ISSN 1066-3622, Radiochemistry, 2019, Vol. 61, No. 4, pp. 464–469. © Pleiades Publishing, Inc., 2019.
Russian Text © The Author(s), 2019, published in Radiokhimiya, 2019, Vol. 61, No. 4, pp. 339–343.

Spectrophotometric Determination of Simultaneously Present Neptunium, Americium, and Plutonium in Aqueous Solutions

V. N. Momotov*[a], E. A. Erin[a], and A. Yu. Volkov[a]

[a] *Research Institute of Atomic Reactors, Zapadnoe shosse 9, Dimitrovgrad, Ulyanovsk oblast, 433510 Russia*
**e-mail: momotov@niiar.ru*

Received August 27, 2018; revised November 12, 2018; accepted November 14, 2018

Abstract—A spectrophotometric method was developed for determining simultaneously present Np, Am, and Pu in sulfuric and perchloric acid solutions. The molar extinction coefficients ε were determined. In the concentration ranges 1.0×10^{-4}–2.0×10^{-3} M for Pu and Am and 5.0×10^{-4}–1.0×10^{-2} M for Np, the overall error does not exceed 5%. The detection limits are 3.0×10^{-5} M for Pu and Am and 1.0×10^{-4} M for Np.

Keywords: spectrophotometric determination, spectrophotometric titration, americium, plutonium, neptunium, absorption spectrum, optical density, wavelength, molar extinction coefficient

DOI: 10.1134/S1066362219040106

Analytical determination of the mass content of Pu, Am, and Np is performed using diverse methods such as radiometric, mass-spectrometric, coulometric, activation, spectrophotometric, etc. [1–3]. The use of these methods for determining Pu, Am, and Np present simultaneously involves certain problems. For example, when using coulometric method, it is possible to reach very low (no more than tenth fractions of percent) overall error in the determination of the mass content of Pu [4] and Np [5], but the determination of Am in this case is impossible because of very high redox potential (E_0^{p}) of the Am(IV)–Am(III) couple in mineral acids [6]. The Am determination in mineral acids becomes possible in the presence of strong complexing agents, e.g., phosphate and phosphotungstate ions [7, 8]. However, such procedure is time-consuming and therefore hardly suitable for prompt monitoring. The use of isotope dilution followed by mass-spectrometric determination requires time-consuming sample preparation with preliminary partitioning of Pu and Am [9, 10]. The radiometric method allows measurement of tracer amounts of these elements, but problems arise, e.g., with the determination of ^{238}Pu and ^{241}Am, because the α-particle energies in the decay of these radionuclides are virtually equal [11]. The radiometric determination of Np requires thorough removal of other α-emitting radionuclides because of relatively low specific α-activity of ^{237}Np (26.08 Bq μg^{-1}).

Analysis of samples containing Pu, Am, and Np simultaneously (e.g., of spent nuclear fuel samples) becomes more and more necessary [9].

This study was aimed at the development of a simple and quick method for joint determination of Pu, Am, and Np without their preliminary separation.

EXPERIMENTAL

A ^{241}Am sample was purified to remove Pu, Np, and nonradioactive impurities by extraction chromatography using HDEHP [11, 12] and TOPO [13]. Monoisotopic ^{239}Pu and ^{237}Np samples were additionally purified using Dowex 1×8 resin [2, 3].

Perchloric, sulfuric, and nitric acids and sodium nitrite ($NaNO_2$) were of chemically pure grade and were used without additional purification. All solutions were prepared using double-distilled water. Spectrophotometric measurements were performed using with Beckman DU-640 and Cary 5000 recording spectrophotometers.

The Pu, Am, and Np concentrations in the initial solutions were determined by independent methods characterized by low overall error.

The mass content of Pu and Am was determined by isotope dilution mass spectrometry [9, 10]. The spike was prepared from branch standard samples prepared at the Khlopin Radium Institute from nitric acid solutions of ^{242}Pu and ^{243}Am.

In the case of Np, we used the radiometric method and spectrophotometric titration [14]. The $KMnO_4$ solution prepared using a standard solution was chosen as a titrant. This choice was governed by the fact that oxidation of NpO_2^+ to NpO_2^{2+} with potassium permanganate occurs quickly and quantitatively; furthermore, the presence of K^+, MnO_4^-, and Mn^{2+} ions does not prevent spectrophotometric determination of both NpO_2^+ at a wavelength of 980 nm and NpO_2^{2+} in the region of 1222 nm [3].

Neptunium was preliminarily stabilized in the pentavalent state by evaporating its solution in 1 M $HClO_4$, introducing excess $NaNO_2$, and precipitating NpO_2^+ hydroxide with excess NH_4OH. The precipitate was separated by centrifugation, washed thrice with distilled water, and dissolved in 1 M $HClO_4$.

RESULTS AND DISCUSSION

It is known [1–3] that Pu, Am, and Np in mineral acid solutions have characteristic absorption bands with relatively high molar extinction coefficients. For example, Am^{3+} in perchloric and sulfuric acid solutions has a characteristic absorption band at 503; PuO_2^{2+}, at 830; NpO_2^+, at 980; and NpO_2^{2+}, at 1222 nm. All these bands are well resolved, are analytical, and allow determination of the concentrations of these elements with high accuracy. Tenfold excess of UO_2^{2+} and $NaNO_3$, and also of Fe^{3+}, Cr^{3+}, and other metal ions does not interfere with the photometric determination of PuO_2^{2+} and Am^{3+}, and nitrate ions up to a concentration of 2.5 M and a tenfold excess of UO_2^{2+}, PuO_2^{2+}, Fe^{3+}, Cl^-, F^-, $Cr_2O_7^{2-}$, MnO_4^-, SO_4^{2-}, $C_2O_4^{2-}$, citrate, and other ions do not interfere with the determination of NpO_2^{2+} [1–3]. When these ratios are exceeded, separation of the interfering ions from Np, Am, and Pu is required. AgO is widely used for quantitative oxidation of Pu^{4+} and NpO_2^+ to the hexavalent state for their quantitative determination [16–20].

First we recorded the individual absorption spectra of the Am^{3+}, PuO_2^{2+}, NpO_2^+, and NpO_2^{2+} ions in perchloric and sulfuric acids. Figure 1 shows the absorption spectra of Am^{3+}, PuO_2^{2+}, NpO_2^+, and NpO_2^{2+} in perchloric acid. In sulfuric acid solutions, the spectra are similar.

As can be seen, the analytical bands of the elements are well resolved and can be used for measuring their concentrations in the case of their simultaneous presence.

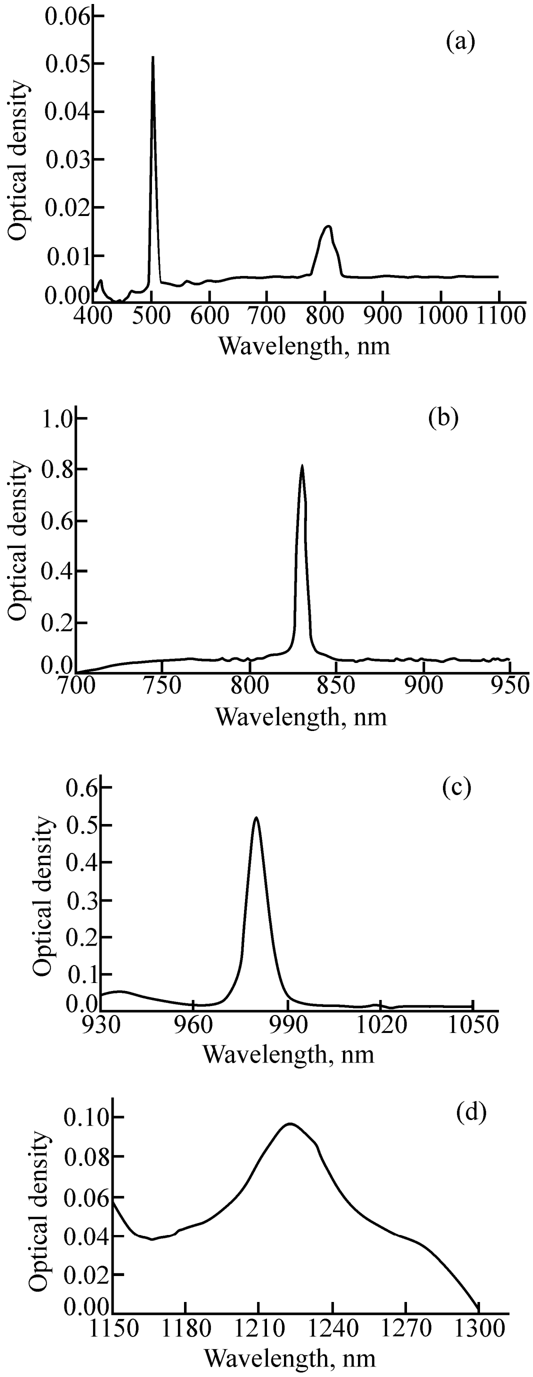

Fig. 1. Integral absorption spectra of (a) Am^{3+} (C_{Am} = 1.30 × 10^{-4} M), (b) PuO_2^{2+} (C_{Pu} = 2.34 × 10^{-3} M), (c) NpO_2^+ (C_{Np} = 1.55 × 10^{-3} M), and (d) NpO_2^{2+} (C_{Np} = 1.64 × 10^{-3} M) in 2.0 M $HClO_4$.

We have studied the influence of the spectrum scanning rate (v) on the optical density of the analytical bands (Table 1). As can be seen, the optical density of the characteristic absorption bands of PuO_2^{2+}, Am^{3+},

Table 1. Optical density (*D*) of PuO_2^{2+}, Am^{3+}, NpO_2^+, and NpO_2^{2+} in various media as a function of the spectrum scanning rate (*v*)

Ion being determined	Medium	Wavelength, nm	*v*, nm min^{-1}	*D*
PuO_2^{2+}	2 M $HClO_4$	830.2	1200	0.178
			600	0.183
			240	0.187
			120	0.186
	1 M H_2SO_4	834.8	1200	0.042
			600	0.064
			240	0.067
			120	0.067
Am^{3+}	2 M $HClO_4$	503.0	1200	0.054
			600	0.063
			240	0.064
			120	0.064
	1 M H_2SO_4	503.2	1200	0.351
			600	0.369
			240	0.380
			120	0.380
NpO_2^+	2 M $HClO_4$	980.0	1200	0.0538
			600	0.0554
			240	0.0544
			120	0.0552
	1 M H_2SO_4	981.0	1200	0.2676
			600	0.2715
			240	0.2722
			120	0.2723
NpO_2^{2+}	2 M $HClO_4$	1222.0	1200	0.2378
			600	0.2389
			240	0.2383
			120	0.2383
	1 M H_2SO_4	1227.0	1200	0.0562
			600	0.0555
			240	0.0542
			120	0.0542

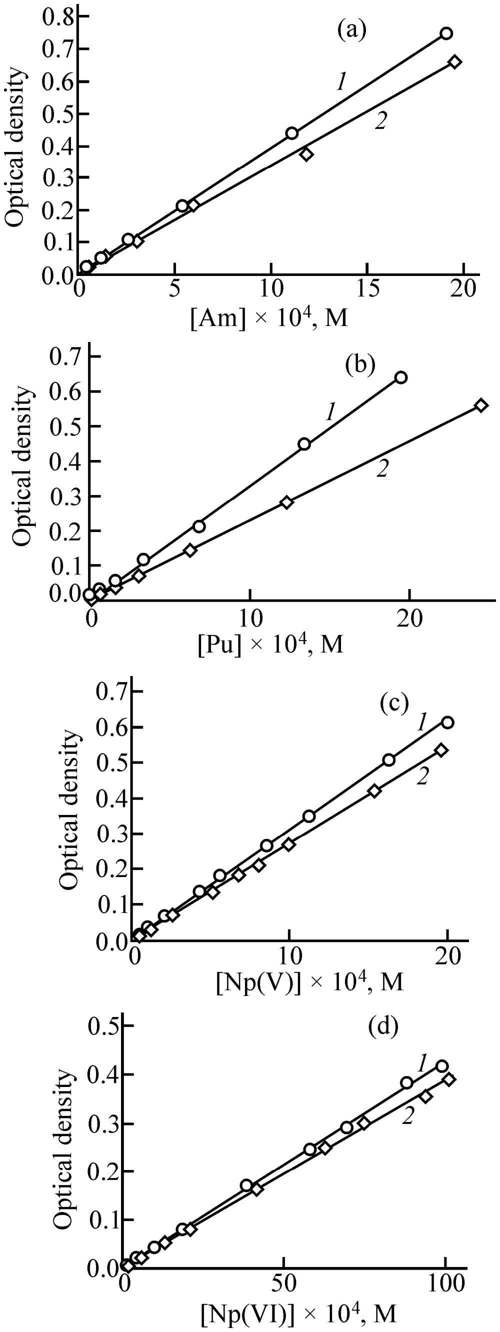

Fig. 2. Concentration dependences of the optical densities of the absorption bands of (a) Am^{3+} at 503.0 nm, (b) PuO_2^{2+} at 830.2 nm, (c) NpO_2^+ at 980.1 nm, and (d) NpO_2^{2+} at 1222.0 nm: (*1*) 2.0 M $HClO_4$ and (*2*) 1 M H_2SO_4.

and NpO_2^+ somewhat increases as the scanning rate is decreased from 1200 to 240 nm min^{-1}. At scanning rates of 240 and 120 nm min^{-1}, the optical densities remain constant within the measurement uncertainty. For the characteristic NpO_2^{2+} absorption band, the optical density slightly decreases as the scanning rate is decreased from 1200 to 240 nm. However, in the scanning rate range 240–120 nm min^{-1} the optical density of the NpO_2^{2+} absorption band also remains constant. Therefore, in the experiments on determination of the mass content of Pu, Am, and Np in solutions, we used the scanning rate of 240 nm min^{-1}.

We studied the observance of the Bouguer–Lambert–Beer law for the characteristic absorption bands of Am^{3+}, PuO_2^{2+}, NpO_2^+, and NpO_2^{2+} in perchloric and sulfuric acid solutions. The results are shown in Fig. 2. As can be seen, the dependences are well fitted

Table 2. Optical density (*D*) of PuO_2^{2+}, Am^{3+}, NpO_2^{+}, and NpO_2^{2+} solutions in various media as a function of the concentration of the element being determined (*C*). Scanning rate 240 nm min^{-1}

Ion being determined	Medium	$C \times 10^4$ M	*D*	ε	ε_{av}
				L mol^{-1} cm^{-1}	
Am^{3+}	2 M $HClO_4$	22.1	0.8421	381	393 ± 6
		11.1	0.4403	398	
		5.56	0.2138	387	
		2.76	0.1060	391	
		1.38	0.0554	401	
		0.69	0.0275	398	
	1 M H_2SO_4	11.9	0.3780	316	360 ± 13
		5.97	0.2186	366	
		2.98	0.1112	372	
		1.49	0.0552	369	
		0.75	0.0275	368	
PuO_2^{2+}	2 M $HClO_4$	13.4	0.4528	338	345 ± 14
		6.87	0.2110	307	
		3.43	0.1216	354	
		1.73	0.0618	357	
		0.85	0.0309	360	
		0.48	0.0154	321	
		0.24	0.0078	325	
	1 M H_2SO_4	24.7	0.5574	226	233 ± 5
		12.4	0.2853	231	
		6.18	0.1427	231	
		3.09	0.0732	237	
		1.55	0.0361	233	
		0.78	0.0179	231	
		0.37	0.0090	233	
		0.28	0.0043	245	
NpO_2^{2+}	2 M $HClO_4$	87.7	0.3852	43.9	41.4 ± 2
		70.1	0.2910	41.5	
		58.5	0.2477	42.3	
		39.0	0.1496	38.4	
		19.5	0.0770	39.5	
		9.75	0.0413	42.4	
		4.88	0.0187	38.5	
		1.63	0.0073	44.8	
	1 M H_2SO_4	93.7	0.3574	38.1	39.0 ± 2
		75.0	0.2997	40.0	
		62.6	0.2492	39.8	
		41.7	0.1628	39.0	
		20.9	0.0834	39.9	
		13.2	0.0538	40.8	
		6.61	0.0249	37.7	
NpO_2^{+}	2 M $HClO_4$	16.2	0.5127	316	319 ± 5
		11.2	0.3520	314	
		8.57	0.2696	315	
		5.72	0.1807	316	
		4.28	0.1373	321	
		2.14	0.0692	323	
		1.07	0.0351	328	
		0.53	0.0171	323	
		0.27	0.0087	322	

Table 2. (Contd.)

Ion being determined	Medium	$C \times 10^4$ M	D	ε	ε_{av}
				L mol^{-1} cm^{-1}	
NpO_2^+	1 M H_2SO_4	10.0	0.2715	272	272 ± 5
		8.09	0.2163	267	
		6.79	0.1833	270	
		5.15	0.1351	262	
		2.58	0.0724	281	
		1.29	0.0357	277	

by straight lines at the PuO_2^{2+}, Am^{3+}, and NpO_2^+ concentrations in the range from 1.0×10^{-4} to 2.0×10^{-3} M and NpO_2^{2+} concentration in the range from 5.0×10^{-4} to 1.0×10^{-2} M.

In these concentration ranges, we determined the molar extinction coefficients ε of PuO_2^{2+}, Am^{3+}, NpO_2^+, and NpO_2^{2+} in sulfuric and perchloric acids and calculated the uncertainty of ε by analysis of variance [21].

Table 2 shows the optical densities in perchloric and sulfuric acid solutions as functions of the element concentrations. As can be seen, the suggested method allows determination of the mass content of Am, Pu, and Np at their comparable amounts. The molar extinction coefficients are relatively high, allowing analysis of low Am and Pu concentrations. The molar extinction coefficients of NpO_2^{2+} are lower than those of Am^{3+}, PuO_2^{2+}, and NpO_2^+ in perchloric and sulfuric acids. Therefore, the detection limit for Np(VI) is higher and the range of measurable concentrations is narrower.

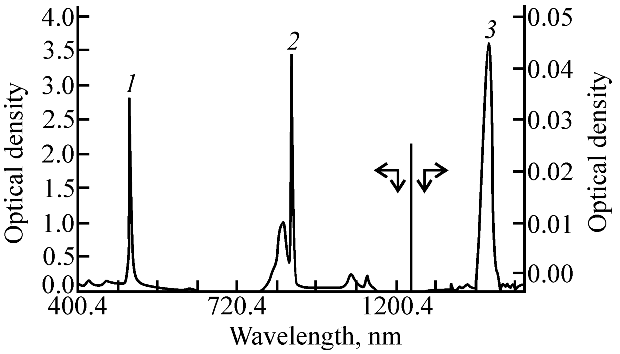

Fig. 3. Total integral absorption spectrum of Am^{3+}, PuO_2^{2+}, and NpO_2^{2+} in 1 M H_2SO_4 (initial solution). Bands: (*1*) Am, (*2*) Pu, and (*3*) Np.

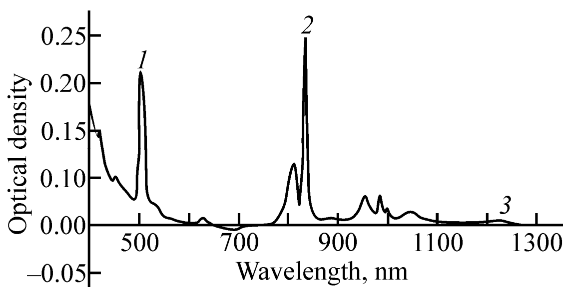

Fig. 4. Total integral absorption spectrum of Am^{3+}, PuO_2^{2+}, and NpO_2^{2+} in 1 M H_2SO_4 (diluted solution). Bands: (*1*) Am, (*2*) Pu, and (*3*) Np.

However, cases when the amount of one or two components considerably exceed the amount of the other component(s) become more and more frequent in the practice. For example, in pyrochemical separation of Am and Pu their content in the sample being analyzed exceeds that of Np by a factor of tens and even hundreds, which considerably complicates determination of the mass Np content [22].

Figure 3 shows the total integral spectrum of all the three elements in a solution at the ratio $C_{Pu} : C_{Am} : C_{Np}$ = 16.2 : 8.3 : 1.

As can be seen, the Np amount is sufficient for its determination in the initial solution, because the optical density is in the range of values suitable for this method. In the case of Pu and Am, the optical densities are too high, so that the Bouguer–Lambert–Beer law is not observed and the concentration determination becomes impossible. Therefore, to determine Pu and Am, the solution should be diluted to obtain optical densities in the range 0.1–0.3. Figure 4 shows the integral absorption spectrum of the diluted solution.

Thus, we have developed a rapid spectrophotometric method for joint determination of Np, Pu, and Am. At Pu and Am concentrations in the range 1.0×10^{-4}–2.0×10^{-3} M and Np concentrations in the range 5.0×10^{-4}–1.0×10^{-2} M, the overall error does not exceed 5%. The detection limits are 3.0×10^{-5} M for Pu and Am and 1.0×10^{-4} M for Np.

The procedure for spectrophotometric determination of Np, Am, and Pu is protected by the Russian patent [23]. The procedure has been tested and is widely used at the Research Institute of Atomic Reactors for determining the mass content of Pu, Am, and Np in solutions obtained in the course of the development of technologies for pyrochemical and hydrometallurgical SNF reprocessing.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Myasoedov, B.F., Guseva, L.I., Lebedev, I.A., et al., *Analiticheskaya khimiya elementov. Transplutonievye elementy Am–Cm* (Analytical Chemistry of Elements. Transplutonium Elements Am–Cm), Moscow: Nauka, 1972, p. 138.
2. Milyukova, M.S., Gusev, N.I., Sentyurin, I.G., and Sklyarenko, N.S., *Analiticheskaya khimiya elementov. Plutonii* (Analytical Chemistry of Elements. Plutonium), Moscow: Nauka, 1965, p. 164.
3. Mikhailov, V.A., *Analiticheskaya khimiya urana* (Analytical Chemistry of Uranium), Moscow: Nauka, 1962, p. 104.
4. Momotov, V.N., Erin, E.A., and Chistyakov, V.M., *Radiochemistry*, 2011, vol. 53, no. 3, pp. 322–326.
5. Kasar, U.M., Joshi, A.R., and Patil, S.K., *J. Radioanal. Nucl. Chem.*, 1991, vol. 150, no. 2, pp. 369–376.
6. Lebedev, I.A., Thermodynamics of formation of simple and complex ions of transplutonium elements in solutions, *Doctoral (Chem.) Dissertation*, Moscow, 1984, p. 310.
7. Chistyakov, V.M., Baranov, A.A., Erin, E.A., and Timofeev, G.A., *Radiokhimiya*, 1990, vol. 32, no. 3, pp. 128–132.
8. Trofimov, T.I., Kulyako, Yu.M., Lebedev, I.A., et al., *Radiokhimiya*, 1981, vol. 23, no. 5, pp. 1051–1053.
9. Erin, E.A., Momotov, V.N., Volkov, A.Yu., et al., *Radiochemistry*, 2017, vol. 59, no. 4, pp. 372–378.
10. Petrov, E.R., Bibichev, B.A., Domkin, V.D., et al., *Radiochemistry*, 2012, vol. 54, no. 4, pp. 379–382.
11. Metz, C.F. and Waterbary, G.R., *Treatise on Analytical Chemistry*, part II, section A, vol. 9: *The Transuranium Actinide Elements*, Interscience, 1962. Translated under the title *Analiticheskaya khimiya transuranovykh elementov*, Moscow: Atomizdat, 1967, pp. 87–97.
12. Erin, E.A., Momotov, V.N., and Baranov, A.A., *Radiochemistry*, 2017, vol. 59, no. 1, pp. 58–64.
13. Erin, E.A., Vityutnev, V.M., Kopytov, V.V., and Vasil’ev, V.Ya., *Radiokhimiya*, 1979, vol. 21, no. 1, pp. 100–104.
14. Charlot, G., *Les methods de la chimie analytique. Analyse quantitative minerale*, Paris: Masson, 1961, 4th ed. Translated under the title *Metody analiticheskoi khimii*, Moscow: Khimiya, 1966, p. 412.
15. Momotov, V.N., Erin, E.A., and Zakharova, L.V., *Radiochemistry*, 2017, vol. 59, no. 2, pp. 175–180.
16. Kosyakov, V.N., Yerin, E.A., and Vitutnev, V.M., *J. Radioanal. Chem.*, 1980, vol. 56, nos. 1–2, pp. 83–92.
17. Davies, W. and Gray, W., *Talanta*, 1964, vol. 11, no. 8, pp. 1203–1211.
18. Simakin, G.A., Baklanova, P.F., Kuznetsov, G.F., et al., *Zh. Anal. Khim.*, 1974, vol. 29, pp. 1585–1588.
19. Momotov, V.N., Erin, E.A., and Chistyakov, V.M., *Radiochemistry*, 2011, vol. 53, no. 3, pp. 322–326.
20. Momotov, V.N., Erin, E.A., and Chistyakov, V.M., *Radiochemistry*, 2014, vol. 56, no. 3, pp. 302–307.
21. Laitinen, H.A. and Harris, W.E., *Chemical Analysis: An Advanced Text and Reference*, McGraw-Hill, 1975, 2nd ed. Translated under the title *Khimicheskii analiz*, Moscow: Khimiya, 1979, pp. 590–595.
22. Benedict, M. and Pigford, T.H., *Nuclear Chemical Engineering*, New York: McGraw-Hill, 1957.
23. Momotov, V.N., Erin, E.A., and Volkov, A.Yu., Patent RU 2647837, Appl. Febr. 22, 2017, Publ. March 19, 2018.

Translated by G. Sidorenko