

DETERMINATION OF URANIUM IN SOLUTIONS BY THE NEUTRON ACTIVATION ANALYSIS METHOD WITH ^{252}Cf RADIONUCLIDE NEUTRON SOURCE

by

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A determination option for ^{238}U in solutions by the neutron activation analysis was investigated. A radionuclide treatment based on ^{252}Cf was used as a neutron source. The limit for the determination of uranium using thermal neutrons of 0.1 mgL^{-1} was determined within the research framework. With the help of the preliminary concentration of the sample via the evaporation method, it is possible to further reduce the detection limit by 2-5 times. It is defined that the optimal time for measuring the induced activity of the sample when working with a short-life isotope of ^{239}U , is 30 minutes. The influence of the effects of scattering and self-absorption of gamma radiation of the uranium line 74.6 keV on the results of the neutron activation analysis was determined. The studies conducted made it possible to determine uranium by the neutron activation analysis method in solutions of various compositions, in a wide range of concentrations.

Key words: natural uranium in solution, neutron activation analysis, gamma spectrometry, detection limit

INTRODUCTION

Uranium is a resource of great commercial interest; it is used in the production of nuclear fuel, nuclear weapons, radiation protection for industrial radioactive sources, and even anti-tank munitions [1]. Unfortunately, human activities associated with uranium mining lead to environmental pollution. Thus, in the course of underground leaching of uranium-containing ores, sulfate complexes of uranyl get into the groundwater, and during the technological cycle of uranium processing, the formation of fluoride-chloride solutions containing uranium is possible. Besides, uranium pollution can be caused by the production of catalysts, coloring pigments, the combustion of fossil fuels (oil and coal), and the production and use of fertilizers [2]. In all these cases, we are talking about trace amounts of uranium that require deep additional purification. Hence, increasing the reliability of monitoring the distribution of radioactive elements in technological and waste solutions is one of the important areas of radiation safety.

To determine the uranium content in solutions, the most widespread methods are alpha and gamma spectrometry, electro-analytical and X-ray fluorescence [1,

3-5]. Gamma spectrometry is attractive primarily for two reasons: it is characterized by the minimum amount of equipment required for measurements, the ability to carry out analyzes *based on volumes* rather than from the surface, and also the low cost of equipment in the case of gamma spectrometers with scintillation detectors. An obvious problem expected when using this method is a long exposure time due to the low activity of uranium in technological solutions and a large sample volume (from 1 to 3 liters in the enclosing Marinelli geometry) [3].

An alternative approach to solving the problem of determining uranium in solutions can be the neutron activation analysis (NAA) method. Currently, for the determination of uranium, various versions of this method are accepted, including analysis for short- and medium-life radionuclides using thermal and epithermal neutrons [6-8]. Analysis on epithermal neutrons using medium-living radionuclides allows one to reach a minimum threshold for the determination of uranium but requires a reactor as a neutron source [6], while when performing instrumental NAA on short-lived isotopes, simpler and more mobile radionuclide neutron sources can be used as a source, for example, based on ^{252}Cf [9].

This work is aimed at developing a method for determining the content of ^{238}U in solutions employing the method of instrumental NAA on thermal neutrons, using a radionuclide neutron source based on ^{252}Cf .

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METHODOLOGY OF THE EXPERIMENT

To prepare the solutions, the research team used uranium nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, with a basic substance content of at least 99.1 %. The samples under study were solutions with a volume of 10 to 1000 mL. The chemical composition was changed by adding sulfate and fluoride ions to a concentration of $5 \cdot 10^{-2} \text{ molL}^{-1}$.

Determination of uranium by the NAA was conducted using a setup developed at the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences, Vladivostok [10]. A radioisotope source based on ^{252}Cf type NK252M11 with a total neutron flux of $8.77 \cdot 10^8 \text{ s}^{-1}$ was used as a neutron source. The activation zone consists of a central channel with ^{252}Cf and 6 vertical irradiation channels up to 16 cm high and 7.0 cm in diameter, fig. 1. Plexiglas was used as a moderator, providing the maximum flux of thermal neutrons in the activation zone [11].

The measurement of the induced activity was carried out using a gamma spectrometer based on a coaxial germanium detector GC2018 manufactured by Canberra, USA, and the SBS-75 pulse signal processor manufactured by Green Star Technologies LLC. The integrated software package for spectrometric analysis eSBS Version 1.6.7.0 and *Gamma analyzer for semiconductor detector* Version 1.0 were used for the collection and processing of spectra. The energy resolution of the spectrometer was 1.8 keV at radiation energy of 1332 keV, and the relative detection efficiency at the 1332 keV peak was 20 %.

To calibrate the gamma spectrometer, closed reference point sources of gamma radiation of the OSGI-3-2 type (^{60}Co , ^{137}Cs , ^{241}Am , ^{152}Eu , ^{22}Na , ^{133}Ba), located directly at the end of the detector, were used.

To determine uranium via the instrumental NAA method, the reaction $^{238}\text{U} + n \rightarrow ^{239}\text{U} + \gamma$ was used, the

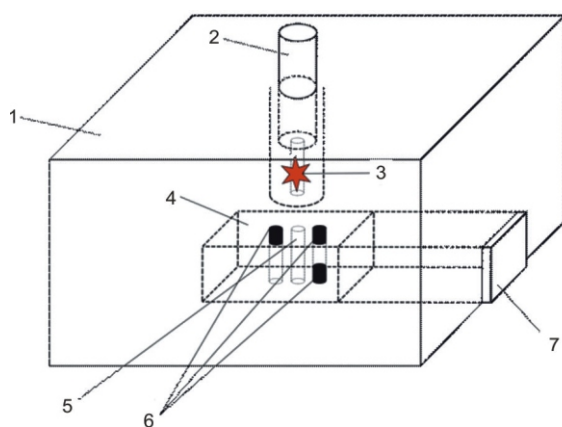


Figure 1. Diagram of the NAA unit with a radionuclide californium neutron source: 1 – radiation protection, 2 – movable rod with a source, 3 – the ^{252}Cf radionuclide source, 4 – plexiglass retarder block, 5 – channel for a neutron source, 6 – samples in activation channels, and 7 – movable loading block

neutron capture cross-section for this reaction is $\sigma = (2740 \pm 60) \cdot 10^{-31} \text{ m}^2$. The sample activation time varied from 30 to 90 minutes. For each sample, a correction was made for the activation time. The measurements were carried out after a 2 minute exposure. The measurement time was 30 minutes. The quantitative determination of uranium was conducted by the photopeak of the isotope ^{239}U with an energy of 74.6 keV. For the determination of uranium, samples with a volume of 1 to 100 mL were used, placed in plastic cassettes with a diameter of 69 mm and a height of 50 mm; in these cassettes, the induced activity was also measured. The samples were installed directly on the end of the gamma-ray detector.

To exclude the influence of the characteristic radiation of lead on the measurement results of the uranium line (74.6 keV), during the experiments, to protect the detector, instead of lead shields, iron shields, 60 mm thick, were used.

RESULTS AND DISCUSSIONS

To construct the calibration curve of the NAA method, the measurement of the intensity of the analytical signal of the ^{239}U line depending on the concentration of uranium in the solution was conducted for samples with a volume of 50 mL. The duration of the measurements was 30 minutes. The change in the concentration of uranium in the samples was set within the range of 0.1-1000 mgL^{-1} . The results of these measurements are presented in fig. 2 (uranium concentration range 50-1000 mgL^{-1}) and fig. 3 (uranium concentration range 0.1-10 mgL^{-1}).

The calibration graph is described by the equation of a straight line

$$I(C) = 0.0637 C + 0.0319 \quad (1)$$

where I is the intensity of the analytical signal and C – the concentration of uranium in the solution.

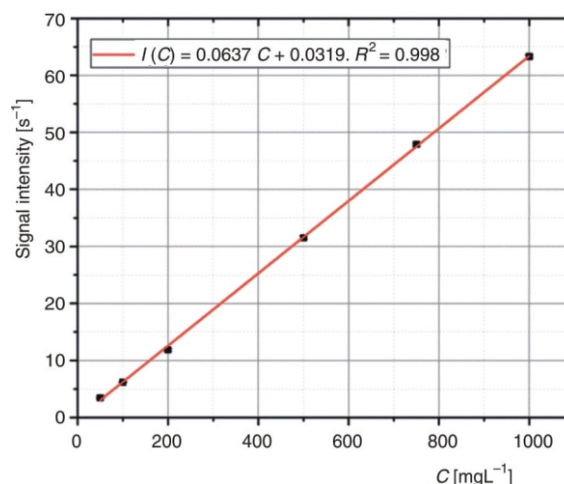


Figure 2. Dependence of the intensity of the analytical signal on the concentration of uranium in solution (concentration range 50-1000 mgL^{-1})

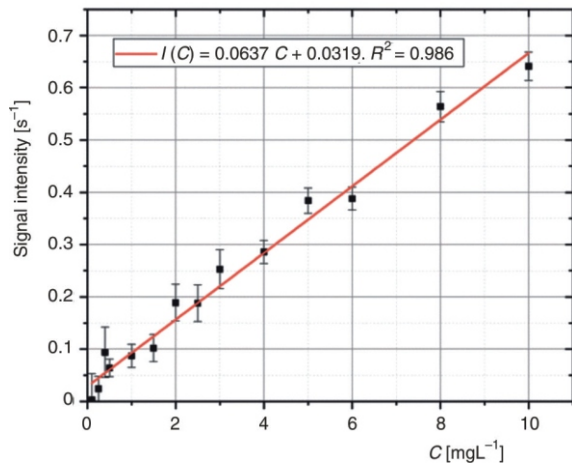


Figure 3. Dependence of the intensity of the analytical signal on the concentration of uranium in solution (concentration range 0.1-10 mgL⁻¹)

The limit of detection (LD) – the minimum amount of an analyte in a sample that can be detected and the limit of quantitative detection (LQ) – the minimum amount of an analyte in a sample that can be quantified with the required accuracy and precision, were calculated

$$LD = 3.3 \frac{S}{a} \quad (2)$$

$$LQ = 10 \frac{S}{a} \quad (3)$$

where S is the standard deviation of the analytical signal, a – the sensitivity coefficient, which is the ratio of the analytical signal to the determined value (the tangent of the slope of the calibration curve).

The calculation of the sensitivity coefficient a and standard deviation S was carried out using the standard formulas of the least square's method.

$$a = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2}, \quad b = \frac{\sum y_i - a \sum x_i}{n} \quad (4)$$

where b is the free member (the value of the analytical signal in the reference experiment without sample).

For a linear calibration graph, the value of the standard deviation of the analytical signal S is equal to the standard deviation S_a of the free term of the equation of this graph, which can be determined by the formula

$$S_a = \sqrt{\frac{(y_i - ax_i - b)^2}{n - 2} \frac{1}{n} \frac{\bar{x}^2}{(x_i - \bar{x})^2}} \quad (5)$$

As the initial data for calculations by eqs. (2)-(5), we used the data presented in figs. 2 and 3 experimental data: values of uranium concentration in solution – x_i , and analytical signal intensity – y_i .

The estimation of the relative error LD and LQ was made according to the formula

$$\delta = \sqrt{\frac{n}{n-k} \frac{\omega_i (\tilde{y}_i - y_i)^2}{\omega_i} \frac{\sqrt{\omega_i}}{\sqrt{\omega_i \tilde{y}_i}}} \quad (6)$$

where n is the number of calibration points, k – the number of independent coefficients in the calibration formula, \tilde{y}_i – the corresponding value for point i obtained from the constructed calibration curve, and w_i – the statistical weight of the point. The relative error in determining the considered values does not exceed 9.5 %.

For a sample with a volume of 50 mL, with a measurement time of the induced activity of 30 minutes, the following results were obtained

$$LD = (0.094 \quad 0.009) \text{ mgL}^{-1}$$

$$LQ = (0.286 \quad 0.027) \text{ mgL}^{-1}$$

Due to the short lifetime of the ²³⁹U radionuclide, the half-life of which (23.45 minutes) is commensurate with the measurement time, LD and LQ will significantly depend on time. The dependence of LD and LQ on the measurement time is influenced by two factors: the improvement of the signal-to-noise ratio over time due to the statistical accumulation of the analytical signal of uranium and the deterioration of the signal-to-noise ratio due to a gradual decrease in the intensity of the analytical signal due to the decay of uranium.

For gamma spectrometry, LD can be determined

$$LD = \frac{1}{a} \sqrt{\frac{I_{\text{back}}}{t_{\text{meas}}}} \quad (7)$$

where t_{meas} is the measurement time, I_{back} – the average value of the background count rate under the peak of total absorption, calculated from the data of n measurements, and a – the sensitivity coefficient.

The sensitivity coefficient is calculated by the formula

$$a = \frac{I_{\text{peak}}}{C_U} \quad (8)$$

where C_U is the concentration of uranium in the solution, and I_{peak} – the intensity of the analytical signal of the sample.

Taking into account that the measurement time of the induced activity of the sample is commensurate with the measurement time when calculating the intensity of the analytical signal, it is necessary to consider the decay of the analyzed radionuclide during the measurement

$$I_{\text{peak}} = I_0 \frac{1 - e^{-\lambda t_{\text{meas}}}}{\lambda t_{\text{meas}}} \quad (9)$$

where I_0 is the intensity of the analytical signal at the beginning of the measurement and λ – the decay constant.

Thus, substituting eqs (8) and (9) into eq. (7), the research team obtained the following formula for calculating LD

$$LD = \frac{C_U}{I_o} \frac{\lambda t_{meas}}{1 - e^{-\lambda t_{meas}}} \sqrt{\frac{I_b}{t_{meas}}} \quad (10)$$

To determine the dependence of LD on the measurement time of the induced activity of the sample, 20 measurements were carried out with experimental data. The measurements were conducted with a 50 mL sample, the uranium concentration in the solution was 10 mgL^{-1} , the activation time was 1 hour, the measurement time varied from 300 seconds to 6000 seconds with an interval of 300 seconds. For each of the spectra, LQ was calculated using eq. (9). The calculation results are presented in tab. 1 and fig. 4.

The results obtained show that the minimum values for LD and LQ are reached at a time of measurement of the induced activity of uranium of the order of 1800 seconds. A further increase in time is impractical.

To take into account the influence of scattering and self-absorption effects on the results of gamma spectrometry of uranium samples, the dependence of the analytical signal of the induced activity of the sample on the volume and density of the sample was investigated.

To plot the dependence of the analytical signal intensity on the volume, a uranium solution with a concentration of 10 mgL^{-1} was used. The samples were packed in plastic cuvettes 69 mm in diameter and 48 mm in height. The measurement results are shown in fig. 5.

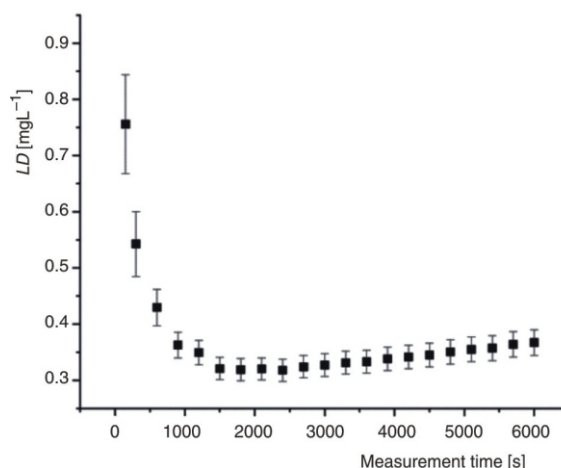


Figure 4. Dependence of LD on the measurement time

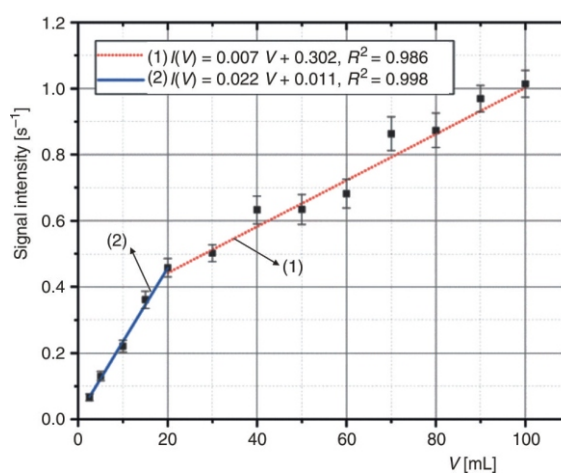


Figure 5. Dependence of the analytical signal intensity on the sample volume

Table 1. Dependence of LD on the measurement time

T_{meas} [s]	I_{peak} [s^{-1}]	I_{back} [s^{-1}]	LQ [mgL^{-1}]	$\sigma(LQ)$ [mgL^{-1}]
150	0.742	0.438	0.756	0.087
300	0.723	0.420	0.543	0.058
600	0.736	0.457	0.430	0.032
900	0.721	0.425	0.363	0.023
1200	0.625	0.459	0.349	0.022
1500	0.539	0.425	0.321	0.020
1800	0.495	0.443	0.319	0.020
2100	0.469	0.460	0.320	0.020
2400	0.450	0.459	0.318	0.020
2700	0.418	0.477	0.324	0.020
3000	0.414	0.482	0.327	0.020
3300	0.411	0.486	0.331	0.020
3600	0.395	0.481	0.333	0.020
3900	0.387	0.484	0.338	0.021
4200	0.381	0.480	0.341	0.021
4500	0.381	0.476	0.345	0.021
4800	0.379	0.476	0.351	0.022
5100	0.388	0.473	0.355	0.022
5400	0.395	0.463	0.357	0.022
5700	0.389	0.465	0.364	0.023
6000	0.371	0.457	0.367	0.023

The measurement results indicate the general nonlinear nature of the dependence of the analytical signal intensity on the sample volume, however, for the range of 2.5-20 mL, a linear portion of the dependence can be distinguished, described by the equation: $I(V) = 0.022 V + 0.011$, which makes it possible to effectively compare the results obtained for samples of different volumes in this range.

To plot the dependence of the analytical signal intensity on the density, $NaNO_3$ was added to the sample by successively increasing the solution density. To take into account the increase in the sample volume and the simultaneous decrease in the volume concentration of uranium in the solution due to the addition of the $NaNO_3$ salt solution, the analytical signal intensities were recalculated based on the previously obtained calibration curves for concentration δC_i and volume δV_i .

$$\delta C_i = \frac{I_i}{I_o} \frac{0.064 C_i}{0.064 C_0} \frac{0.032}{0.032} \quad (11)$$

$$\delta V_i \frac{I_i}{I_o} \frac{0.007V_i}{0.007V_o} \frac{0.302}{0.302} \quad (12)$$

The entered correction factors represent the ratio of the analytical signal intensity for a given concentration and sample volume to the intensity value of the original reference sample. The final value of the signal intensity is obtained by multiplying the value of the analytical signal intensity by the value of the correction factors

$$I = I_{APP} \delta C_i \delta V_i \quad (13)$$

The calculation results are shown in tab. 2.

Based on the data obtained, a graph of the dependence of the analytical signal intensity on the density of the test solution was constructed. The resulting graph is shown in fig. 6.

The obtained dependence of the analytical signal intensity on the sample density is described by a weakly decreasing function. In the range of densities from 1.0 to 1.2 mg cm⁻³, the spread of the results of changes in the analytical signal does not exceed the statistical measurement error, thus, in this range of changes in the density of the sample, one can ignore.

CONCLUSIONS

The studies conducted show that for the determination of natural uranium in solutions via the NAA method using a radionuclide neutron source based on ²⁵²Cf, for a sample with a volume of 50 mL, with a measurement time of 1800 seconds, it is possible to achieve *LD* and *LQ* no more than 0.1 mgL⁻¹ and 0.3 mgL⁻¹, respectively. Additional reduction of *LD* and *LQ* values by 2-5 times is possible due to preliminary concentration of the sample, for example by evaporation.

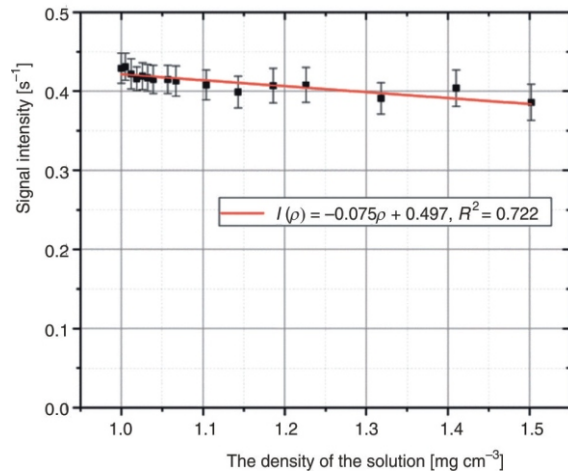


Figure 6. Dependence of the analytical signal intensity on the sample density

The dependence of *LD* and *LQ* on the measurement time of the induced activity of the sample was obtained. It has been established that the maximum accuracy of determining ²³⁸U is achieved with a measurement time of the induced activity of about 1800 seconds.

The influence of the effects of scattering and self-absorption of gamma radiation of the uranium line 74.6 keV on the results of neutron activation analysis is established. The linear sections of the dependence of the intensity of the analytical signal of uranium on the volume (from 2.5 to 20 mL) and density (from 1.0 to 1.2 mg cm⁻³) were determined.

The carried out studies make it possible to determine uranium by the NAA method in solutions of various compositions, in a wide range of concentrations, and with different sample volumes. Thus, the NAA method with a radionuclide source based on ²⁵²Cf can be successfully used to solve a wide range of problems of detection and quantitative determination of uranium concentration in solutions.

Table 2. Study results of the dependence of the analytical signal intensity on the density of the solution

Density of solution [gcm ⁻³]	<i>I</i> _{APP} [s ⁻¹]	Volume error correction δV_i	Concentration error correction δC_i	<i>I</i> corrected [s ⁻¹]	Absolute measurement error [s ⁻¹]
1.000	0.429	1.000	1.000	0.429	0.034
1.005	0.432	1.003	0.995	0.431	0.027
1.012	0.423	1.004	0.993	0.422	0.031
1.019	0.418	1.006	0.990	0.416	0.028
1.026	0.421	1.007	0.987	0.419	0.037
1.032	0.420	1.009	0.984	0.417	0.036
1.039	0.418	1.011	0.981	0.415	0.038
1.057	0.419	1.012	0.980	0.415	0.038
1.067	0.418	1.017	0.971	0.413	0.036
1.104	0.415	1.022	0.962	0.408	0.036
1.143	0.407	1.027	0.955	0.399	0.039
1.186	0.416	1.029	0.951	0.407	0.044
1.226	0.418	1.032	0.946	0.408	0.044
1.318	0.401	1.033	0.944	0.391	0.039
1.410	0.414	1.034	0.943	0.404	0.047
1.502	0.396	1.035	0.942	0.386	0.046

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AUTHORS' CONTRIBUTIONS

The idea for the study and experiment design was put forward by V. Zheleznov. The samples were prepared by S. Ivannikov and N. Markin. The activations and measurements were carried out by S. Ivannikov and N. Markin. The discussion and interpretation of the results was carried by S. Ivannikov, N. Markin and V. Zheleznov. The manuscript and figures were prepared by S. Ivannikov and N. Markin.

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ОДРЕЂИВАЊЕ УРАНИЈУМА У РАСТВОРИМА МЕТОДОМ НЕУТРОНСКЕ АКТИВАЦИОНЕ АНАЛИЗЕ СА ^{252}Cf ИЗВОРОМ НЕУТРОНА

Испитана је опција одређивања ^{238}U у растворима неутронском активационом анализом. Третман радионуклида заснован је на коришћењу ^{252}Cf извора неутрона. У оквиру истраживања утврђена је граница од 0.1 mgL^{-1} за одређивање уранијума помоћу термичких неутрона. Уз помоћ прелиминарне концентрације узорка методом испаравања, могуће је додатно смањити границу детекције за 2-5 пута. Дефинисано је да је 30 минута оптимално време за мерење индиковане активности узорка при раду са краткорживећим изотопом ^{239}U . Утврђен је утицај расејања и самоапсорпције гама зрачења уранијумске линије од 74.6 KeV на резултате анализе неутронске активације. Спроведена истраживања омогућила су одређивање уранијума у широком опсегу концентрације методом неутронске активационе анализе у растворима различитих састава.

Кључне речи: природни уранијум у раствору, неутронска активациона анализа, гама спектрометрија, граница детекције