U content were obtained through the basis solution dilution with 2 % HNO_3 . The aerosols of final solutions were introduced into the ionization region of the mass spectrometer with the speed-controlled peristaltic pump.

RESULTS AND DISCUSSIONS

The ion current contribution of uranium hydrides to the intensity of analytical signals from the isotopes ^{234}U , ^{235}U , ^{236}U , ^{238}U was estimated by measuring the mass spectra of the uranium ore concentrate CRM 124-1 with the use of the masses $m = 236$ (ion current contribution from $^{235}\text{U}^1\text{H}^+$) and $m = 239$ (ion current contribution from $^{238}\text{U}^1\text{H}^+$) on the assumption that there are no ^{236}U and ^{239}Pu isotopes in the measured sample. The efficiency of hydride ion

formation was calculated as the intensity ratios of $^{235}\text{U}^1\text{H}^+ / ^{235}\text{U}$ and $^{238}\text{U}^1\text{H}^+ / ^{238}\text{U}$. Then the analytical signal intensities of the isotopes in CRM U100 and CRM U200 were corrected and the isotope ratios $R_{meas.}$ were calculated with and without regard for the hydride ion current contribution. Obtained data were compared with the certified isotope ratio values $R_{cert.}$ given in Table 1.

The efficiency of the uranium hydride ion formation was found to be 3.54×10^{-5} , this corresponding to the $^{235}\text{U}^1\text{H}^+$ hydride ion current of 1 cps at the ^{235}U analytical peak current intensity of 3.54×10^5 cps.

In the studies of the sample CRM U100, the analytical peak intensities were determined to be 8.53×10^6 cps and 3.16×10^4 cps for ^{235}U and ^{236}U , respectively, then the ion current contribution of $^{235}\text{U}^1\text{H}^+$ hydride to the analytical signal intensity at $m = 236$ (polyatomic interference effect) was determined to be 24 cps or $\sim 0.1\%$.

Fig. 1 shows the calculated isotope ratios $R_{cert.} / R_{meas.}$ as a functions of the difference of the isotope mass numbers (Δm) in the CRM U100 isotope standard, with and without regard for the ion current contribution of the $^{235}\text{U}^1\text{H}^+$ hydride.

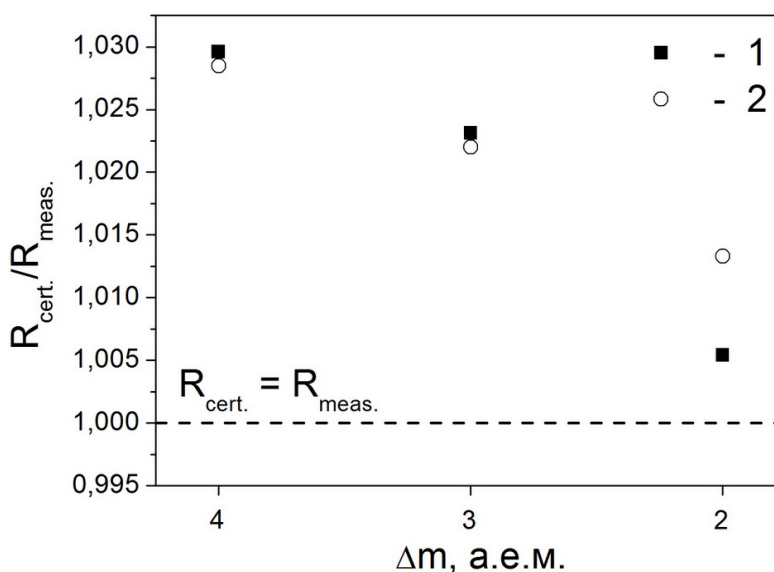


Figure 1. Isotope ratios versus their mass number difference Δm in the isotope standard CRM U100: 1 – initial value $R_{cert.} / R_{meas.}$ without regard for the ion current contribution from $^{235}\text{U}^1\text{H}^+$ hydride; 2 – corrected value $R_{cert.} / R_{meas.}^{corr.}$ with due regard for the ion current contribution from $^{235}\text{U}^1\text{H}^+$ hydride

From the data given at Fig. 1 it is evident that the polyatomic interference effect is the most significant during measuring the $^{236}\text{U} / ^{238}\text{U}$ isotope ratios, i.e., at $\Delta m = 2$ a.m.u.; for the ratios $^{234}\text{U} / ^{238}\text{U}$ ($\Delta m = 4$ a.m.u.) and $^{235}\text{U} / ^{238}\text{U}$ ($\Delta m = 3$ a.m.u.) the given effect is less pronounced. Nevertheless, the values of all measured isotope ratios $R_{meas.}$ appear underestimated by 1...3 % relative to their certified values (the underestimating increases with increase in Δm), this bearing witness to the influence of other factors on the measurement results, one of which is mass bias effect.

To investigate the influence of the mass bias effect on the determinations of uranium isotope ratios, the external standardization calibration was used with three models (linear, power, exponential) describing the behavior of the specific discrimination coefficient β versus the mass of measured isotopes. The external standardization calibration implies that on measuring the ion signal ratios of isotopes in the probe, the parallel measurement of ion signals from the certified isotope standard is performed. After that, based on the measured isotope ratio and the exactly known isotope ratio in the standard the mass discrimination factor B and the specific discrimination coefficient β is calculated and the correction for the mass bias effect is introduced [12].

The mass discrimination factor characterizes the magnitude of the mass bias effect, and in the case of light-to-heavy isotope ratio measurements is determined as:

$$B = R_{cert.} / R_{meas.} \quad (1)$$

In addition to the mass discrimination factor, for quantitative description of the mass bias effect (the degree of ion mass discrimination in % a.m.u.⁻¹) the specific discrimination coefficient β is also used:

$$\beta = [(B - 1) \cdot 100] / \Delta m \quad (2)$$

Formula (2) describes the linear model dependence of the specific discrimination coefficient β from the measured isotope masses. Then the isotope ratio value in the sample under study, corrected for the mass bias effect, is determined as:

$$R_{corr.}^{lin.} = R_{meas.} (1 + \beta \cdot \Delta m) . \quad (3)$$

For the power and exponential models, the dependence of the specific discrimination coefficient β from the measured isotope masses is written as:

$$\beta = \ln B / \Delta m \quad (4)$$

and the isotope ratios in the sample, corrected for the mass bias effect, are given by equations (5) and (6), respectively:

$$R_{corr.}^{pow.} = R_{meas.} (1 + \beta)^{\Delta m} , \quad (5)$$

$$R_{corr.}^{exp.} = R_{meas.} \cdot \exp(\beta \cdot \Delta m) . \quad (6)$$

In the present studies, the isotope standard CRM U200 was chosen as an external standard for taking into account the mass bias effect in the CRM U100 sample (conditionally unknown).

Table 3 lists the values of measured isotopic ratios in the sample CRM U100, which were corrected for the mass bias effect with the use of the linear, power and exponential dependence models of the specific discrimination coefficient β from the measured isotope masses (eqs. (3), (5) and (6), respectively). The table also gives the calculated values $R_{cert.} / R_{corr.}$ and the relative measurement error δ .

Table 3.

Results of isotope ratio determinations in the CRM U100 adjusted for mass bias effect

	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
$R_{cert.}$	0.00075359	0.11359	0.00042250
$R_{corr.}^{lin.}$	0.00076296	0.11444	0.00042583
$R_{corr.}^{pow.}$	0.00075613	0.11361	0.00042371
$R_{corr.}^{exp.}$	0.00075647	0.11364	0.00042380
$R_{cert.} / R_{corr.}^{lin.}$	0.988	0.993	0.992
$R_{cert.} / R_{corr.}^{pow.}$	0.997	0.999	0.997
$R_{cert.} / R_{corr.}^{exp.}$	0.996	0.999	0.997
$\delta^{lin.}, \%$	1.243	0.746	0.788
$\delta^{pow.}, \%$	0.338	0.015	0.287
$\delta^{exp.}, \%$	0.382	0.047	0.308

The degree of ion mass discrimination calculated by formula (2) varies from 0.60×10^{-3} (0.6 %) at $\Delta m = 4$ a.m.u. to 1.20×10^{-2} (1.2 %) at $\Delta m = 2$ a.m.u. Dependences of the specific discrimination coefficient β versus Δm , calculated by formulas (2) and (4), as well as the results of their approximation by linear and exponential functions are shown at Fig. 2.

It can be seen that at determining the uranium isotope ratios the mass bias effect can be compensated through their correction by means of the linear, power and exponential models of the $\beta = F(\Delta m)$ relationship. Nevertheless, taking into account the need for fulfillment of the conditions $(R_{cert.} / R_{corr.}) \rightarrow 1$ and $\delta \rightarrow 0$, the application of the power/exponential models is preferable. Besides, the approximation data in Fig. 2 confirm the advantage of the exponential function by the coefficient of determination $R^2 = 1$, that can be treated as full correspondence of the regression model to the experimental data.

Fig. 3 a-c shows the results of isotope ratio determination in the CRM U100 during seven consecutive measurements. The relative error of $^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurements was $< 0.5 \%$, while for the $^{235}\text{U}/^{238}\text{U}$ ratio it was less than 0.1 %.

Mass spectra of the uranium ore concentrate CRM 124-1 on the mass $m = 237$ (contribution of the $^{238}\text{U}^+$ ion peak "tail") were measured to estimate the effect of isobaric overlapping of the "tail" of the high-intensity peak of mass m on the intensities of the peaks of masses $(m-1)$, $(m-2)$, $(m-3)$. The estimated value was found to be 8.17×10^{-6} , this being in agreement with the data [13]. Thus, the contribution of scattered $^{238}\text{U}^+$ ions to the intensities of less abundant $^{236}\text{U}^+$ and $^{235}\text{U}^+$ is insignificant and can be neglected.

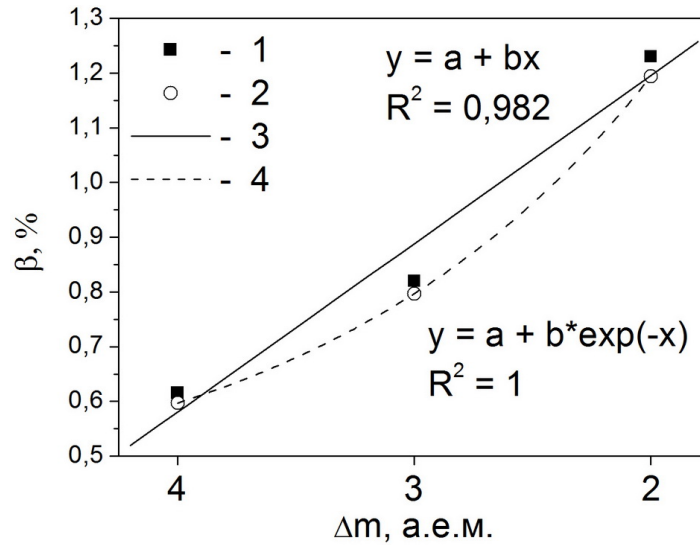


Fig. 2. Specific discrimination coefficient β versus mass numbers difference of the measured isotopes Δm : 1 – linear model calculated data; 2 – exponential model calculated data; 3 – approximation of points 1 by the linear function; 4 – approximation of points 2 by the exponential function

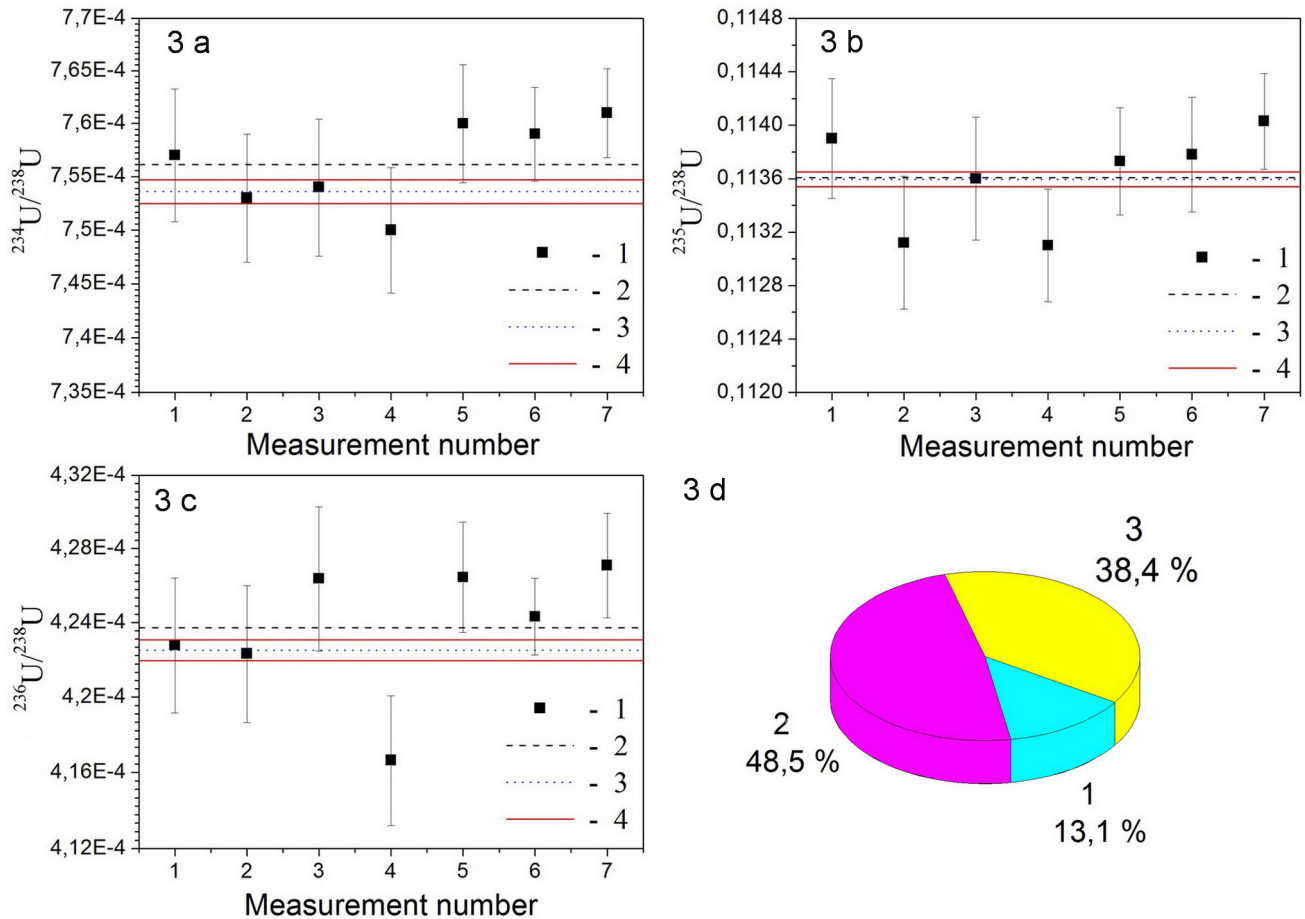


Fig. 3 a, 3 b, 3 c. Isotope ratios $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ in the CRM U100, corrected for the mass bias effect using exponential model for $\beta = F(\Delta m)$: 1 – experimental data; 2 – mean value of experimental data; 3 – certified value; 4 – certified value uncertainty bounds

Fig. 3 d. Measurement uncertainty budget for the $^{235}\text{U}/^{238}\text{U}$ isotope ratio in the CRM U100: 1 – contribution of the certified value $^{235}\text{U}/^{238}\text{U}$ uncertainty; 2 – contribution of intensity measurement uncertainty for the analytical ^{235}U and ^{238}U peaks in the CRM U100; 3 – contribution of intensity measurement uncertainty for the analytical ^{235}U and ^{238}U peaks in the external standard CRM U200

In addition to the relative error, another metrological characteristic of the measurements is uncertainty, i.e., the parameter, which characterizes the spread of measured values. The calculated standard uncertainty u of the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurements in the CRM U100 was 0.563, 0.322 and 0.856 %, respectively. These are reasonable estimates in comparison with the uncertainties of certified values of 0.296, 0.097 and 0.265 %.

Finally, the uncertainty budgets of the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratios measurements were calculated for the CRM U100, i.e., the contribution values of the uncertainty components (see Fig. 3 d).

The major contribution to the measurement uncertainty of the $^{235}\text{U}/^{238}\text{U}$ isotope ratio comes from the intensity measurement uncertainties for the analytical ^{235}U and ^{238}U peaks. For the other ratios under study, the measurement uncertainty budget is similar to that given at Fig. 3 d.

CONCLUSIONS

The influence of the ion interaction processes in the sector-field mass spectrometer (ICP-SFMS) on the measurements of $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios in uranium oxide was studied.

It has been demonstrated that the mass bias effect has most influence on the results of uranium isotope ratios determination. The degree of discrimination has been found to vary from 6.00×10^{-3} to 1.20×10^{-2} , and the grounds have been given for the use of the power/exponential models of the relationship $\beta = F(\Delta m)$ for correction of the measurement results.





Consideration has been given to the influence of the effects of isobaric and polyatomic interferences on the results of uranium isotope ratios determination. The efficiency of uranium hydride ion ($^{235}\text{U}^1\text{H}^+$) formation has been calculated to be 3.54×10^{-5} , while the contribution of scattered $^{238}\text{U}^+$ ions to the intensities of less abundant ^{236}U and ^{235}U reached 8.17×10^{-6} .

Metrological characteristics of analytical results have been analyzed, in particular, the relative measurement error for $^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ isotope ratios has made < 0.5 %, while for the $^{235}\text{U}/^{238}\text{U}$ ratio it was less than 0.1 %. This points to the applicability of the ICP-SFMS method for the quality control and certification of uranium products in nuclear power industry.

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REFERENCES

- [1] V.A. Kalashnikov, Synopsis of Ph.D. dissertation, Federal State Unitary Enterprise Ural Electromechanical Plant, 2006. (in Russian)
- [2] G.V. Shishalova, M.A. Kulakova, and E.E. Varlashova, *Analytics and Control*. **7**(2), 186-189 (2003) (in Russian)
- [3] A.V. Saprygin, V.M. Golik, A.A. Makarov, B.G. Dzhavayev, and V.N. Kudryavtsev, *Standard Samples*. **2**, 39-48 (2007). (in Russian)
- [4] I.T. Platzner, *Modern isotope ratio mass-spectrometry*. (Chichester, Wiley, 1997), pp. 83-108.
- [5] A.V. Saprygin, B.G. Dzhavayev, and A.A. Makarov, *Analytics and Control*. **7**(1), 68-73 (2003). (in Russian)
- [6] A.V. Saprygin, B.G. Dzhavayev, and A.A. Makarov, *Analytics and Control*. **7**(1), 64-67 (2003). (in Russian)
- [7] S. Lapshin, O. Proshenkina, *Equipment and materials*. **3**, 28-36 (2012). (in Russian)
- [8] A.V. Khoroshilov, E.L. Silakova, and P.I. Ivanov, *Advances in Chemistry and Chemical Technology*, **29**(6), 56-58 (2015). (in Russian)
- [9] A.N. Baranova, in: *Материалы Конференции «Современные Проблемы Геохимии» [Materials of the Conference "Contemporary Issues of Geochemistry"]* (Irkutsk, Russia, 2011), pp. 84-86. (in Russian)
- [10] M. Zoriy, L. Halicz, M. Ketterer, C. Pickhardt, P. Ostapczuk, and J. Becker, *J. Anal. At. Spectrom.* **19**, 362-367 (2004).
- [11] A.Yu. Leikin, and P.V. Yakimovich, *Journal of Analytical Chemistry*, **67**(8), 752-762 (2012). (in Russian)
- [12] A.A. Pupyshv, and B.A. Sermyagin, *Дискриминация ионов по массе при изотопном анализе методом масс-спектрометрии с индуктивно-связанной плазмой [Ion mass discrimination in the isotope analysis by the method of inductively coupled plasma mass spectrometry]* (Ural State Technical University, Yekaterinburg, Russia, 2006), pp. 16-68. (in Russian)
- [13] V.A. Stebel'kov, O.V. Erokhin, N.R. Stankov, and A.I. Yermakov, *Mass-Spectrometry*. **1**(3), 221-230 (2004). (in Russian)

ВИЗНАЧЕННЯ ІЗОТОПНИХ СПІВВІДНОШЕНЬ $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ В ОКСИДІ УРАНУ МЕТОДОМ МАС-СПЕКТРОМЕТРІЇ З ПОДВІЙНИМ ФОКУСУВАННЯМ (ICP-SFMS)

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Досліджено вплив ефектів дискримінації іонів по масах, ізобарних і поліатомних інтерференцій на результати вимірювань ізотопних співвідношень $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ в оксиді урану методом мас-спектрометрії з подвійним фокусуванням. Для проведення досліджень використовували сертифіковані ізотопні стандарти на основі октаоксида триурана (U_3O_8) CRM U100, CRM U200 і одноколлекторний мас-спектрометр ICP-SFMS ELEMENT 2. Показано, що основним ефектом, що впливає на результати визначення ізотопних співвідношень урану, є дискримінація іонів по масах. Для вивчення впливу ефекту дискримінації іонів по масах на результати визначення ізотопних співвідношень урану, застосовували спосіб зовнішнього стандарту з трьома моделями (лінійної, ступеневої та експоненціальної) залежності питомого коефіцієнта дискримінації β від мас вимірюваних ізотопів. Розрахований коефіцієнт ступеня дискримінації для лінійної, ступеневої та експоненціальної моделей залежності питомого коефіцієнта дискримінації від мас ізотопів варіюється від $6,00 \times 10^{-3}$ до $1,20 \times 10^{-2}$. Обґрунтовано перевагу використання ступеневої або експоненційної моделей залежності $\beta = F(\Delta m)$ для коригування ізотопних співвідношень, що вимірюються. При виникненні поліатомних інтерференцій ефективність утворення іонів гідриду урану ($^{235}\text{U}^1\text{H}^+$) становить $3,54 \times 10^{-5}$, а величина ефекту ізобарних накладень внаслідок вкладу розсіяних іонів $^{238}\text{U}^+$ в інтенсивності менш розпроторених $^{236}\text{U}^+$ і $^{235}\text{U}^+$ – $8,17 \times 10^{-6}$. Проаналізовано метрологічні характеристики аналітичних результатів, зокрема, відносна похибка вимірювань ізотопних співвідношень $^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ склала $< 0,5\%$, а для співвідношення $^{235}\text{U}/^{238}\text{U}$ – менше $0,1\%$. Розрахована стандартна невизначеність вимірювань ізотопних співвідношень u в стандарті CRM U100 склала $0,563$; $0,322$ і $0,856\%$ відповідно, що виглядає задовільно в порівнянні з величинами невизначеності сертифікованих значень: $0,296$; $0,097$ і $0,265\%$.

КЛЮЧОВІ СЛОВА: мас-спектрометрія з індуктивно-зв'язаною плазмою, оксид урану, ефект дискримінації іонів по масах, поліатомні інтерференції, ізобарні накладення, співвідношення ізотопів урану

ОПРЕДЕЛЕНИЕ ИЗОТОПНЫХ ОТНОШЕНИЙ $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ В ОКСИДЕ УРАНА МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ С ДВОЙНОЙ ФОКУСИРОВКОЙ (ICP-SFMS)

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Исследовано влияние эффектов дискриминации ионов по массам, изобарных и полиатомных интерференций на результаты измерений изотопных отношений $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ в оксиде урана методом масс-спектрометрии с двойной фокусировкой. Для проведения исследований использовали сертифицированные изотопные стандарты на основе октаоксида триурана (U_3O_8) CRM U100, CRM U200 и одноколлекторный масс-спектрометр ICP-SFMS ELEMENT 2. Показано, что основным эффектом, влияющим на результаты определения изотопных отношений урана, является дискриминация ионов по массам. Для изучения влияния эффекта дискриминации ионов по массам на результаты определения изотопных отношений урана, применяли способ внешнего стандарта с тремя моделями (линейной, степенной и экспоненциальной) зависимости удельного коэффициента дискриминации β от масс измеряемых изотопов. Рассчитан коэффициент степени дискриминации для линейной, степенной и экспоненциальной моделей зависимости удельного коэффициента дискриминации от масс измеряемых изотопов, который варьируется от $6,00 \times 10^{-3}$ до $1,20 \times 10^{-2}$. Обосновано преимущество использование степенной либо экспоненциальной моделей зависимости $\beta = F(\Delta m)$ для корректирования измеряемых изотопных отношений. При возникновении полиатомных интерференций эффективность образования ионов гидрида урана ($^{235}\text{U}^1\text{H}^+$) составляет $3,54 \times 10^{-5}$, а величина эффекта изобарных наложений вследствие вклада рассеянных ионов $^{238}\text{U}^+$ в интенсивности менее распространенных $^{236}\text{U}^+$ и $^{235}\text{U}^+$ – $8,17 \times 10^{-6}$. Проанализированы метрологические характеристики аналитических результатов, в частности, относительная погрешность измерений изотопных отношений $^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ составила $< 0,5\%$, а для отношения $^{235}\text{U}/^{238}\text{U}$ – менее $0,1\%$. Рассчитанная стандартная неопределенность u измерений изотопных отношений $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ в стандарте CRM U100 составила $0,563$; $0,322$ и $0,856\%$ соответственно, что выглядит удовлетворительно по сравнению с величинами неопределенности сертифицированных значений: $0,296$; $0,097$ и $0,265\%$.

КЛЮЧЕВЫЕ СЛОВА: масс-спектрометрия с индуктивно-связанной плазмой, оксид урана, эффект дискриминации ионов по массам, полиатомные интерференции, изобарные наложения, отношения изотопов урана