Cold vapor atomic absorption determination of Mercury in environmental samples after cloud point extraction

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Received: 29 June 2012 / Accepted: 2 September 2012

The possibility to use capric acid and octylamine for mercury (II) preconcentration by the cloud point extraction and later cold vapor atomic absorption spectrometry (AAS) determination was investigated. Under the optimum conditions, preconcentration of 50 ml of sample in the presence of 0.5% non-ionic surfactant Triton X-114, 0.01 mol L^{-1} capric acid and octylamine permitted the detection of 3 ng L^{-1} mercury. The experimental enrichment factor was 25 (for 50 mL of sample solution, 50 mL/2mL). The relative standard deviation for 10 replicates containing 50 ng $L^{-1}$of mercury was 5.8%. The proposed method was successfully applied to determination of mercury in some river of Ukraine and in sediments of south-west seacoast of Crimea.

В.А. ДОРОЩУК, М.С. МИГЛОВЕЦ, А.Н. ГОРБАЧЕВСКИЙ. *АТОМНО-АБСОРБЦИОННОЕ ОПРЕДЕЛЕНИЕ РТУТИ В ПРИРОДНЫХ ВОДАХ С ПРЕДВАРИТЕЛЬНЫМ МИЦЕЛЛЯРНО-ЭКСТРАКЦИОННЫМ КОНЦЕНТРИРОВАНИЕМ. Изучена мицеллярная экстракция ртути(II) в присутствии каприновой кислоты и октиламина фазами неионного ПАВ при температуре помутнения. Предложены условия атомно-абсорбционного определения металла в природных водах и донных отложениях с предварительным мицеллярно-экстракционным концентрированием.*

Ключевые слова: неионные ПАВ, мицеллярная экстракция, определение ртути, природные воды

Keywords: non-ionic surfactant; cloud point extraction; Mercury determination; natural waters

Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment [1]. Mercury has a number of effects on humans, that can be simplified into the following main effects: disruption of the nervous system, damage to brain functions, DNA and chromosomal damage, allergic reactions, resulting in skin rashes, tiredness and headaches and negative reproductive effects [2, 3]. Mercury from soils can accumulate in mushrooms. Acidic surface waters can contain significant amounts of mercury. When the pH values are between five and seven, the mercury concentrations in the water will increase due to mobilization of mercury in the ground. Once mercury has reached surface waters or soils microorganisms can convert it to methylmercury, a substance that can be absorbed quickly by most organisms and is known to cause nerve damage. Fish organisms absorb great amounts of mercury from surface waters every day. The mercury compounds can get to the surface waters due to alloying ore, decomposition of water microorganisms that accumulate mercury. Great amount of mercury compounds are received to surface waters from sewage of dye, pesticides and pharmaceutical factories. Other way of getting mercury compounds is from thermal power-stations and coal-mining industry. They throw out in the atmosphere a lot of different compounds including compounds of mercury that get to the surface waters from precipitation. In general, concentration of mercury in natural waters is about several ng/l. Therefore the determination of mercury often requires a method offering low detection limit. Since atomic spectrometric methods are a powerful analytical tool for the determination of trace elements in environmental samples, preconcentration techniques combined with atomic absorption spectrometry (AAS) are still necessary [5].

Several methods for ultra-trace mercury analysis in environmental samples are used including atomic absorption spectrometry with cold vapor, inductively coupled plasma mass spectroscopy [6]. Mercury determination in natural water samples is of a great interest for pollution control. However, mercury is at such a low concentration in this kind of sample that the determination requires a preconcentration step of the analyte before applying the above mentioned techniques [5,6].

Separation and preconcentration based on cloud point extractions (CPE) are becoming an important and practical application surfactants using in analytical chemistry [7-9]. Non-ionic surfactants (NS) dissolves in the water due to the hydrogen

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bonds formation between oxygen atoms of polyoxyethyl chain and water molecules [10]. Heating of aqueous NS solutions until a definite temperature, namely cloud point, results in a destruction of these bonds and a further system separation into phases. As a result two phases are formed. The first one is the surfactant-rich phase, which consists of large hydrated micelles, and the second one is the aqueous solution of NS with the concentration level near critical micelle concentration. The surfactant-rich phase is used for preconcentration [10].

The use of CPE methodology for extraction and/or preconcentration of metal ions, organic compounds, biological and clinical samples, and environmental clean-up procedures has been reported [11-13]. The main advantage of the cloud point extraction is the achievement of high values of the concentrating factor using small volume of samples for analysis in comparison with traditional extraction by organic solvents. Cloud point extraction also provide a decrease of the relative detection limit value due to absolute preconcentration and an efficient modification of the analyte by a non-ionic surfactant. The simplicity of cloud point extraction combination with spectral, atomic absorption, chromatographic and electrochemical analysis allows the using of extraction with surfactant-rich phases for elaborating of high-sensitive and convenient hyphenated analytical methods [14-19]. Especially outstanding results were obtained at the cloud point separation of biomaterials including proteins, peptides, hormones and viruses [7].

In the present work we report the results obtained in a study of the cloud point preconcentration of mercury (II), after the formation of a complex with capric acid and octylamine, and following analysis by cold vapor atomic absorption spectroscopy using Triton X-114 as surfactant. The proposed method is also applied to the determination of mercury in water samples.

EXPERIMENTAL

Apparatus

The distribution of mercury between the aqueous and surfactant-rich phases was controlled by atomic absorption spectroscopy. We used a cold vapor atomic absorption mercury analyzer Julia-2 (Start Ltd., Russia) with DB-4 lamp. Detection of mercury was performed at 285 nm. The operating conditions were those recommended by the manufacturer. As reducing agent $SnCl_2$ was used.The acidity of the solutions was controlled by pH meter pH-340. A Universal 320 (Labor-Technik) centrifuge and GFL 1023 (Labor-Technik) water bath were used throughout the work.

Reagents and solutions

The non-ionic surfactant Triton X-114 (TX-114) was produced by Merck and was used without previously purification. The choice of Triton X-114 is related to its quicker phase formation than other non-ionic surfactants under heating as well as high viscosity and the compactness of the surfactant-rich phases. The solutions of Triton X-114 were prepared by dissolving the exact mass of the substance in the distilled water. The standard sample MSO 0345:2002 with mercury concentration 0.1 mg ml^{-1} (Ukrainian State Standard Sample of Metal Solution) for preparation of the mercury solutions was used. Working solutions were obtained by appropriate dilution of the stock standard solutions. Capric acid and octylamine from the «REACHEM» Company were of analytical reagent grade. Capric acid was additionally purified by re-crystallization from the ethanol - acetone mixture. The acid and amines solutions were prepared by dissolving the definite mass of reagents in the aqueous solutions of Triton X-114. Nitric acid (Merck), methanol (Merck) and potassium hydroxide (Merck) were used.

General Procedure for Cloud Point Extraction

Aqueous solutions of Triton X-114 containing all required components in calibrated 10 ml volumetric flasks were placed into water bath. The temperature of the solutions was controlled by the thermometers dived both in the cylinders and in the bath. Heating was performed at the rate 0.5°C/min. The cloud point was registered by the appearance of characteristic opalescence. The solution was kept at 40 °C for 10 min for equilibration and then centrifuged for 5 min at 3500 rpm. After phase separation and cooling the solutions to room temperature, the water phase was decanted and the surfactant-rich phase was diluted with nitric acid and methanol to required volume before determination.

Preparation of Water Samples

The probes of natural water were preserved by adding of nitric acid. Water samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter. Before mercury determination the water was treated with ultrasound energy to destruction of mercury complexes with natural ligands, such as fulvic and guminic acids. An ultrasonic bath Ultrasons (Selecta) was used for sonication of sample. The water solution was acidified to pH 1.0 using 65 % HNO_3 and exposed to ultrasound at 44 kHz, at an intensity of $\leq$ 10 W cm^{-2} for 3 min.

Procedure for Mercury Determination in Natural Water

0.25 g of Triton X-100 was dissolved in 50 ml of the water sample. Capric acid (86 mg) and octylamine (64.5 mg) were added to the pretreated water and then it was stirred. The solution pH was adjusted to 8.0 using KOH. The solution was kept at 40°C for 10 min for equilibration and then centrifuged for 5 min at 3500 rpm. After phase separation, 1 ml of methanol solution containing 0.1 mol L^{-1} nitric acid

was added to surfactant-rich phase and the cold vapor atomic absorption mercury determination was performed. The final volume of the surfactant-rich phase was 2 ml. The concentration of mercury in the sample was found using a calibration graph.

Procedure for Mercury Determination in Sediments

A 5.0 g sediments were placed into 100 ml glass, followed by the addition of 50 ml of 0.1 mol L^{-1} nitric acid. The mixture was stirred during 30 min. After filtration the mercury was extracted following the procedure described in Section 2.5.

RESULTS AND DISCUSSION

The choice of reagents for cloud point extraction of mercury

Aliphatic and aromatic carboxylic acids were proposed for various metal extractions from aqueous solutions with organic solvents [20]. Such systems are characterized by the large extraction capacitance which has a great importance for analysis of composite multicomponent objects. At the same time advantages of carbon acids are ability to regeneration, absence of toxicity and high boiling temperature.

Despite this adding of aliphatic hydrophobic amines facilitate formation of highly hydrophobic aminocarboxylic complexes. These formations are efficiently extracted to surfactant-rich phase. The mixtures of hydrophobic capric acid and octylamine were proposed for cloud point extraction of a lot of metals before analysis by atomic absorption spectroscopy [21]. Therefore capric acid and octylamine were chosen for the subsequent experiments.

Effect of pH

Cloud point extraction of mercury was performed at different pH-values. The cloud point extraction involves prior formation of a complex with sufficient hydrophobic chelating agent to be extracted into surfactant-rich phase. Extraction recovery depends on the pH at which complex formation is carried out.

The study of the cloud point extraction of mercury with capric acid and octylamine has shown complete metal extraction (R>99%) into the surfactant-rich phase in the pH range 7.0-10.2 (Fig. 1).

Decreasing of the metal extraction efficiency at pH<7.0 is explained by the complex destruction, whereas at pH>10.2 hydrolysis of the metal takes place upon heating of the alkaline solutions. This experiment showed that specific binding and cloud point extraction was maximal at pH 8.0. So, all subsequent experiments were carried out at pH 8.0.

Effect of reagents concentrations

Fig. 2. shows the effect of capric acid concentration on the mercury cloud point extraction at constant octylamine concentration (C_{OctAm} = 0.01 mol L^{-1}). The concentration of capric acid tested in range from 0.001 to 0.018 mol L^{-1}.

As capric acid concentration increase from 0.001 to 0.008 mol L^{-1}, the extraction recovery of mercury increases and the maximum values reaches at 0.008 mol L^{-1} capric acid concentration. Therefore, a capric acid excess concentration of 0.01 mol L^{-1} was chosen for other experiments. The extraction recovery of mercury as a function of the octylamine concentration (at C_{Cap} = 0.01 mol L^{-1}) is shown in Fig. 3. The extraction recovery increases towards octylamine concentration to 0.006 mol L^{-1} and reaches >99% extraction efficiency. Therefore, a 0.01 mol L^{-1} octylamine excess concentration was chosen for the subsequent experiments.

The analysis of the dependencies lg D=f(lgC_{Cap}) and lg D=f(lgC_{OctAm}) allows to determine the number of ligands in the extracted complex (D – distribution coefficient of mercury between water and surfactant-rich phases).

The slope of curves on the Fig. 2 and Fig. 3 in lgD=f(lgC) coordinates is nearly ≈2, therefore the unsaturated complex with Hg : Cap : OctAm ratio 1 : 2 : 2 is extracted into the surfactant-rich phase.

Effect of Triton X-114 concentration

It was found that at a Triton X-114 concentration of 0.4 – 1.0 % (w/v), the extraction recovery of mercury into surfactant-rich phase was >99% (Fig. 4). A decrease of the Triton X-114 concentration in the solution somewhat reduces the extraction efficiency of mercury. This can be explained by the insufficient solubilization capacity of dilute Triton X-114 solutions. 0.5 % (w/v) Triton X-114 concentration was chosen in order to achieve a good preconcentration factor.

Interferences

Solutions containing 2 μg L^{-1} of Hg and 80 μg L^{-1} of Ca^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Mo^{4+} and Mn^{2+} for evaluate the effects of other metal ions on the preconcentration procedure were prepared and analyzed. Commonly encountered matrix components such as alkali and alkali-earth elements generally are not extracted into the surfactant-rich phase. The results showed that concomitant ions in these concentrations do not interfere on the determination of mercury by the proposed method.

Calibration and detection limits

The calibration equation obtained after preconcentration and determination of mercury by cloud point extraction of standard solutions under the optimum conditions was $I = (1.10 \pm 1.79) + (1.86 \pm 0.03) \times C_{Hg}(ngL^{-1})$ r^2=0.9991) in the range from 10 ng L^{-1} to 100 ng L^{-1}. The experimental enrichment factor was 25 (for 50 mL of sample solution, 50 mL/2mL). The relative standard deviation for 10 replicates containing 50 ng $L^{-1}$of mercury was 5.8%. The limits of detection (3σ) and quantification (10σ) were 3 ng L^{-1} and 10 ng L^{-1}, respectively.

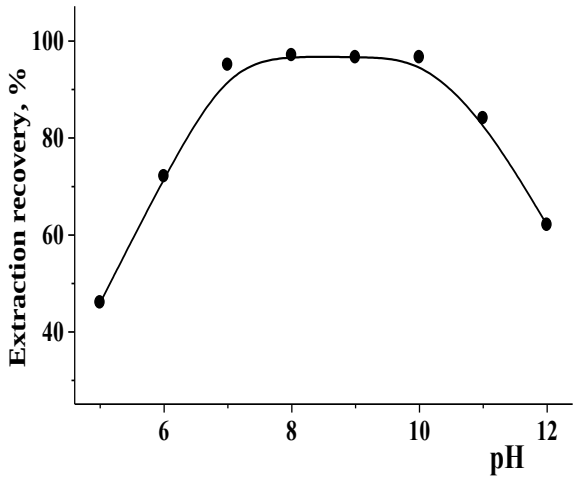

Figure 1. Effect of pH on the extraction recovery of mercury with capric acid and octylamine into surfactant-rich phase.C_{Hg} =2 μg L^{-1},C_{Cap} = 0.01 mol L^{-1}, C_{OctAm} = 0.01 mol L^{-1}, C_{TX-114} = 0.5 % (w/v)

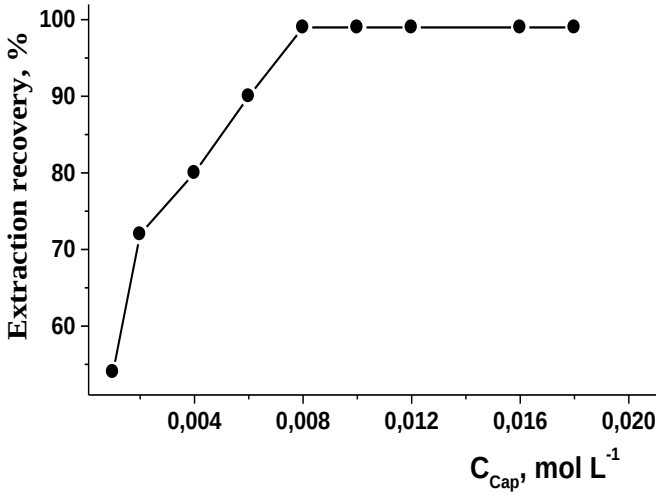

Figure 2. Effect of capric acid concentration on the extraction recovery of mercury into surfactant-rich phase. C_{Hg} = 2 μg L^{-1}, C_{OctAm} = 0.01 mol L^{-1}, pH= 8.0, C_{TX-114} = 0.5 % (w/v).

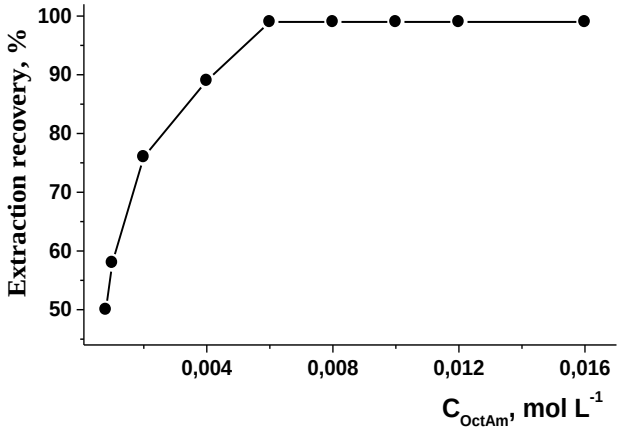

Figure 3. Effect of octylamine concentration on the extraction recovery of mercury into surfactant-rich phase. C_{Hg} = 2 μg L^{-1}, C_{Cap} = 0.01 mol L^{-1}, pH= 8.0, C_{TX-114} = 0.5 % (w/v)

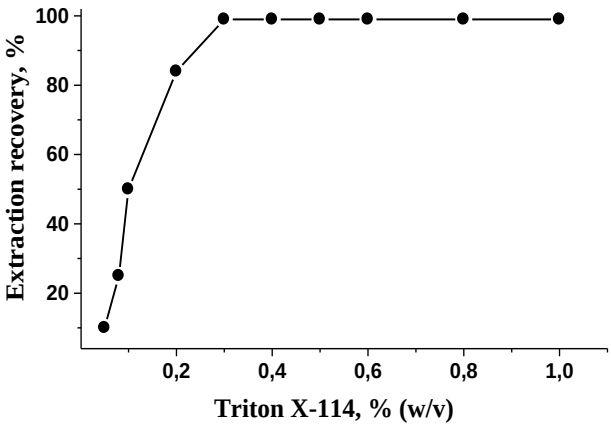

Figure 4. Effect of Triton X-114 concentration on the extraction recovery of mercury with capric acid and octylamine into surfactant-rich phase. C_{Cap}=0.01 mol·L^{-1}, C_{Hg} = 2 μg L^{-1}, C_{OctAm}=0.01 mol L^{-1}, pH= 8.0

Table 1. Determination of the mercury additions in some river waters of Ukraine with the elaborated procedure (n=4, P=0.95)

Samples	Hg (II) added, ng L^{-1}	Hg (II) found, ng L^{-1}	RSD,%
Distilled water	50	51 ± 4	2.3
River Uzh (Zhytomyr region, Ukraine)	50	48 ± 6	5.2
River Teteriv (Zhytomyr, Ukraine)	50	49 ± 3	4.4
River Dnipro (Kyiv, Ukraine)	50	50 ± 2	4.7

Table 2. Determination of the mercury in sediments of south-west seacoast of Crimea, Ukraine (n=4, P=0.95)

Sample number	Mercury found, mg kg^{-1}	RSD, %
1	0.39 ± 0.03	6.8
2	4.8 ± 0.1	1.9
3	0.27 ± 0.01	3.7
4	3.8 ± 0.4	9.3
5	8.5 ± 0.7	7.1

Determination of mercury(II) in natural waters and sediments. On the basis of obtained data the method of cold vapor atomic absorption mercury(II) determination in the natural waters and sediments using cloud point extraction preconcentration with capric acid and octylamine has been elaborated. The procedure was verified by the analysis of standard reference material SRM 1944: informed value - 3.4±0.5 mg kg^{-1}, found value - 3.3±0.2 mg kg^{-1}, RSD 4.7 %. The results of mercury determination in natural waters and sediments are presented in tabl. 1 and 2.

CONCLUSIONS

Cloud point extraction of mercury(II) with capric acid and octylamine into the surfactant-rich phase of non-ionic surfactant Triton X-114 was investigated.

The molar ratio of the extracted complex was determined. The method for cold vapor atomic absorption determination of mercury in the natural waters and sediments using preconcentration by cloud point extraction was elaborated. The sensitivity, metrological characteristics, ecological safety, simplicity and convenience of the suggested procedure excels its analogues based on the extraction with organic solvents. The proposed method was successfully applied for determination of mercury in some rivers of Ukraine and in sediments of south-west seacoast of Crimea.

REFERENCES

1. Clarkson T.W. The toxicology of mercury and its chemical compounds. *Crit. Rev. Toxigology.* 2006, 36, 609-662.
2. Barkay T., Miller S.M., Summens A.O. Bacterial mercury resistance from atoms to ecosystems. *Microbiol. Rev.* 2003, 27, 355-384.
3. Ballaroti N., Gatmaitan Z., Truong A.T. Impaired biliary excretion and whole body elimination of methylmercury in rats with congenital defect in biliary glutathione excretion. *Hepatology.* 1995, 22, 1469-1473.
4. Barregard L., Horvat M., Shutz A. No indication of *in vivo* methylation of inorganic mercury in chloralkali workers. *Environ. Res.* 1994, 67, 160-167.
5. R.-D. Wilken, H Hintelman, Analysis of Mercury – Species in Sediments, NATO ASI Series, Vol. G 23. Metal Sediments in the Environment /Edited/ by J.A.C. Broekaert, S Guser, F. Adams – Berlin Heidelberg: Springer Verlag, 1990.
6. Garrido M., Di Nezio M.S., Lista A.G., Palomeque M., Fernández Band B.S. Cloud-point extraction/preconcentration on-line flow injection method for mercury determination. *Anal. Chim. Acta.* 2004, 502, 173-177.
7. Quina F.H., Hinze W.L. Surfactant-mediated cloud point extractions: an environmentally benign alternative separation approach. *Ind. Eng. Chem. Res.* 1999, 38(11), 4150-4168.
8. Hinze W.L., Pramauro E. A critical review of surfactant-mediated phase separations (cloud point extractions): theory and applications. *CRC Crit. Rev. Anal. Chem.* 1993, 24(2) 133-177.
9. Chang Z., Yan H.T. Cloud point extraction-fluorimetric combined methodology for the determination of trace arfarin based on the sensitization effect of supramolecule. *J. Luminescence.* 2012, 132(2) 811-817.
10. Pramauro E. and Pelezetti E. Surfactants in analytical chemistry. Elsevier, Amsterdam, 1996. P.521.
11. Doroschuk V.O., Lelyushok S.O., Ishchenko V.B., Kulichenko S.A. Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction. *Talanta.* 2004, 64(4), 853-856.
12. Paleologos E.K., Giokas D.L., and Karayannis M.I. Micelle-mediated separation and cloud point extraction. *Trends Anal.Chem.* 2005, 24, 426-436.
13. Zou Y., Li Y., Jia H., Tang H., Zou D., Liu M., Yang Y. Determination of estrogens in human urine by high-performance liquid chromatography/diode array detection with ultrasound-assisted cloud-point extraction. *Anal. Biochem.* 2012, 421(2), 378-384.
14. Bezerra M.A., Nogueira A.N.A., Lemos S.G., Ferreira S.L.C. Multivariate optimization of a procedure for Cr and Co ultratrace determination in vegetal samples using GF AAS after cloud-point extraction. *Intern. J. Environ. Anal. Chem.* 2008, 88(2), 131-140.
15. Beiraghi A., Babaee S. Separation and preconcentration of ultra trace amounts of beryllium in water samples using mixed micelle-mediated extraction and determination by inductively coupled plasma-atomic emission spectrometry. *Anal. Chim. Acta.* 2008, 607, 183-190.
16. Wen X., Deng Q., Ji S., Yang S., Peng L. Design of rapidly synergistic cloud point extraction of ultra-trace lead combined with flame atomic absorption spectrometry determination. *Microchem J.* 2012, 100, 31-35.
17. Doroschuk V.O., Kulichenko S.A., Lelyushok S.O. The influence of substrate charge and molecular structure on interphase transfer in cloud point extraction systems. *J. Colloid Interf. Sci.* 2005, 291(1), 251-255.
18. Fontana A.R., Silva M.F., Martinez L.D., Wuilloud R.G., Altamirano J.C. Determination of polybrominated diphenyl ethers in water and soil samples by cloud point extraction-ultrasound-assisted back-extraction-gas chromatography-mass spectrometry. *J.Chromatogr.A.* 2009, 1216(2), 4339-4346.
19. Fontana A.R., Camargo A.B., Altamirano J.C. Coacervative microextraction ultrasound-assisted back-extraction technique for determination of organophosphates pesticides in honey samples by gas chromatography-mass spectrometry. *J. Chromatogr.A.* 2010, 1217(1), 6334-6341.
20. Charykov A.K., Osipov N.N. *Karbonovye kisloty i karboxilatnye komplexy v khimicheskom analize [Carboxylic Acids and Carboxylates in Chemical Analysis].* Khimiya, Leningrad, 1991. P.240.
21. Kulichenko S.A., Doroschuk V.O., Lelyushok S.A. The cloud point extraction of copper(II) with monocarboxylic acids into non-ionic surfactant phase. *Talanta.* 2003, 59(4), 767-773.