SORPTION
AND ION EXCHANGE PROCESSES

Sorption Recovery of Transition Metals with Dithiooxamidated Polysiloxane

A. S. Kholmogorova[a], L. K. Neudachina[a], I. S. Puzyrev[b], and A. V. Pestov[b]

[a] *Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia*
[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences,*
ul. Kovalevskoi 22, Yekaterinburg, 620137 Russia
e-mail: kholmogorovaa@mail.ru

Abstract—Effect of the acidity of the sorption solution on the recovery of Cu(II), Ni(II), Co(II), Ag(I), and Pd(II) ions was studied for dithiooxamidated polysiloxanes with degrees of modification of 0.10 and 0.21. The constant acidity of the solution was maintained with ammonia, acetate, and ammonia-acetate buffer solutions. The optimal sorption conditions of metal ions from individual solutions were found. The distribution coefficients and pairwise selectivity coefficients were calculated for all the ions studied. It was fund on the basis of the selectivity coefficients that introduction of dithiooxamide groups into the structure of polysiloxane yields an effective sorbent for recovery of Pd(II) and Ag(I).

To priority tasks in environment protection belongs a search for effective and ecologically safe techniques for purification of industrial wastewater with sorbents [1, 2]. A no less topical task is to recover noble metals from complex-composition objects to which belong ores, ore-processing wastes, catalysts, biological materials, and medicinal preparations.

Rubeanic acid is widely used to detect and determine trace amounts of transition metal ions in various media. The acid forms with metal ions colored poorly soluble intracomplex compounds having a large stability constant [3–7].

In recent years, rubeanic acid has been rather frequently used to modify the surface of sorbents. A rather large number of studies are known, concerned with the fixation of dithiooxamides on an organic surface: chitosan [8], various resins [9–11], fullerene [12], and cellulose [13]. The number of studies using an inorganic matrix is substantially smaller: only silica gels [14, 15] and silicas [16] are mentioned among representatives of silicon-containing sorbents.

Meanwhile, sorbents based on silicon compounds possess certain advantages: they show no swelling and are distinguished by a rather high rate of mass exchange; the time in which equilibrium is attained between a solution and a sorbent occasionally does not exceed several tens of seconds [17]. In addition, sorbents based on silicon compounds exhibit high heat resistance and radiation hardness and have a high mechanical strength. These sorbents are irreplaceable as stationary phases for modern high-performance liquid chromatography, one of the most effective and versatile methods of instrumental analysis [18–21].

The known organosilicon sorbents with dithiooxamide groups [13–15] demonstrate a high sorption affinity and selectivity for transition metal ions, and especially for Pd(II) and Pt(IV) ions. Despite the positive results, their capacity remains rather low (0.19 mmol g^{-1}) and the concentration of grafted groups does not exceed 0.24 mmol g^{-1}. Hence follows the need to improve the synthesis methods of sorbents of this kind and to test their sorption properties.

Sorbents with grafted dithiooxamide groups onto a polysiloxane matrix by the sol-gel technique have been synthesized at the Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences [22]. Polysiloxanes

differ from the conventional chemically synthesized silicas by the higher exchange capacity and the innovative way to synthesize sorbents, the sol-gel method, can modify the matrix to improve its thermal and chemical stability and change the general structure of the matrix. For example, it has been found [21] that the reaction of reamidation of rubeanic acid with aminopropylpolysiloxane (APPS) can yield dithiooxamidated polysiloxanes with a surface group content of up to 0.78 mmol g^{-1} at a general degree of substitution of up to 0.25.

The goal of our study was to examine the sorption properties of polysiloxanes modified with dithiooxamide groups (DAPPS) for Cu(II), Ni(II), Co(II), Ag(I), and Pd(II) ions.

EXPERIMENTAL

Solutions of Cu(II), Ni(II), Co(II), and Ag(I) ions with a concentration of 2.5×10^{-3} M were prepared by dissolution of precisely weighed portions of the corresponding nitrate salts of chemically pure grade in distilled water. The solution of Pd(I) ions was prepared by dissolution of a precisely weighed portion of palladium chloride in a 0.1 M solution of hydrochloric acid.

Sorption solutions were prepared by dilution of the starting solutions immediately prior to an experiment. The required acidity was created and maintained in the solutions with ammonia, acetate, and ammonia-acetate buffer solutions; the precise pH value was monitored with an I-160MI ion meter with glass (ES-10603) and silver chloride (ESr-10103) electrodes.

The acid-base properties of the polysiloxanes synthesized in the study were studied using the limited-volume method [23] by the following scheme: weighed portions of sorbents (10 mg each), 50.0 cm^3 of a working solution of a metal, with a metal ion concentration of 1×10^{-4} M and a certain pH value, were placed in conical vessels and allowed to stay for 48 h under periodic agitation. Then the solutions were filtered through a Blue ribbon filter and the sorbent was washed with distilled water to remove the residual mother liquor. Each experiment was performed in three parallel runs.

The concentration of metal ions in the solutions before and after the sorption was determined with a Solaar M6 atomic-absorption spectrometer (Thermo Electron) with atomization in acetylene–air flame by using the preliminarily plotted calibration plot. Working parameters of the spectrometer: flow rate of acetylene, 1.0 dm^3 min^{-1};

three parallel runs; time of each measurement, 4 s; lamp current 50%; no background compensation; wavelengths (nm): 324.8 for copper, 240.7 for cobalt, 232.0 for nickel, and 328.1 for silver. The width of the absorbing layer was chosen in relation to the required range of calibration concentrations.

The concentrations of palladium ions before and after the sorption were determined with an iCAP 6500 Duo atomic-emission spectrometer with inductively coupled plasma (Thermo Electron) by using a calibration plot. The analytical line at 342.109 nm was used for analysis.

To evaluate the sorption, the distribution coefficient D was calculated by the formula

$$D = \frac{(c - c_{eq})V}{c_{eq}g},$$

where c and c_{eq} are the metal ion concentrations in solution before and after the sorption, respectively (mol dm^{-3}); V, volume of the sorption solution (cm^3); and g, mass of the sorbent (g).

RESULTS AND DISCUSSION

The synthesized sorbents were identified by elemental analysis and IR Fourier spectroscopy. The degree of modification was calculated from the elemental analysis data to be 0.10 (DAPPS 0.10) and 0.21 (DAPPS 0.21), and the concentration of grafted groups, 0.31 and 0.68 mmol g^{-1}, respectively.

The structure of the modified polysiloxanes can be represented as
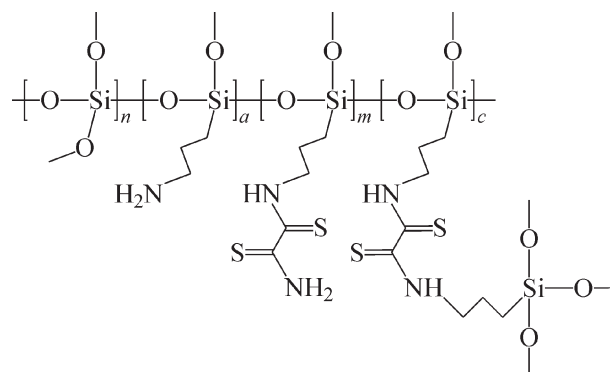
The presence of dithiooxamide groups on the sorbent surface suggest that complex compounds with metal ions are formed. Most of complex-forming sorbents has

the maximum sorption capacity for ions of a particular metal in a rather narrow range of solution acidities, which provides conversion of all the functional groups to the coordination-active (deprotonated) form, with formation of precipitated hydroxides and basic metal salts ruled out [24]. Thus, a selective recovery of metal ions from solution on the background of accompanying ions can be achieved.

Because the interaction between metal ions and the sorbent surface is largely affected by the form in which a metal ion is present in solution, the dependence of the sorption of Cu(II), Ni(II), Co(II), Ag(I), and Pd(II) ions on the acidity of the medium was studied using ammonia (pH 6.5–10.5), acetate (pH 2–6), and ammonia-acetate (pH 2–10) buffer solutions.

To describe the state of equilibrium in the solution–sorbent system, we plotted dependences of the distribution coefficients of metal ions on the solution pH (Figs. 1 and 2). The absence of a linear relationship between the logarithm of the distribution coefficients and the acidity of the medium indicates that a coordination bond is formed between metal ions and functional groups of the sorbents [25]. In the course of sorption, the sorption bed is differently colored, depending on the metal ion: black for C(II), blue for Co(II), red for Ni(II), and dark brown for Ag(I) and Pd(II), which indirectly confirms that the metals are sorbed by the complexation mechanism.

We found, judging from the maximum sorption capacity, that the optimal solutions for recovery of the metal ions are ammonia and ammonia-acetate buffer solutions with pH 6.5–9.0 for Cu(II), 7.0–9.5 for Ni(II), and 7.5–10.0 for Co(II), which was confirmed in [26, 27]. It was shown in [28] that Cu(II) ions are present in dilute solutions as hydrated ions at pH < 6.0, and Ni(II) and Co(II) ions, at pH values smaller than 7.0 and 7.5, respectively. As the solution pH increases, ammonia complexes are formed, which is a probable reason for the shift of the optimal pH range for sorption of Ni(II) and Co(II) to the more alkaline range, compared with Cu(II) ions.

Ag(I) ions are quantitatively sorbed in all the pH ranges under study, which may be due to their low concentration in the sorption solution. Pd(II) ions are optimally recovered in an acid medium (pH 2–4); in this pH range, metal ions are present in the form of mixed chloride and hydroxide complexes [29].

Based on the dependences obtained (Fig. 1), we can arrange metal ions in order of increasing affinity: Co(II) <

Ni(II) < Cu(II) << Pd(II) ≈ Ag(I). The sequence Co(II) < Ni(II) < Cu(II), which corresponds to a fragment of the Irving–Williams stability series, is also confirmed by the decrease in the solubility products of the corresponding rubeanates [30]. However, the stability constants of these compounds, determined in [31], are arranged in a different order: Ni(II) < Cu(II) < Co(II).

With increasing degree of sorbent modification, the general run of the dependences is preserved. The values of the distribution coefficients for Ag(I) and Pd(II) ions reach in some cases seven orders of magnitude, which points to a high affinity of the functional groups of the sorbent for these ions. At the same time, the distribution coefficients for Cu(II), Ni(II), and Co(II) ions are 3–4 orders of magnitude smaller in all the pH ranges under study. This fact indicates that the sorbents exhibit selectivity for Ag(I) and Pd(II) ions to a greater extent.

To quantitatively characterize the capacity of polysiloxanes modified with dithiooxamide groups for separation of Ag(I) and Pd(II) ions, we determined the selectivity coefficients $\beta_{M1/M2}$ (see table) where M_1 = Ag(I) or Pd(II); and M_2 = Cu(II), Ni(II), Co(II), Ag(I), and Pd(II). A quantitative separation of a mixture of two elements by the selective sorption method is possible if the selectivity coefficient is on the order $\beta \geq 10$–30 [32].

It follows from the data in the table that quantitative separation of Ag(I) from accompanying Cu(II), Ni(II), and Co(II) is possible in all the pH ranges under study; Pd(II) ions can be separated in ammonia–acetate buffer solutions with pH 2.0–4.0 and in acetate buffer solutions with pH 3.0–6.0. Separation of noble metal ions [Ag(I) and Pd(II)] is possible at pH 8.0–10.0 with ammonia buffer systems and at pH 2.0–3.0 with ammonia–acetate buffer systems.

It should be taken into account that, if selectivity is performed in the dynamic mode, the selectivity coefficients will be higher in all probability.

The whole set of the data available in the present communication evidences that introduction of dithiooxamide groups into the polysiloxane matrix yields materials with high sorption selectivity for Ag(I) and Pd(II) ions.

CONCLUSIONS

(1) The sorbability of Cu(II), Ni(II), Co(II), Ag(I), and Pd(II) ions was studied in relation to the acidity of
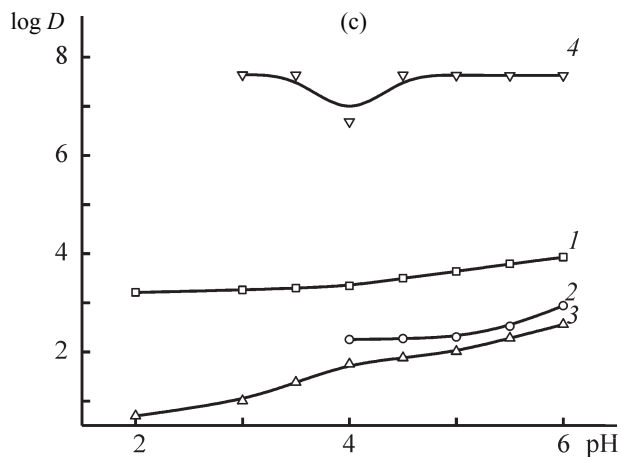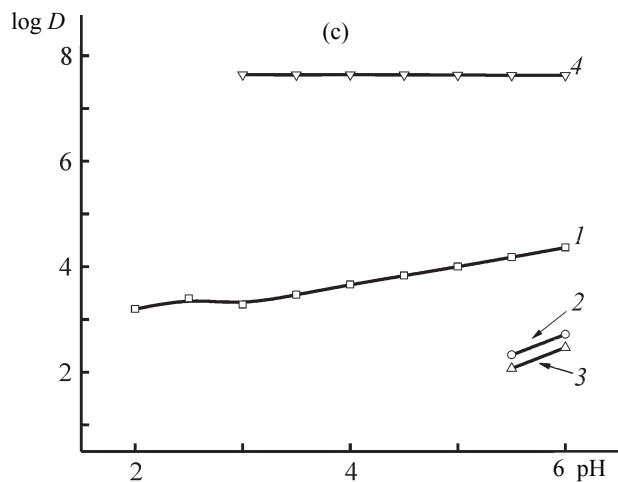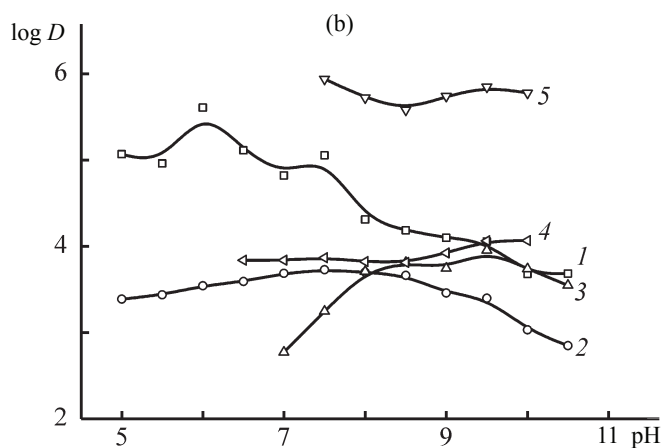
Fig. 1. Logarithm of the distribution coefficients, log D, of (*1*) Cu(II), (*2*) Ni(II), (*3*) Co(II), (*4*) Pd(II), and (*5*) Ag(I) ions on DAPS 0.10 vs. the solution pH in static conditions with (a) ammonia–acetate, (b) ammonia, and (c) acetate buffer solutions.
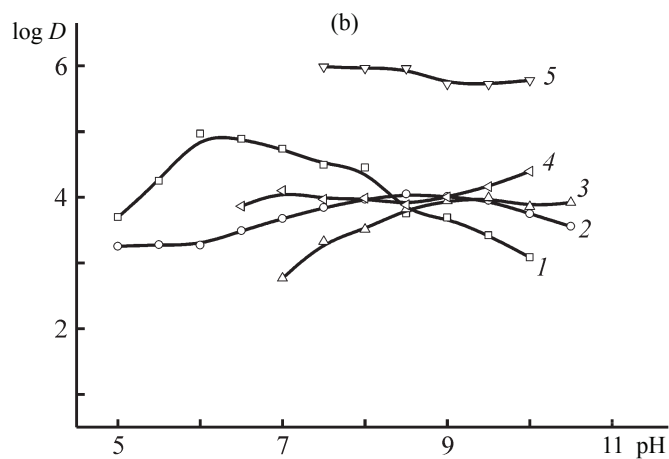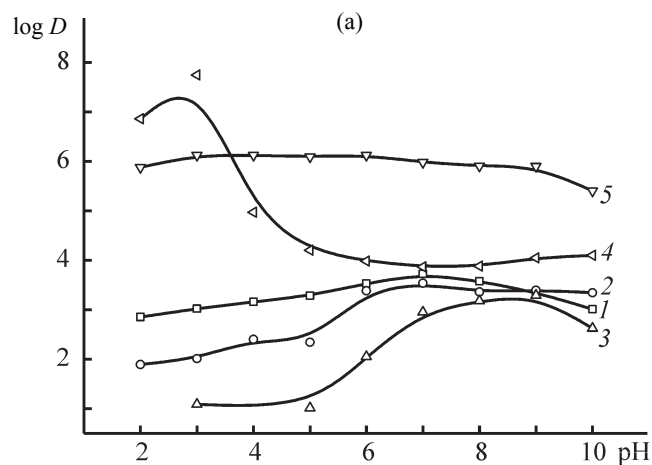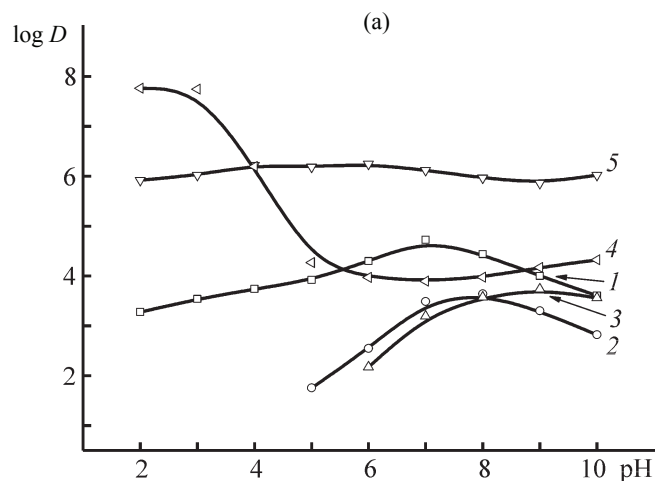
Fig. 2. Logarithm of the distribution coefficients, log D, of (*1*) Cu(II), (*2*) Ni(II), (*3*) Co(II), (*4*) Pd(II), and (*5*) Ag(I) ions on DAPS 0.21 vs. the solution pH in static conditions with (a) ammonia–acetate, (b) ammonia, and (c) acetate buffer solutions.

Values of the selectivity coefficients

	βAg/M								βPd/M							
	Cu(II)		Ni(II)		Co(II)		Pd(II)		Cu(II)		Ni(II)		Co(II)		Ag(I)	
pH	0.10	0.21	0.10	0.21	0.10	0.21	0.10	0.21	0.10	0.21	0.10	0.21	0.10	0.21	0.10	0.21
	Ammonia–acetate buffer solution															
2	1.0×10^4	438	9.6×10^4	–	–	–	0	0	1.0×10^5	3.0×10^5	9.2×10^5	–	–	–	9	70
3	1.3×10^4	308	1.3×10^5	–	1.1×10^6	–	0	0	5.2×10^4	1.6×10^5	5.4×10^6	–	4.5×10^7	–	41	53
4	920	307	5.3×10^4	–	–	–	14	1	64	288	374	–	–	–	0	1
5	643	185	5.5×10^4	2.7×10^4	1.2×10^6	–	77	83	8	2	71	325	1.5×10^4	–	0	0
6	391	90	554	5.0×10^4	1.2×10^5	1.2×10^5	138	189	2	0	4	27	86	63	0	0
7	179	25	277	433	1.0×10^4	848	129	169	1	0	2	3	8	5	0	0
8	213	34	352	213	536	247	106	99	2	0	3	2	5	3	0	0
9	353	73	323	364	409	133	71	49	4	2	4	7	5	3	0	0
10	247	262	114	1.6×10^4	600	292	20	50	12	5	5	32	29	6	0	0
	Ammonia buffer solution															
5.0	0	–	0	–	–	–	–	–	0	–	0	–	–	–	–	–
5.5	0	–	0	–	–	–	–	–	0	–	0	–	–	–	–	–
6.0	0	–	0	–	–	–	–	–	0	–	0	–	–	–	–	–
6.5	0	–	0	–	–	–	0	–	0.1	0.1	2	2	–	–	–	–
7.0	0	–	0	–	0	–	0	–	0.1	0.2	1	2	11	21	–	–
7.5	7	31	163	139	495	459	118	104	0.1	0.3	1	1	4	4	0	0
8.0	26	32	105	99	103	284	79	95	0.3	0.3	1	1	1	3	0	0
8.5	25	163	82	82	58	139	58	120	0.4	1	1	1	1	1	0	0
9.0	44	108	191	52	99	61	66	53	0.7	2	3	1	1	1	0	0
9.5	62	199	280	59	78	53	60	36	1	6	5	2	1	1	0	0
10.0	125	496	556	108	109	84	51	24	2	20	11	4	2	3	0	0
10.5	0	0	0	0	0	0	–	–	0	–	0	0	0	0	–	–

the medium and nature of a buffer solution. It was found that dithiooxamidated polysiloxane recovers Cu(II), Ni(II), and Co(II) ions mostly from the ammonia buffer solution; an acid medium is the optimal for extraction of Pd(II) ions; and Ag(I) ions are predominantly sorbed from ammonia and ammonia–acetate buffer solutions in the whole range of pH values.

(2) The selectivity coefficients were calculated for Ag(I) and Pd(II) ions. It was demonstrated that these ions can be selectively separated from accompanying Cu(II), Ni(II), and Co(II) on dithiooxamidated polysiloxanes.

ACKNOWLEDGMENTS

REFERENCES

1. Zav'yalov, V.S., *Ekol. Prom-st. Ross.*, 2006, no. 8, pp. 7–9.

2. Valinurova, E.R., Kadyrova, A.D., Sharafieva, L.R., and Kudasheva, F.Kh., *Russ. J. Appl. Chem.,* 2008, vol. 81, no. 11, pp. 1939–1941.

3. Mustafa, S. and Nilgun, D.E., *J. Hazard. Mater.*, 2006, vol. 137, pp. 1035–1041.

4. Sandell, E.B. and Onishi, H., *Photometric Determination of Traces of Metals, General Aspects,* New York: John Wiley & Sons, Inc., 1978, 4th ed., vol. 3.

5. Saha, M.B. and Chakraburtty, A.K., *J. Indian Chem. Soc.*, 1983, vol. 60, pp. 281–282.

6. Abdullin, I.F., Turova, E.N., and Budnikov, G.K., *J. Anal. Chem.*, 2000, vol. 55, no. 6, pp. 567–569.

7. Saha, M.B. and Chakraburtty, A.K., *J. Indian Chem*. Soc., 1983, vol. 60, pp. 176–177.

8. Guibal, E., Von Offenberg Sweeney, N., Vincent, T., and Tobin, J.M., *React. Funct. Polym.*, 2002, vol. 50, no. 2, pp. 149–163.

9. Dutta, S. and Das, A.K., *J. Appl. Polym. Sci.*, 2007, vol. 103, pp. 2281–2285.

10. Chanda, M. and Rempel, G.L., *J. Appl. Polym. Sci.*, 1989, vol. 27, no. 10, pp. 3237–3250.

11. Ibrahim, D., Ibrahim, T., Remziye, G., and Recep, Z., *Asian J. Chem.*, 2009, vol. 21, no. 1, pp. 165–175.

12. Mucoz, J., Gallego, M., and Valcórcel, M., *J. Anal. At. Spectrom.*, 2006, vol. 21, no. 12, pp. 1396–1402.

13. Jorgetto, A.O., Silva, R.I.V., Longo, M.M., et al., *Appl. Surf. Sci.*, 2013, vol. 264, pp. 368–374.

14. Schilling, T., Schramel, P., Michalke, B., and Knapp, G., *Mikrochim. Acta*, 1994, vol. 116, nos. 1–3, pp. 83–90.

15. Kravchenko, O.V., Yatsimirskii, K.B., Belyakova, L.A., et al., *Theor. Exp. Chem.*, 1998, vol. 34, no. 6, pp. 338–342.

16. Polonskaya, I.N. and Belyakova, L.A., *Ukr. Khim. Zh.*, 1995, vol. 61, no. 11, pp. 26–30.

17. Stremilova, N.N., Viktorovskii, I.V., and Zigel', V.V., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 1, pp. 19–23.

18. *Modifitsirovannye kremnezemy v sorbtsii, katalize i khromatografii* (Modified Silicas in Sorption, Catalysis, and Chromatography), Lisichkin, G.V., Ed., Moscow: Khimiya, 1986.

19. Kudryavtsev, G.V., Lisichkin, G.V., and Ivanov, V.M., *Zh. Anal Khim.,* 1983, vol. 38, no. 1, pp. 22–31.

20. Savvin, S.B., Dedkova, V.P., and Shvoeva, O.P., *Russ. Chem. Rev.*, 2000, vol. 69, no. 3, pp. 187–200.

21. Zolotov, Yu.A., Tsysin, G.I., Morosanova, E.I., and Dmitrienko, S.G., *Russ. Chem. Rev.*, 2005, vol. 74, no. 1, pp. 37–60.

22. Puzyrev, I.S., Kholmogorova, A.S., Neudachina, L.K., et al., *Russ. J. Appl. Chem.*, 2014, vol. 87, no. 6, pp. 715–719.

23. Myasoedova, G.V. and Savvin, S.B., *Khelatoobrazuyushchie sorbenty* (Chelate-Forming Sorbents), Moscow: Nauka, 1984.

24. Saprykin, A.I. and Shelpakova, I.R., *Zh. Anal. Khim.*, 1972, vol. 27, no. 6, pp. 1207–1208.

25. Rieman., W. and Walton, H.F., *Ion Exchange in Analytical Chemistry*, Oxford: Pergamon, 1970.

26. Pestov, A.V., Petrova, Yu.S., Bukharova, A.V., et al., *Russ. J. Appl. Chem.*, 2013, vol. 86, no. 2, pp. 269–272.

27. Lakiza, N.V., Neudachina, L.K., Yatluk, Yu.G., et al., *Anal. Kontrol.*, 2005, vol. 9, no. 4, pp. 391–398.

28. Neudachina, L.K. and Lakiza, N.V., *J. Inorg. Chem.*, 2014, vol. 59, no. 6, pp. 632–636.

29. Semikolenov, V.A., *Russ. Chem. Rev.*, 1992, vol. 61, no. 2, pp. 168–174.

30. Kolling, O.W., *Dithiooxamide as an Analytical Reagent,* Kansas State College of Agriculture and Applied Science, 1958.

31. Burger, K., Szanto-Horvath, G., and Papp-Molnar, E., *ACHUDC, Acta Chim. Hung.*, 1972, vol. 71, no. 2, pp. 127–136.

32. *Ion Exchangers in Analytical Chemistry. Their Properties and Use in Inorganic Chemistry*, Marhol, M., Ed., Elsevier Science & Technology, 1982.