Studying the possibility of applying spectral methods for the analysis of chemical elements and radionuclides

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Abstract. This article presents the results of a study of the possibility of using spectral methods for analyzing chemical elements and radionuclides. As is known, in uranium production processes, chemical elements and radionuclides behave differently and they are distributed in different concentrations. Therefore, the main tasks of analytics are to determine the concentration and specific activity values of chemical elements and radionuclides in samples taken from various uranium products of uranium production. The magnitude of radiation factors at a local location of a uranium product is assessed by determining the values of these factors and the amount of various radionuclides contained in these samples. In laboratory conditions, the concentrations of U were determined by X-ray fluorescence analysis, the specific activity of 230Th, 226Ra, 40K and 137Cs was determined by gamma spectrometric analysis, and the isotope concentrations of 234U, 235U, 238U were determined by alpha spectrometric analysis. The results obtained were compared with the passport data of standard samples - SOUR, OSK-6, OSK-9, OSGI. Determining the concentration and specific activity values of various chemical elements and radionuclides in uranium products is of scientific and practical interest, and solving this issue is an urgent task of nuclear physics and analytics.

1 Introduction

The X-ray fluorescence method is based on the excitation of characteristic X-ray radiation from the atom of the element under study using X-ray tubes and a source in awakening. X-ray fluorescence methods an instrumental and express method for determining the elemental composition [1-3]. Gamma spectrometric and alpha spectrometric methods of analysis are based on the registration of gamma and alpha radiation of radioactive elements contained in the samples under study.

To carry out spectrometric methods for analyzing uranium-containing samples and products in nuclear analytics, they are used X-ray spectrometers type XRF-1800, EDX-7000, EDX-8000 from SHIMADZU (Japan), enon-dispersive X-ray spectrometers type ARF-6, ARF-7 (Russia), gamma spectrometer type “GAMMA PROGRESS” and alpha spectrometer

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type α-ANALIST "CANBERRA" (USA). Using these spectrometers, the concentrations of more than 40 chemical elements and radionuclides are determined [4-6].

The purpose of this study was studying the possibility of using spectral methods for the analysis of uranium-containing samples and products. As is known, X-ray fluorescence, gamma spectrometric and alpha spectrometric methods of analysis are instrumental, operational and express. The study of uranium-containing samples and products using spectrometric analysis methods is of scientific and practical interest. Based on the above, studying the possibility of using spectral methods for the analysis of uranium-containing samples and products is an urgent task of nuclear physics, nuclear analytics and terotechnology [7-11].

2 Materials and methods

To determine the concentration of chemical elements and radionuclides in uranium-containing samples and products, spectrometers XRF-1800, EDX-7000, EDX-8000 from SHIMADZU (Japan), ARF-6, ARF-7 (Russia), GAMMA PROGRESS and α were used - ANALIST "CANBERRA" (USA) [1-3].

3 Results and discussion

To determine the concentration of chemical elements and radionuclides in uranium-containing samples and products using the X-ray spectral method, methods for the determination of uranium have been studied in detail. Analyzes were carried out on the distribution of uranium in each sample taken.

During studying the distribution of uranium in uranium-containing technogenic samples using the X-ray spectral method; from a technological point of view, uranium is of certain industrial interest as a radioactive product.

The analyzed uranium contents were determined from the spectrum of the obtained X-ray spectral analysis. The given spectrum in Figure 1, obtained on the basis of X-ray spectral analysis of uranium-containing samples.

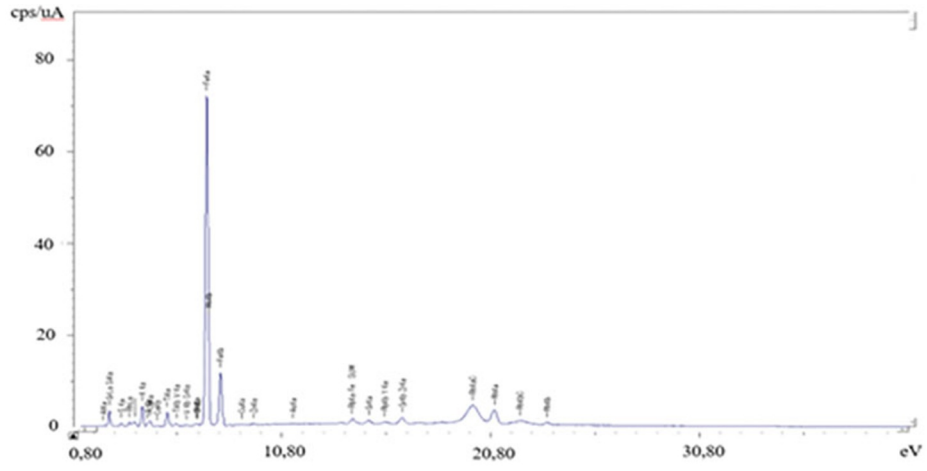

Fig. 1. Obtained spectrum uranium in uranium-containing samples by X-ray spectral analysis.

It can be seen from Figure 1 that more than 15 chemical elements have been identified in this spectrum. Based on this spectrum, it is possible to quantify the elements under study.

The correct determination of the content of chemical elements in the studied samples is in a wide range, that is, from 10 g/t to 1500 g/t and is cross-checked using standard samples with certificates of compliance.

Methods for determining the content of chemical elements in the studied samples are certified by the Uzstandard Agency and the list of certified "Methods for performing measurements" of the Republic of Uzbekistan is included in the register.

This spectrum confirms that the X-ray spectral method of analysis is suitable for identifying uranium and rock-forming chemical elements in uranium-containing samples.

It can be seen from the results obtained in Table 1, based on the x-ray fluorescence analysis methods carried out in 10 selected samples, the average uranium content was determined in 5 parallels. The uranium content in these samples varies in the range from 0.0123% to 0.0232%.

Table 1. Results of determination of the average uranium content in 10 uranium-containing samples in 5 parallels using the X-ray fluorescence analysis method.

No. - samples	U content in parallel samples, (%)				U_{md}, %
	1	2	3	4	
1	0.0138	0.0133	0.0134	0.0137	0.0136
2	0.0135	0.0130	0.0134	0.0131	0.0132
3	0.0124	0.0129	0.0131	0.0132	0.0129
4	0.0161	0.0159	0.0167	0.0160	0.0162
5	0.0119	0.0121	0.0127	0.0123	0.0123
6	0.0138	0.0141	0.0139	0.0137	0.0138
7	0.0153	0.0149	0.0147	0.0156	0.0151
8	0.0143	0.0139	0.0142	0.0145	0.0142
9	0.0213	0.0216	0.0214	0.0219	0.0212
10	0.0224	0.0229	0.0231	0.0232	0.0229

In addition to the X-ray fluorescence method for analyzing uranium in uranium-containing samples, the alpha spectrometric method for analyzing the isotopic composition of uranium in uranium samples is used. Below are the results of determining the isotopic composition of uranium 234U, 235U and 238U in uranium samples. As is known, the alpha spectrometric method for analyzing the isotopic composition of uranium in uranium samples differs from the X-ray fluorescence method for analyzing uranium in uranium samples in the number of peaks. In the alpha spectrometric method for analyzing the isotopic composition of uranium in uranium samples, single peaks are obtained. In the X-ray fluorescence method for analyzing uranium in uranium samples, the number of peaks is numerous.

It is known that natural uranium consists of three isotopes: 234U, 235U and 238U, the relative content of which in the mixture is 99.27%, 0.71% and 0.0056%, respectively.

In Table 2 the specific activities and relative contents of uranium isotopes are given.

Table 2. Specific activities and relative contents isotopes ^{234}U, ^{235}U and ^{238}U.

Isotope	Specific activity, Bq/g	Relative content, %.
^{234}U	$2.31*10^{8}$	0.0056
^{235}U	$7.91*10^{4}$	0.71
^{238}U	$1.25*10^{4}$	99.27

As can be seen from Table 2, the 234U isotope has a high specific activity of 2.31*108 Bq/g than the other two isotopes 235U and 238U.

As part of the research into the possibility of using spectral methods for analyzing uranium products, a series of analyzes of the isotopic composition of uranium 234U, 235U was carried out. 238U in uranium chemical concentrates and in uranium oxide-oxide, depending on the geotechnological processes of uranium leaching.

Figure 2 shows the alpha spectrum of the standard sample OSK-3, No. 02.08.2K20N, with a total activity of 7.5 Bq, prepared by the radiochemical method and measured on an alpha spectrometer of the α-Analyst type (Canbera, USA) for 6 hours.

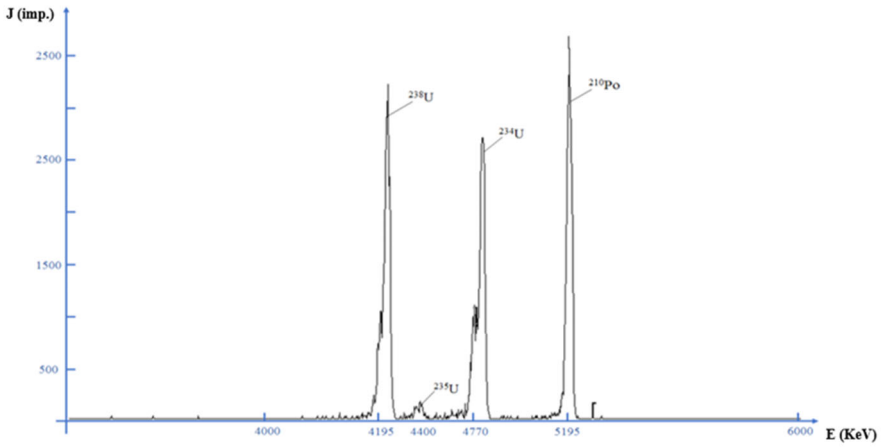

Fig. 2. Alpha spectrum of the OSK-3 standard sample.

As can be seen from the spectrum, in addition to uranium isotopes ^{234}U, ^{235}U. ^{238}U is also registered as the ^{210}Po isotope. Based on this spectrum, the efficiency of the alpha spectrometer is checked, uranium isotopes ^{234}U, ^{235}U, ^{238}U are identified and their quantity is determined. It can be seen that the yield energy of the ^{234}U isotope is 4770 keV, ^{235}U is 4400 keV and ^{238}U is 4195 keV, and the yield energy of the ^{210}Po isotope is 5195 keV,

Figure 3 shows the alpha spectrum of a chemical concentrate sample taken from a geotechnological mine for underground leaching of uranium. At this site, acid leaching of uranium is used.

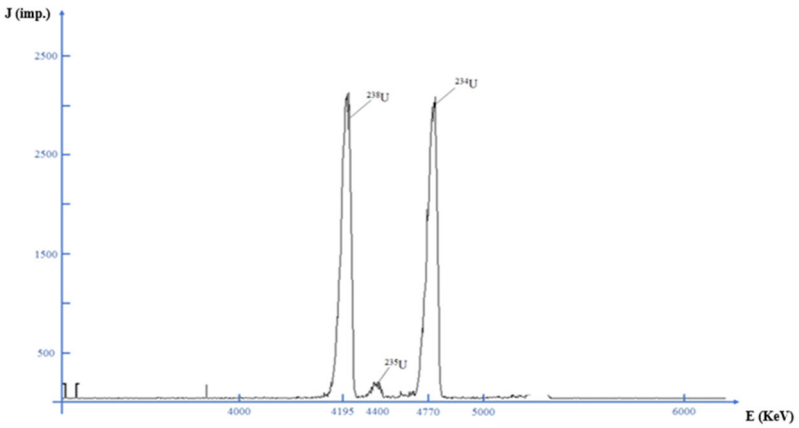

Fig. 3. Typical alpha spectrum of a chemical concentrate sample taken from a geotechnological mine for underground leaching of uranium.

As can be seen in Figure 3, the height of the peak of the ^{238}U isotope is higher than the height of the peak of the ^{234}U isotope and, in turn, the number of pulses is greater. And the number of pulses is directly proportional to the concentration of the isotope ^{234}U and ^{238}U. Based on this spectrum, the $^{234}U/^{238}U$ activity ratio and the relative mass content of ^{234}U (mg/g) in samples of chemical concentrates or uranium oxide are determined.

The results of determining the average concentration of ^{234}U (mg/g) in chemical concentrates selected by quarter during 2022 are given in Table. 3.

Table 3. Results of determining the average concentration of ^{234}U in chemical concentrates (mg/g) during 2022.

Place of selection	I quarter	II quarter	III quarter	IV quarter	Avg. meaning
R-3	50.1	49.9	50.8	48.5	49.8
R-2	50.4	49.5	51.1	49.4	50.1
R-1	51.1	49.3	47.1	50.1	49.4
WITH	53.1	51.7	51.9	53.0	52.4
TO	57.8	56.7	56.2	56.0	56.7
Wed	54.9	56.5	55.1	56.7	56.3

As can be seen from Table 3, during 2022, the average concentration of ^{234}U in samples of chemical concentrates R-1, R-2 and R-3 varies from 49.4 mg/g to 50.1 mg/g and does not exceed the equilibrium content, that is, 53.41 mg /g., in sample C, the concentration of ^{234}U in the 1st and 2nd quarters of 2022 approaches the equilibrium content of 53.41 μg/g and averages 52.4 mg/g, and in samples K and Cp varies from 54. 9 mg/g to 56.7 mg/g and exceeds the equilibrium content.

To carry out spectral analyzes using the method of instrumental neutron activation analysis of chemical elements in samples from uranium dumps, multi-element, instrumental, express and informative methods are required that meet the requirements of accuracy and sensitivity. To study the coefficients of geochemical enrichment of chemical elements in uranium dumps, a method of multi-element instrumental neutron activation analysis was chosen that meets the above requirements. To determine the concentration of chemical elements in samples of off-balance uranium dumps, an instrumental neutron activation method of analysis was used using the VVR-SM reactor of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan with a neutron yield of $5 * 10^{12}$ neutrons/s * cm^2 for sample irradiation. The concentration of elements was determined by gamma spectrometric measurement of induced activity using standard samples with known contents of the studied elements.

The gamma spectrometer consists of a Ge(Li) detector with a resolution of 2.7 keV along the 1170 keV 60Co line and a multichannel programmable analyzer of the LP-4900B type. The reproducibility of the method was studied by repeating the same type of samples 5 times using antimony as an example. It was determined that the standard deviation of the average results is no more than 10%.

Analysis of samples from off-balance uranium dumps was carried out in two time modes of irradiation and measurement. For the analysis of chemical elements - As, La, Sm, W, Au, U for medium-living radionuclides, the irradiation time is 1 hour, and the “cooling” time is 3 days. When analyzing the elements - Sc, Fe, Co, Ni, Rb, Ag, Sb, Cs, Ce, Eu, Tb, Lu, Hf, Hg for long-lived radionuclides, the irradiation time is 10 hours, and the “cooling” time is 20 days.

The limits of determination of chemical elements in samples of off-balance uranium dumps at the VVR-SM reactor of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan meets the analytical requirements. The distributions of the chemical elements Sm, Mo, Lu, U, Yb, Au, Nd, As, W, Br, La, Ce, Se, Hg, Tb, Th, Cr, Hf,

Sr, Ag, Cs, Ni, Sc, Rb, Zn, Co, Ta, Eu and Sb in uranium dump samples. Based on the research carried out and the data obtained on the amount of chemical elements, it is possible to make an approximate calculation of the reserves of chemical elements in these dumps.

To determine the concentration of 35 chemical elements in uranium dumps, 12 solid samples were taken. The selected samples were dried at a temperature of 105 °C to constant weight, the dried samples weighed 200 g, of which three parallel 10 g samples were packed in plastic bags and wrapped in aluminum foil.

The concentrations of 35 chemical elements were determined; as an example, the results were taken from 8 samples, irradiated and measured in 4 samples (in 12 samples in threefold parallelism), the results of which are given in Table. 4.

Table 4. The results of determining the concentrations of chemical elements, their average content, enrichment factor – Cob and the ratio of the enrichment factor - Cob to the average content of the analyzed samples - Sk, that is Cob / Sk.

№	Elements	Content,		Sample numbers				Cob	Cob / Sk
		Clark,	Average,	1	2	3	4		
1.	As	1.7	15.3	14.3	15.8	14.9	16.2	9.0	5.3
2.	Se	0.5	4.3	4.0	4.6	4.1	4.5	8.6	16.6
3.	Mo	0.34	15	15.3	14.9	14.8	15.2	44.12	129.74
4.	Yb	0.34	2.6	2.2	3.0	1.8	3.4	7.64	22.5
5.	Au	0.00047	0.011	0.009	0.012	0.015	0.008	23.4	49787.2
6.	W	0.16	0.82	0.92	0.85	0.78	0.73	5.12	32.0
7.	Br	0.16	4.1	3.9	4.5	5.2	2.8	25.63	160.2
8.	U	2.5	110	112	108	106	114	44.00	17.6

The results obtained show that the multi-element INAA method has a clear advantage over other existing methods. Using the INAA method, it is possible to determine their concentrations with a lower threshold of detectable content - NGOS below $10^{-6\%}$. Of certain chemical elements, the geochemical enrichment coefficient values are U-44.00, Au-23.4, Br-160.2.

Four chemical elements – Mo-129.7, U-17.6, Au-49787.0, Br-160.2 – have high ratios of geochemical enrichment coefficient to Clarke content – C_{ob}/S_c. This fact shows that in mineral deposits, along with radioactive elements, accompanying elements are localized.

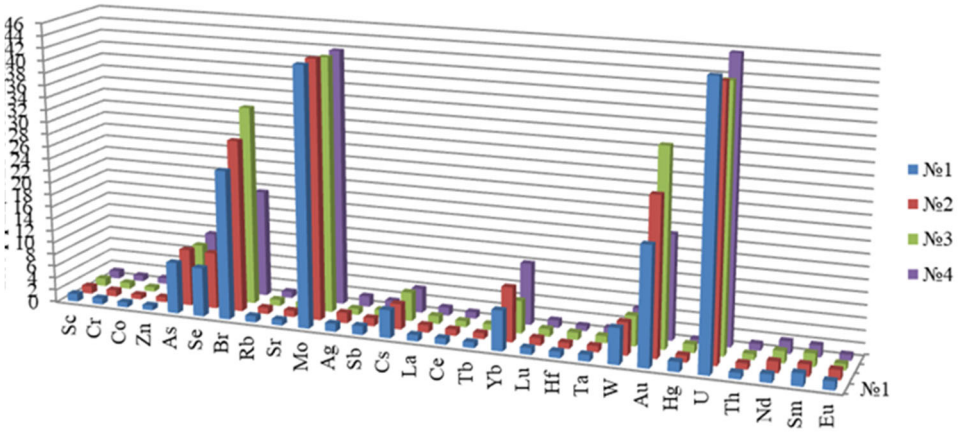

Fig. 4. Change in enrichment coefficients of chemical elements in 4 - No. 1, 2, 3, 4 samples of uranium dumps.

Based on the data obtained (Table 4), graphical changes in the enrichment coefficients of chemical elements in samples No. 1, 2, 3, 4 were constructed. This dependence clearly shows that uranium dumps are technogenic deposits.

From Figure 4 shows that U and more than 30 chemical elements, Mo, U, Au and Br, determined by the INAA method in 4 samples No. 1, 2, 3, 4 have high geochemical enrichment coefficients. In Figure 4 shows 4 obvious peaks of samples No. 1, 2, 3, 4 related to Mo, U, Au and Br by enrichment coefficient in the range from 5.12 to 44.11.

In all 4 samples No. 1, 2, 3, 4, selected from different uranium dumps, the distribution of chemical elements and enrichment factors obeys the pattern of the same uniform change.

Based on the research carried out using the multi-element method of instrumental neutron activation analysis in selected samples of uranium dumps, it was established that it is possible to determine more than 35 chemical elements. The coefficients of geochemical enrichment - K_{ob}, the ratio of the enrichment coefficient - K_{ob} to the Clarke content - K_{ob}/S_k were found and the dependences of the enrichment coefficients of chemical elements to the Clarke content of chemical elements were plotted.

4 Conclusion

Based on the study of the possibility of using spectral methods for the analysis of uranium-containing samples and products, it can be concluded that x-ray fluorescence, gamma spectrometric and alpha spectrometric methods of analysis are suitable and promising for the quantitative determination of chemical elements and radionuclides.

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