

Sorption Preconcentration of Cadmium and Lead Ions as Complexes with Unithiol on a Silica Surface Modified by Quaternary Ammonium Salt Groups

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Abstract—A method of the preconcentration of cadmium and lead as complexes with 2,3-dimercaptopropane-1-sulfonic acid (Unithiol) on a silica surface with the immobilized quaternary ammonium salt groups in the dynamic mode has been developed. The conditions of preconcentration (pH, flow rate and volume of solution) and the subsequent elution of cadmium and lead by a nitric acid solution have been optimized. The proposed method allows the separation of heavy metals from the cationic matrix (Ca^{2+} , Mg^{2+} , Na^+ , K^+) with the preconcentration coefficient equal to 100. The limits of detection for cadmium and lead by flame atomic-absorption spectrometry are 0.3 and 2 $\mu\text{g/L}$, respectively.

Keywords: Unithiol, flame atomic-absorption spectrometry, preconcentration, chemically modified silica gels, quaternary ammonium salt

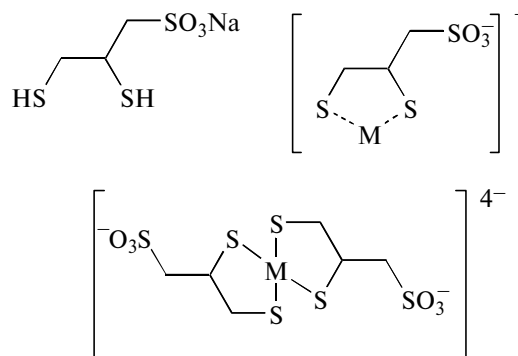
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INTRODUCTION

It is known that cadmium and lead are toxic elements that have detrimental effect on the environment and human health. In particular, compounds of Cd(II) and Pb(II) cause gastric diseases and diseases of the nervous system and are mutagens [1]. Therefore, it is necessary to control the content of these metals in natural and waste waters, food, and technological objects. The maximum permissible concentrations (MPC) for Cd(II) and Pb(II) in the natural waters are 1 and 30 $\mu\text{g/L}$, respectively [2]. The determination of these elements in natural waters at the MPC level and lower requires the use of highly sensitive methods of analysis or sample preconcentration. The method of the sorption preconcentration allows the extraction of the analyzed elements from the large sample volume and their separation from matrix components, thus enhancing the sensitivity and selectivity of analysis [3]. Of promise is the use of chemically modified silica gels, which combine the chemical selectivity of organic reagents with the good dynamic and mechanical characteristics of porous inorganic supports as a phase for the sorption preconcentration [3–5].

One of the simplest organic reagents that forms stable complexes with Cd(II) and Pb(II) (as well as with other heavy metals) is sodium 2,3-dimercaptopropane-1-sulfonate (Unithiol, UT) synthesized in 1950s as an antidote for heavy metal poisoning [6]. It should be noted that the regular cationic components of a matrix, such as Ca^{2+} , Mg^{2+} , Al^{3+} , Na^+ , and K^+ , do not form complexes with UT [7]. The sulfo-group of

Unithiol is strongly acidic ($\text{p}K_1 < 1$), and the thiol groups are weakly acidic ($\text{p}K_2 = 8.6$; $\text{p}K_3 = 10.6$) [8]. In acidic media, unithiol predominantly forms with Cd(II) and Pb(II) complexes of the composition 1 : 1, and in a neutral and weakly basic media, 1 : 2 (Scheme 1), with the stability constants determined by pH-potentiometry, $\log\beta_1[\text{Cd}(\text{UT})] = 16.2$; $\log\beta_2[\text{Cd}(\text{UT})_2] = 25.3$; $\log\beta_1[\text{Pb}(\text{UT})] = 16.4$; $\log\beta_2[\text{Pb}(\text{UT})_2] = 22.2$ [9, 10].



Scheme 1.

Thus, Unithiol complexes of Cd(II) and Pb(II) in neutral and weakly basic media have high negative charge, which should facilitate their ion-exchange adsorption.

The aim of the present work was the sorption preconcentration of Cd(II) and Pb(II) complexes with unithiol on silica with immobilized trimethylammonium bromide ($\text{SiO}_2\text{-N}(\text{CH}_3)_3\text{Br}^-$) groups, their sub-

sequent acidic elution and determination by flame atomic-absorption spectrometry.

EXPERIMENTAL

A laboratory ion meter I-160M Antech (Belarus) with a combined semi-microelectrode ESK-10614, a peristaltic pump LAB-NP-1-20M (Russia), an atomic-absorption spectrophotometer AAS-1N (Carl Zeiss Jena, Germany) equipped with an acetylene burner and a set of spectral lamps were used in this work. The conditions of atomic-absorption determination of metals are presented in Table 1.

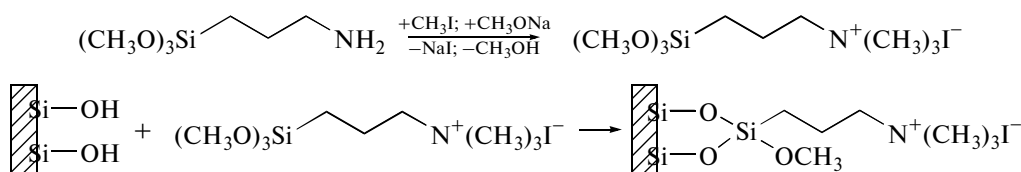
Unithiol, potassium chloride, potassium bromide, sodium nitrate, potassium nitrate, potassium sulfate, sodium acetate, potassium hydrogen phosphate, ferric chloride, calcium chloride, and also sodium hydroxide, conc. nitric acid, hydrochloric acid, and acetic acid of analytical grade were used without additional purification. Acetonitrile was dehydrated by distillation over calcium hydride according to [11]. The accurate concentration of the unithiol solution was found by iodometric titration [8]. Stock solutions of cadmium(II) and lead(II) were prepared by dissolving nitrates of corresponding metals in distilled water with the subsequent determination of accurate concentration by complexometric titration [12]. Solutions with

Table 1. Conditions of atomic-absorption determination of metals in the acetylene–air flame

Metal	Cd(II)	Pb(II)
Wavelength, nm	228.8	217.0
Spectral slit width, nm	0.5	0.2
Lamp current, mA	4.0	8.0
Acetylene flow, L/min	0.5	0.5
Air flow, L/min	4.0	4.0

the concentration less than 1 µg/mL were prepared in the day of use by the dilution of stock solutions. The solutions of cadmium and lead for the calibration of atomic-absorption spectrophotometer were prepared by the dilution of the corresponding State Standard Sample RM-23 (Bogatsky Physicochemical Institute, National Academy of Sciences of Ukraine).

The modification of silica with anion-exchange groups was performed according to the previously proposed method for the modification of porous silicon [13]. The starting organosilicon compound trimethyl-(3-trimethoxysilylpropyl)ammonium iodide (TMAI) was obtained from aminopropyltrimethoxysilane by the Hoffman reaction (Scheme 2).



Scheme 2.

Silica (Silica gel 60, Merck) with a particles size of 0.063–0.2 mm, pore volume 0.84 cm³/g, surface area 480–540 m²/g was used. Weighed 10 g of the silica gel were calcined for 8 h at 450°C in air and mixed with 10 mmol of TMAI in 50 mL of acetonitrile. The reaction mixture was heated in an oil bath for 15 h at 80°C under argon, then silica was filtered and washed with acetonitrile in a Soxhlet apparatus. To convert SiO₂-N(CH₃)₃⁺I⁻ into the bromide form, it was washed with a saturated solution of potassium bromide, then with water to a negative reaction for halide ions, and after that dried at 120°C in air.

The concentration of anion-exchange groups in SiO₂-N(CH₃)₃⁺Br⁻ was determined by argentometric titration with the potentiometric indication of the equivalence point, which was 282 µmol/g.

The pH dependence of sorption of the metal ions on SiO₂-N(CH₃)₃⁺Br⁻ and the solution flow rate were studied in the dynamic mode on a glass column with the diameter 0.5 cm filled with 0.400 g of the sorbent (the sorbent layer height was 3 cm). The solutions were

passed through the column using a peristaltic pump. In the study of the conditions of the sorption of the complexes, 50 mL of a solution containing 8 × 10⁻⁵ M of a metal salt and 8 × 10⁻⁴ M of Unithiol (ratio SiO₂-N(CH₃)₃⁺Br⁻ : UT : metal was 28 : 10 : 1) were passed through the column. The concentration of metal ions in the solutions passed through the column was determined by atomic-absorption spectrometry, recovery (*R*) was calculated according to the formula:

$$R, \% = \frac{(c - [c]) \times 100}{c},$$

where *c* is the concentration of metal ion in the solution before sorption, M; and [*c*] is the equilibrium concentration of metal ion after sorption, M.

The desorption of metals from the sorbent surface was studied as a function of concentration and eluent (5 mL of nitric acid) flow rate. The desorption of metal from the surface was calculated according to the formula:

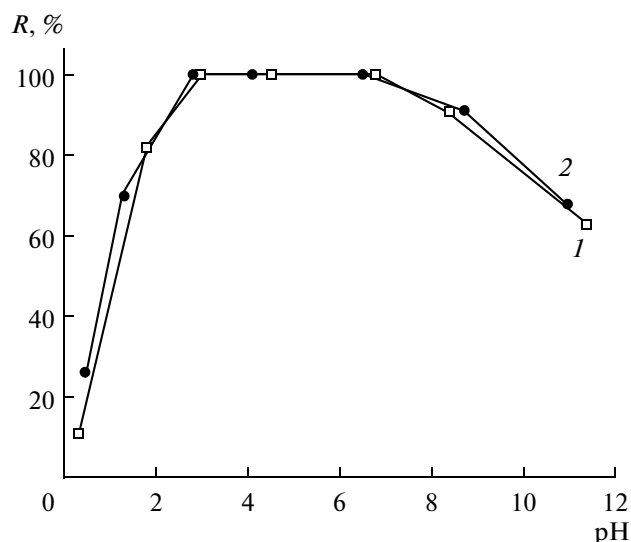


Fig. 1. The pH dependence of the recovery of Unithiol complexes of (1) Cd and (2) Pb at the solution flow rate 2 mL/min.

$$R_{\text{desorp}}, \% = \frac{cV \times 100}{v},$$

where c is the concentration of a metal ion passed into the solution, M; v is the amount of absorbed metal, mol; and V is the volume of solution, L.

The dynamic volume capacity (DVC) before the breakthrough and the total dynamic volume capacity (TDVC) were determined by passing solutions with pH 5, containing 8×10^{-5} M of a metal salt and 8×10^{-4} M of Unithiol, at a flow rate of 1.5 mL/min. The 10-mL portions of the eluted solution were collected and the concentration of metal ions was determined in the eluates by atomic-absorption spectrometry (AAS). The DVC was determined as the sum of the amounts of metal ions adsorbed by the adsorbent prior to their concentration at the column outlet will exceed 5% of the inlet concentration. TDVC corresponded to the amount of metal ions bound by the sorbent at the time when their concentration in the eluate became equal to the concentration in solution prior to passing through the adsorbent.

To determine the maximum preconcentration coefficient for metal ions, samples of the volume from 50 mL to 1 L, containing 2×10^{-7} mol of a metal salt and 2×10^{-6} mol of Unithiol, were passed at a flow rate of 1.5 mL/min and pH 5. Then desorption of cadmium and lead was conducted with 5 mL of 0.1 M nitric acid, and their concentrations were determined by AAS.

To study the interference of the components of natural waters, they were added to solutions containing 2.8×10^{-5} M of a metal salt and 2.8×10^{-4} M of Unithiol. Twenty five milliliters of such solution were passed through the column with the sorbent, eluted

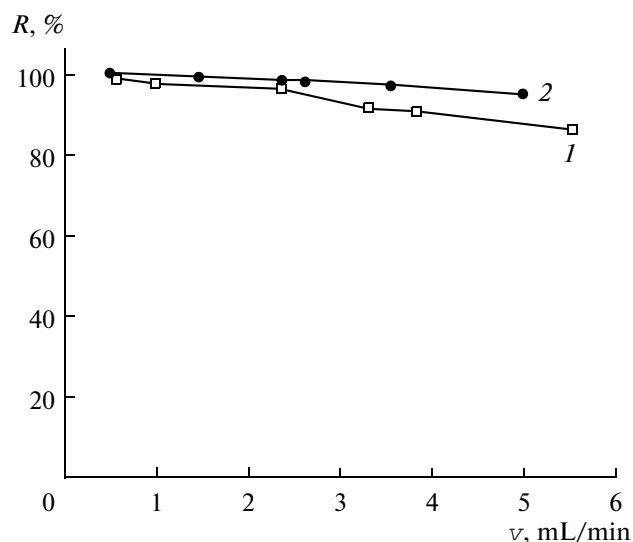


Fig. 2. The dependence of the recovery of Unithiol complexes of (1) Cd and (2) Pb on the solution flow rate through the column at pH 5.

with 5 mL of 0.1 M nitric acid, and metal concentration was determined by AAS.

RESULTS AND DISCUSSION

The dependences of the recovery of cadmium and lead on pH are presented in Fig. 1. In the pH range 3.5–7, lead and cadmium are virtually completely extracted by the sorbent, but in strongly acidic and strongly basic media, their recovery significantly decreases. Probably, this is associated with the decomposition of Unithiol complexes of lead and cadmium in the acidic medium because of the protonation of the thiol groups of the ligand, and with the abstraction of immobilized surface groups of the sorbent; and also with the decomposition of Unithiol complexes through the formation of metal hydroxides in the basic medium. Therefore, pH value 5.0 ± 0.5 may be considered optimal for the extraction of cadmium and lead; the subsequent experiments were performed at this pH value.

Another parameter that determines the efficiency of extraction of metal ions by the sorbent under dynamic conditions is the flow rate of sample loading to the column. The dependences of the recovery of metal ions on this parameter are presented in Fig. 2. The quantitative extraction of lead ($R > 95\%$) occurs at the sample loading flow rate less than 4 mL/min, and of cadmium, less than 2.4 mL/min; therefore, in the following experiments the solution flow rate was 2 mL/min for lead and 1.5 mL/min for cadmium. The breakthrough of metal ions at high flow rates is, probably, associated with the limited diffusion rate of the solution into the sorbent particles. However, carrying out the experiment with the above loading flow rates

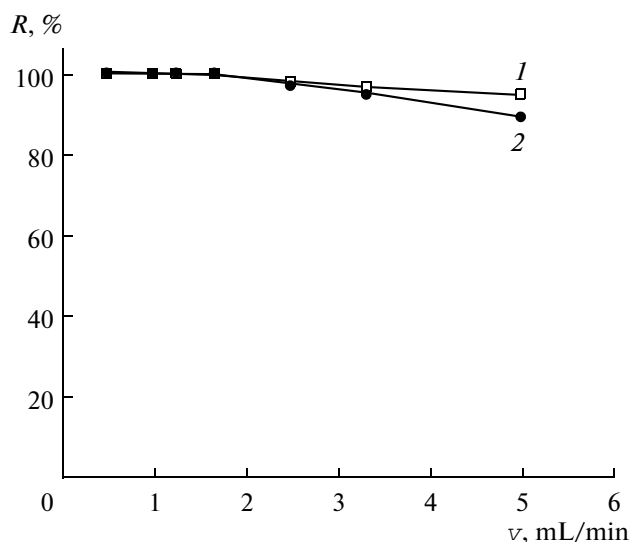


Fig. 3. The dependence of the desorption rate of Unithiol complexes of (1) Cd and (2) Pb on the eluent (0.1 M solution of nitric acid) flow rate.

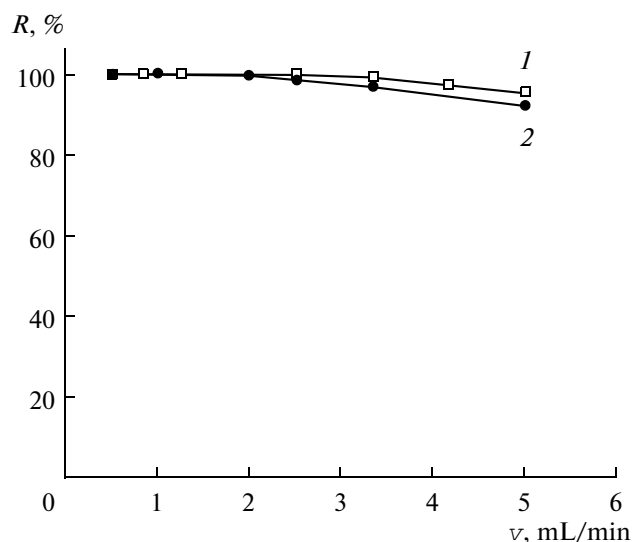


Fig. 4. The dependences of the desorption rate of Unithiol complexes of (1) Cd and (2) Pb on the eluent (1 M solution of nitric acid) flow rate.

allows the achievement of sufficiently high values of DVC before the breakthrough, 2.1 mg/g (10 $\mu\text{mol/g}$) for lead and 1.3 mg/g (12 $\mu\text{mol/g}$) for cadmium, which indicates the strong retention of metal complexes by the sorbent under these conditions. Here with the values of TDVC were 3.3 mg/g (16 $\mu\text{mol/g}$) for lead and 2.7 mg/g (24 $\mu\text{mol/g}$) for cadmium, which is correspondingly 17 and 12 times less than the concentration of ion-exchange groups of the sorbent (282 $\mu\text{mol/g}$). Probably, upon the conditions of the experiment, free Unithiol present in the solution in a tenfold excess compared to the metal ions is strongly adsorbed by the ion-exchange groups of the sorbent and is not displaced by the complex ions. The impurities present in Unithiol, for example, disulfide compounds formed upon its oxidation, may have identical properties.

Metal complexes with Unithiol were eluted from the sorbent with 5 mL of 0.1 and 1 M solutions of nitric acid, the plots of the dependences of the rate of metal desorption on the eluent flow rate are presented in Figs. 3 and 4. It can be seen that both eluents quantitatively desorb cadmium and lead at the flow rate lower than 3 mL/min. From here on desorption was performed with a 0.1 M nitric acid solution at a flow rate of 1.5 mL/min.

The plots of the recovery of metal ions vs. sample volume are presented in Fig. 5. The quantitative extraction of the metals ($R > 95\%$) can be performed from a sample of the volume not larger than 500 mL; consequently the sample may be concentrated 100-fold.

To assess the interfering effect of extraneous impurities, model solutions were prepared that represented

the average concentrations of the macrocomponents of natural waters [14]. To these solutions a constant amount of Pb(II) and Cd(II) was added, and their sorption–desorption was conducted under the previously determined optimal conditions. In Table 2 the typical concentration ranges of the macrocomponents in natural waters and their limiting concentration values at which the recovery of Pb(II) and Cd(II) is 95–100% are presented. At high concentrations of the

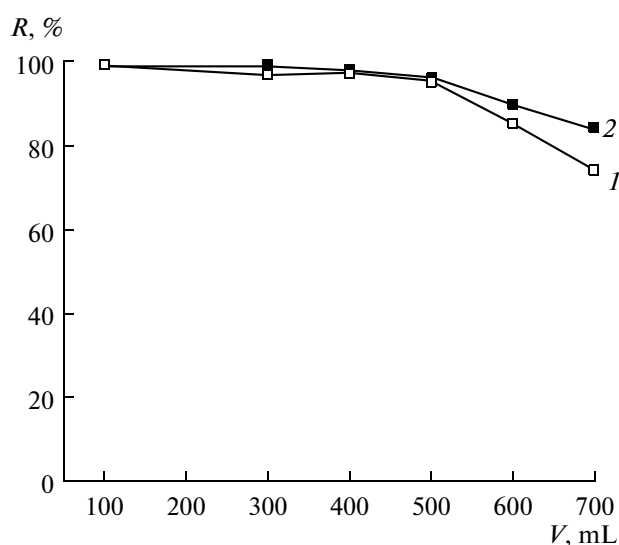


Fig. 5. The dependence of the recovery of Unithiol complexes of (1) Cd and (2) Pb on the volume of solution containing 2×10^{-7} mol of a metal salt and 2×10^{-6} mol of Unithiol.

Table 2. Influence of water macrocomponents on the determination of lead and cadmium

Matrix component	Concentration in natural waters, mg/L [14]	Does not interfere with the determination, mg/L
Na ⁺ + K ⁺	1–75	2000
Ca ²⁺	10–120	2000
Fe ³⁺	0.5–2	5
HPO ₄ ²⁻	0.05–5	500
SO ₄ ²⁻	12–120	300
Cl ⁻	3–100	2000

Table 3. Results of analysis of tap water (City of Kyiv) by the sorption–atomic-absorption method ($n = 3$, $P = 0.95$)

Element	c , µg/L	
	Added	Found
Pb(II)	0	0*
Pb(II)	50	48 ± 9
Cd(II)	0	0*
Cd(II)	2	1.8 ± 0.5

* Lower than the limit of detection.

macrocomponent, the recovery of at least one of the metals became less than 95%. It can be seen that the main macrocomponents do not interfere with the determination of cadmium and lead. The influence of

iron(III) is probably associated with its ability to oxidize Unithiol and form complexes with it. Subsequently the interference of iron was eliminated by adding excess Unithiol.

Based on the study performed, a sorption–atomic-absorption method of Pb(II) and Cd(II) determination in surface waters was proposed. The evaluation of the performance characteristics of the method was performed according to [15]. At the sample volume 500 mL, the limits of detection of Pb(II) and Cd(II) calculated according to [16] are 2 and 0.3 µg/L, respectively. The reproducibility of the results (expressed as the relative standard deviation) of determining Pb(II) and Cd(II) at the MPC level 7.5 and 10%, respectively. The results of analysis of tap water of the city of Kyiv are presented in Table 3. It can be seen that the method is characterized by an acceptable accuracy and precision.

The comparison of the characteristics of the developed method for Pb(II) and Cd(II) determination with the published analogues (methods of concentration of the same elements on silica gels with the aim of subsequent analysis by AAS were considered) demonstrates, that the proposed method possesses the concentration coefficient and sorption capacity as good as the analogues methods (Table 4). Herein the time of analysis by the proposed method is shorter or comparable with the results of most of the methods with high concentration coefficients. The proposed method is less labor-intensive, and the modified sorbent is easily available. In addition, unlike most of the methods proposed in the literature, the current method may be

Table 4. Analytical characteristics of methods of sorption preconcentration of Pb(II) and Cd(II) on the surface of chemically modified silica gels

Modifier	Analytes	Sorption capacity, µmol/g	S_k	Time of analysis, h	Literature
Trimethyl-(3-trimethoxysilylpropyl)ammonium bromide	Pb(II)–Unithiol	16	100	2	Present work
	Cd(II)–Unithiol	24	100	2	
Methyl tricapryl ammonium chloride	Cd(II)	20	75	2	[17]
4-Amino-2-mercaptopyrimidine	Pb(II)	2.9	7.2	0.2	[18]
1-Methyl-3-butylimidazole bromide	Pb(II)	–	185	10	[19]
Trioxybenzoic acid	Pb(II)	60	200	8	[20]
	Cd(II)	53	200		
Amido-triaminoantraquinone	Pb(II)	500	100	0.3	[21]
	Cd(II)	70			
8-Hydroxyquinoline	Pb(II)	100	150	20	[22]
	Cd(II)	70	150		
5,5'-Dithiobis(2-nitrobenzoic acid)	Cd(II)	–	150	2	[23]

S_k is preconcentration coefficient;

“–” not specified.

extended to the determination of other heavy metals forming stable complexes with Unithiol.

REFERENCES

1. Ershov, Yu.A. and Pleteneva, T.V., *Mekhanizmy toksicheskogo deistviya neorganicheskikh soedinenii* (Mechanism of Toxic Effects of Inorganic Substances), Moscow: Meditsina, 1989.
2. Fomin, G.S., *Voda. Kontrol' khimicheskoi, bakterial'noi i radiatsionnoi bezopasnosti po mezhdunarodnym standartam. Entsiklopedicheskii spravochnik* (Water: Monitoring of Chemical, Microbial, and Radiation Safety According to International Standards. Encyclopedic Handbook), Moscow: Protektor, 2000, 3rd ed.
3. Camel, V., *Spectrochim. Acta B*, 2003, vol. 58, p. 1177.
4. Lisichkin, G.V., Fadeev, A.Yu., Serdan, A.A., et al., *Khimiya privitykh poverkhnostnykh soedinenii* (Chemistry of Immobilized Surface Substances), Moscow: Fizmatlit, 2003.
5. Zaitsev, V.N., *Kompleksoobrazuyushchie kremnezemy: sintez, stroenie privitogo sloya i khimiya poverkhnosti* (Complexation Silica: Synthesis, Structure of Immobilized Layer, and Surface Chemistry), Kharkov: Folio, 1997.
6. Petrun'kin, V.E., *Ukr. Khim. Zh.*, 1956, vol. 22, no. 5, p. 603.
7. Ryabushko, O.P., *Cand. Sci. (Chem.) Dissertation*, Kiev: Kiev Gos. Univ., 1967.
8. Pilipenko, A.T. and Ryabushko, O.P., *Ukr. Khim. Zh.*, 1962, vol. 28, no. 8, p. 955.
9. Ryabushko, O.P., *Ukr. Khim. Zh.*, 1968, vol. 34, no. 12, p. 1299.
10. Pilipenko, A.T., Ryabushko, O.P., and Makarenko, T.K., *Ukr. Khim. Zh.*, 1968, vol. 34, no. 8, p. 823.
11. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, Wiley, 1972.
12. Schwarzenbach, G. and Flaschka, H.A., *Complexometric Titration*, Methuen, 1969.
13. Mery, E., Alekseev, S.A., Zaitsev, V.N., and Barbier, D., *Sens. Actuators B*, 2007, vol. 126, no. 1, p. 120.
14. Linnik, P.N. and Nabivanets, B.I., *Formy migratsii metallov v poverkhnostnykh vodakh* (Ways of Metal Migration in Surface Waters), Leningrad: Gidrometeoizdat, 1986.
15. *The Fitness for Purpose of Analytical Methods*, 1998, ISBN 0-948926-12-0.
16. *GOST (State Standard) ISO 11843-3-2005: Statistical Methods. Capability of Discovery. Methodology for Determination of a Critical Value of Respond without Use of Calibration Data*, 2005.
17. Akatsuka, K., Yoshida, Y., Nobuyama, N., Hoshi, S., Nakamura, S., and Kato, T., *Anal. Sci.*, 1998, vol. 14, no. 3, p. 529.
18. Ferreira, G., Renata, L.C., Castro, S.D., Padilha, P.M., and Castro, G.R., *Clean Technol. Environ. Policy*, 2011, vol. 13, no. 3, p. 397.
19. Ayata, S., Bozkurta, S.S., and Ocakoglu, K., *Talanta*, 2011, vol. 84, no. 1, p. 212.
20. Xie, F., Lin, X., Wu, X., and Xie, Z., *Talanta*, 2008, vol. 74, no. 4, p. 836.
21. Ngeontae, W., Aeungmaitrepirom, W., and Tuntulani, T., *Talanta*, 2007, vol. 71, no. 3, p. 1075.
22. Goswami, A., Singh, A.K., and Venkataramani, B., *Talanta*, 2003, vol. 60, no. 6, p. 1141.
23. Zolfonouna, E., Rouhollahia, A., and Semnanib, A., *Int. J. Environ. Anal. Chem.*, 2008, vol. 88, no. 5, p. 327.