

## EXTRACTION OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS INTO THE *IN SITU* FORMED IONIC LIQUIDS WITH SUBSEQUENT DETERMINATION BY ATOMIC EMISSION SPECTROMETRY WITH MICROWAVE PLASMA

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**Abstract.** Ionic liquids based on quaternary ammonium cations – tetrahexylammonium dioctyl sulfosuccinates (**THADOSS**) and tetrabutylammonium are obtained *in situ* by mixing salts in an aqueous solution – suppliers of the cation and anion, constituting the ionic liquid, and studied for the extraction of heavy metal ions from aqueous solutions. Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) ions are quantitatively extracted in the presence of 4-(2-pyridylazo)resorcinol ( $1 \times 10^{-3}$  M) into the *in situ* formed THADOSS at pH 4.9 in 1 min. The possibility of determining metals by microwave plasma atomic emission spectrometry after extraction into ionic liquids is demonstrated; the detection limits are from 2 to 25  $\mu\text{g/L}$ .

**Keywords:** metal ion extraction, ionic liquids, microwave plasma atomic emission spectrometry

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The unique properties of ionic liquids (**IL**) – low vapor pressure, low flammability and electrical conductivity – have attracted the attention of researchers over the past few decades as an alternative to volatile organic solvents. The structural diversity of IL, due to the combined nature of these compounds and a wide range of cations and anions suitable for the production of low-melting salts, is a distinctive feature of this class of compounds. The problems associated with low biodegradability, biocompatibility, hydrolytic stability, as well as the availability and cost-effectiveness of using classical dialkylimidazolium ions with fluorinated anions are solved by replacing the components of ions, cations and anions with more affordable, environmentally friendly ones, including those with complexing ability. The most common hydrophobic ionic liquids, in addition to dialkylimidazolium, are tetraalkylammonium and tetraalkylphosphonium salts. The longer the length of the alkyl substituents and, consequently, the larger the size and hydrophobicity of the IL cation, the less the nature of the anion affects the hydrolytic stability of IL. Thus, trioctylmethylammonium chlorides (Aliquat 336) and trihexyl(tetradecyl)phosphonium (Cyphos® IL 101) are liquid hydrophobic salts with low solubility in water [1]. Hydrophobic anions are required to produce hydrophobic ionic liquids with cations with short-chain alkyl substituents.

Previously, we obtained hydrophobic ionic liquids based on tetraalkylammonium cations and anions of surfactants (**surfactants**), dihexylsulfosuccinate and

N-lauroylsarcosinate, and studied them for the extraction of organic compounds with various functionalities and metal complexes [1, 2]. The synthesis and some physico-chemical properties of ionic liquids based on quaternary ammonium and phosphonium salts with surfactant anions (alkysulfosuccinates, dodecyl sulfates) are described in the literature [3, 4], some of them have been used in liquid extraction for the separation [5, 6] and preconcentration of metal ions [7]. It is worth noting that IL with surfactant anions are readily available and relatively inexpensive compared to typical fluorinated and complexing IL. Dioctyl sulfosuccinate anion has low toxicity, is a part of pharmaceutical and cosmetic preparations; in addition, it is able to exhibit complexing properties with respect to metal ions [8].

We have previously shown [9] that IL based on tetraalkylammonium cations can be obtained *in situ* by mixing solid salts in an aqueous solution, which are suppliers of the IL cation and anion for the metathesis reaction. *In situ* dispersive microextraction into ionic liquids (**in situ DME**) eliminates the need for preliminary synthesis of the extractant (IL), reduces the consumption of IL, and the dispersion of IL at the time of formation ensures high efficiency and extraction speed.

The determination of heavy metals in water is one of the main tasks of environmental monitoring. Despite the fact that some heavy metals (Co, Cu, Zn, etc.) are

involved in biological processes and play a vital role in the normal functioning of living organisms, their excess can be dangerous for humans, animals and plants. Cd and Pb are among the most dangerous, polluting components that have harmful effects on living organisms. The most toxic metals included in the group of mineral ecotoxicants also include Cu, Co and Ni [10]. In water bodies of fishery importance, the maximum permissible concentrations are as follows (μg/L): 5 for Cd, 10 for Pb, 5 for Cu, 5 for Co, 10 for Ni and 50 for Zn [11]. Heavy metals enter the aquatic environment as a result of natural processes, for example, due to leaching from rocks and groundwater. However, the main contribution to environmental pollution is made by anthropogenic impact. The determination of heavy metals at the required level, especially in samples with a complex matrix or high salt content, is usually carried out by atomic emission and atomic absorption spectrometry, often after preliminary preconcentration and separation. For this purpose, liquid-liquid and solid-phase extraction are most often used, which makes it possible to separate the matrix components before introducing the sample into the spectrometer and lower the detection limits of elements in complex samples [12].

Our previous studies have shown that the group preconcentration of metal ions in extraction systems based on organic salts, including ionic liquids, can be combined with detection by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and nitrogen microwave plasma atomic emission spectrometry (MP-AES) [7, 13, 14]. Sensitive multi-element detection, versatility, safety of nitrogen plasma and low operating costs are the obvious advantages of the NMP-AES method and make it a promising alternative to flame atomic absorption spectroscopy (FAAS) and flame atomic emission spectroscopy. Compared with the ICP-AES, the equipment for MP-AES is more affordable, however, the MP-AES method is characterized by a lower plasma temperature and, as a rule, lower sensitivity; detection limits ( $c_{\min}$ ) for a number of elements in simple matrices are 0.1–33 μg/l [15, 16]. The detection limits of elements can increase by more than an order of magnitude due to non-spectral interference from matrix components in the presence of significant amounts of inorganic acids, salts, or organic substances [17–20]. It shows at least a 2–20-fold increase in the detection limits obtained in 1% nitric acid [19] and seawater [13] for Cd, Ni, Cu and Pb, and a 60-fold increase for Zn compared to  $c_{\min}$  for deionized water [15, 16]. It has recently been shown [13] that extraction preconcentration makes it possible to eliminate the influence of matrix components and increase the sensitivity of the MP-AES method, expanding its application possibilities for samples with a high salt content.

The purpose of this work is to obtain *in situ* IL based on quaternary ammonium cations – tetrahexylammonium dioctylsulfosuccinate (THADOSS) and tetra-

butylammonium dioctylsulfosuccinate (TBADOSS) by simultaneously dissolution of tetraalkylammonium bromides and sodium dioctylsulfosuccinate in water, to study the extraction of Cd(II), Co(II), Cu(II), Ni(II) ions into the formed ILS, Pb(II) and Zn(II), and subsequent determination of metals by MP-AES.

## METHODS AND MATERIALS

**Reagents, solutions, and equipment.** Sodium dioctyl sulfosuccinate (DOSSNa) (98%, Sigma, USA), tetrahexylammonium bromide (THAB) (99%, Sigma, USA), and tetrabutylammonium bromide (TBAB) (99%, Sigma, USA) were used to obtain IL.

Aqueous solutions of metal salts for extraction and for constructing calibration dependences were prepared by diluting standard solutions of metal nitrates of 1.00 g/l (Inorganic Ventures, USA) with deionized water (purified at the Millipore plant, France; resistivity not lower than 18.2 mΩ·cm) with the addition of conc. hydrochloric acid to a final concentration of 0.2 M.

Initial solutions: 0.62 M solution of TBAB, 0.025 M solution of 4-(2-pyridylazo) resorcinol (PAR) (97%, Sigma, USA), solutions of sodium, calcium, and magnesium chlorides (0.1–500 mg/L) were prepared by dissolving their exact weights in deionized water. The working solutions were prepared by diluting the initial ones with deionized water. A model seawater solution was prepared by dissolving precise mixtures of the following salts: 22.0 g NaCl reagent grade (Reakhim, Russia), 9.7 g MgCl<sub>2</sub>·6 H<sub>2</sub>O (Reakhim, Russia), 3.7 g Na<sub>2</sub>SO<sub>4</sub> (Reakhim, Russia), 1.0 g CaCl<sub>2</sub> (Reakhim, Russia), 0.7 g KCl (Reakhim, Russia), 0.2 g NaHCO<sub>3</sub> (99.7%, Panreac, Spain), 0.02 g H<sub>3</sub>BO<sub>3</sub> (>98%, Reakhim, Russia) in 1000 ml of deionized water [21]. All reagents and solvents used in the work of analytical or higher grade. Hydrochloric acid 37% (Panreac, Germany), orthophosphoric acid 85% (Panreac, Germany), acetic acid 99.7% (Panreac, Germany) and sodium hydroxide (98%, Panreac, Germany) were used.

To establish the required pH values of the aqueous phases, 2 and 3.75 M HCl, 0.5 and 5 M NaOH solutions and universal buffer solutions based on a mixture of boric, phosphoric and acetic acids and sodium hydroxide were used. Isopropanol analytical grade (Ruskhim, Russia) was used to dilute the extracts. Paper filters "white ribbon" (ApexLab, Russia) were used for filtration.

The concentration of metals in the aqueous phase after extraction was determined using an Agilent ICP-OES 5100 SVDV, inductively coupled plasma spectrometer in the axial plasma view mode (Agilent Technologies, Australia), the main parameters of the spectrometer are shown in Table 1. The Agilent ICP Expert II software was used. The concentration of metals in the extracts after concentration in THADOSS IL was determined using the Agilent MP-AES 4200 microwave plasma spectrometer (Agilent Technologies, Australia), its

**Table 1.** Parameters of inductively coupled and microwave plasma spectrometers

Parameter	Meaning	
	Agilent ICP-OES 5100 SVDV	Agilent MP-AES 4200
Generator power, kW	1.4	1.4
Plasma-forming flow, l/min	14	
Axial flow, l/min	1.1	
Spray flow, l/min	0.9	0.4 (spray flow, l/min)
Sample feed delay, s	12	35
Pump, rpm	12	7
Delay in stabilization, with	20	10
Replica, reading time, s	20	5
Replicates	2	1
Spectral lines, nm	Cd 226.502; 228.802 Co 228.615; 238.892 Cu 324.754; 327.395 Ni 231.604 Pb 220.353 Zn 213.857	Cd 228.802 Co 345.351 Cu 327.395 Ni 305.082 Pb 283.305 Zn 213.857
Sample feed line configuration	Glass double-pass spray chamber, 5-channel peristaltic pump, glass nebulizer, axial quartz burner (2.4 mm injector diameter), automatic sample feeding	Glass single-pass spray chamber, 5-channel peristaltic pump, polymer nebulizer One Neb, axial quartz burner (2.4 mm injector diameter), manual sample feeding

operating parameters are shown in Table 1. The Agilent MP Expert software was used.

The pH values were measured with a pH meter pH-410 (Aquilon, Russia) with a combined glass microelectrode ESC-10601/7. A Hettich EBA-20 centrifuge (Tuttlingen, Germany) was used for centrifugation. An ELMI-3 orbital shaker (ELMI, Latvia) was used for mixing. Weighing was carried out on ViBRA HT analytical scales (Shinko Denshi, Japan). The water content in the extracts was determined by Karl Fischer titration using an 870 KF Titrino plus titrator (Metrohm, Switzerland), elemental analysis was performed using a Flash EA 1112 CHNS analyzer (Thermo Electron Corp., USA).

**Extraction into the *in situ* formed ionic liquids** was carried out in 10-ml polypropylene centrifuge tubes at  $21 \pm 3$  °C. 0.5 ml of an aqueous solution containing the studied metal ions was placed in a test tube, 0.8 ml of a 5 mM PAR solution, and 2.7 ml of a buffer solution were added. To obtain *in situ* THADOSS, 112 mg of DOSSNa was added to an aqueous solution, placed in a water bath ( $85 \pm 5$  °C) for 5 minutes to dissolve the solid, then 110 mg of THAB was added and shaken for 1 min. To obtain *in situ* IL TBADOSS, 135 mg of DOSSNa was added to an aqueous solution containing metal complexes with

PAR and a buffer solution, placed in a water bath for 5 minutes to dissolve the sample, then 0.5 ml of 0.62 M TBAB solution was added and shaken for 1 min. After centrifugation for 3 min at 6000 rpm, the aqueous phase was separated by decantation and passed through a paper filter "white ribbon" to separate from the organic phase. The main amount of ionic liquid was retained due to adhesion on the walls of the tube. The pH of the aqueous phases was measured after extraction. The content of the studied metals was determined in the aqueous phase by the ICP-AES; the metal content in the organic phase was determined by the difference.

**Determination of metals in extracts by atomic emission spectrometry with microwave plasma.** To construct the calibration curves, a series of standard solutions were prepared, each of which contained 0, 5, 10, 20, 50, 70, 100 mcg/l of Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Zn(II). 0.32 ml of 0.025 M PAR solution and 5.0 ml of universal buffer solution with pH 4.9 were added to each solution. The total volume was 8.0 ml. To obtain *in situ* ionic liquid THADOSS of a volume of  $200 \pm 50$  µl, 112 mg of DOSSNa was added, placed in a water bath ( $85 \pm 5$  °C) for 5 min to dissolve the solid, then 220 mg of THAB was added, shaken for 1 min and centrifuged for

3 min at 6000 rpm. 75  $\mu$ l of the extract was taken, added to a micro-sample, 300  $\mu$ l of isopropanol was added, mixed, and metals were determined using the MP-AES method. A blank sample containing all the components except the metals being determined was subjected to a similar procedure.

The extraction efficiency ( $R$ , %) and the distribution coefficient ( $D$ ) were calculated using the formulas:

$$D = V_w \cdot \frac{(c_w^0 - c_w)}{c_w V_o},$$

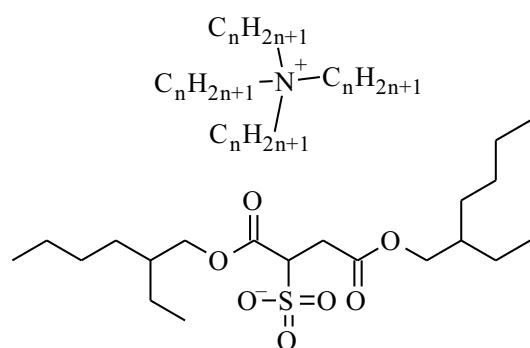
$$R, \% = D/(D + V_w/V_o) \times 100\%,$$

where  $c_w^0$ ,  $c_w$  are the initial and final concentrations of the metal ion in the aqueous phase, respectively, mg/l;  $V_w$ ,  $V_o$  are the volumes of the aqueous and organic phases, ml.

**Determination of metals in artificial seawater.** A 3.0 ml sample of artificial seawater containing the studied metal ions was placed in a test tube, 5.0 ml of a buffer solution with a pH of 4.9 containing 1.6 mM PAR was added. 112 mg of DOSSNa was added, placed in a water bath ( $85 \pm 5$  °C) for 5 min to dissolve the sample, then 220 mg of THAB was added, shaken for 1 min and centrifuged for 3 min at 6000 rpm. 75  $\mu$ l of the extract was taken, added to a microtube, 300  $\mu$ l of isopropanol was added, mixed, and metals were determined by the MP-AES method.

## DISCUSSION OF RESULTS

**Extraction of metal ions into *in situ* ionic liquids.** Preliminary studies have shown that the hydrophobic IL THADOSS and TBADOSS can be obtained directly in an aqueous solution during the exchange reaction between DOSSNa (the cationic component of IL) and tetraalkylammonium bromide (TBAB or THAB, the anionic component of IL). The structural formulas of IL THADOSS and TBADOSS are shown in Scheme 1.



**Scheme 1.** Chemical structure of tetrabutylammonium (TBADOSS,  $n = 4$ ) and tetrahexylammonium (THADOSS,  $n = 6$ ) dioctylsulfosuccinates.

All salts used for the production of IL are solid substances in their initial state. After adding solid DOSSNa to the aqueous solution, a test tube was placed in a water bath ( $85 \pm 5$  °C) for 5 min to accelerate its dissolution. During the preparation of THADOSS, a stoichiometric amount of solid THAB was added; during the preparation of TBADOSS, an aqueous solution of TBAB was introduced, due to its good solubility in water. When tetraalkylammonium bromide was added, the solution instantly became turbid. The appearance of the turbidity indicated the formation of a finely dispersed emulsion of the resulting ionic liquid. Similar phenomena occur as a result of the dispersion of hydrophobic ionic liquid formed *in situ* [9]. Separation of a noticeable volume of hydrophobic IL (more than 10  $\mu$ l) was observed when equimolar amounts of DOSSNa and tetraalkylammonium bromide were mixed at a total concentration  $c_{\text{DOSSNa+THAB}} \geq 1 \times 10^{-2}$  M and  $c_{\text{DOSSNa+TBAB}} \geq 7.5 \times 10^{-2}$  M. The separation of hydrophobic TBADOSS from water occurred at higher concentrations of the initial salts due to its higher solubility in water compared with THADOSS [3].

The composition of the IL obtained *in situ* was confirmed by elemental analysis. The content of C, N, S, and H in THADOSS was 69.2, 2.05, 3.45, and 12.3 wt.%, respectively; calculated content of C, N, S and H in THADOSS – 68.1, 1.8, 4.13 and 11.5 wt.%. The slightly lower C/N ratio (33.8) and higher C/S (20.1) and N/S (0.60) ratios compared to the theoretical values of 37.8, 16.5, and 0.44, respectively, may be associated with incomplete substitution of bromide for the DOSS anion during the exchange reaction and the formation of a mixed salt of the composition THA (DOSS<sub>x</sub>)(Br<sub>1-x</sub>). Calculations show that with a change in  $x$  from 1 to 0, the C/N ratios decrease, while C/S and N/S ratio increase; the experimental values obtained for these ratios correspond to the formation of the salt THA (DOSS<sub>0.8</sub>)(Br<sub>0.2</sub>). The results of elemental analysis of IL TBADOSS, wt. %: 65.2 C, 2.32 N, 4.40 S and 12.1 H, the obtained ratios of C/N (28.1), C/S (14.8) and N/S (0.53) confirm the formation of a mixed salt of the composition TBA(DOSS<sub>x</sub>)(Br<sub>1-x</sub>), where  $x = 0.9$ . The calculated content was (wt%) 65.12 C, 2.11 N, 4.83 S and 10.00 H for TBADOSS.

The water content in the THADOSS and TBADOSS obtained *in situ* was  $4.7 \pm 0.2$  and  $9.1 \pm 0.2$  wt. %, which is in good agreement with the water content after saturation in the pre-synthesized THADOSS and TBADOSS: 4.5 and 8.9% by weight, respectively [3]. The Immiscibility with water and the high water content in ILs allow them to be classified as hydrophobic-hydrophilic ionic liquids with low solubility in water and high water content upon saturation [2].

The possibility of group extraction of Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions was investigated. To perform extraction in the *in situ* DME variant, DOSSNa, an aqueous solution of TBAB or solid THAB were added to an aqueous solution containing metal ions and PAR. The

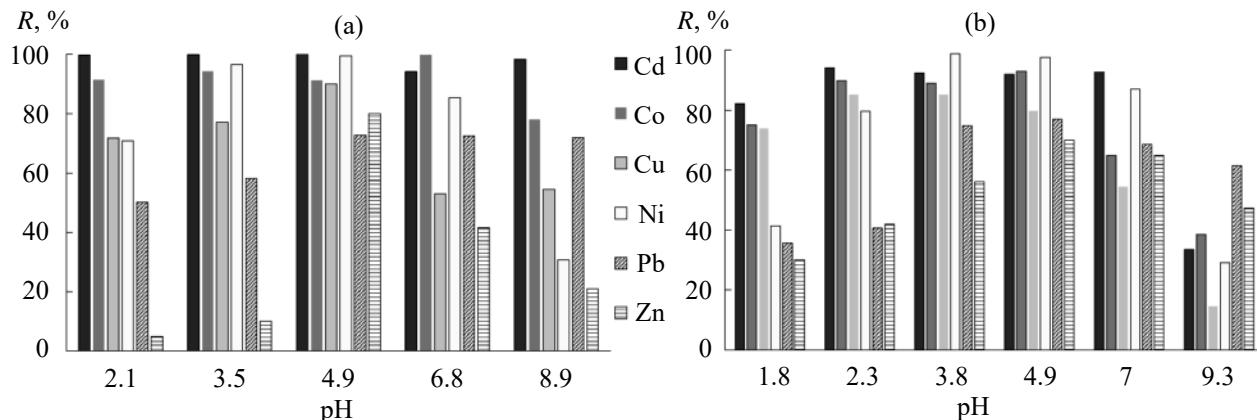
amount of DOSSNa, THAB and TBAB were calculated to obtain 100  $\mu$ l of IL. The parameters, such as pH, the concentration of the complexing reagent, the phase cationic and anionic components of IL during its preparation, the phase volume ratio and contact time were varied.

The dependences of the extraction efficiency of metal ions (on their simultaneous presence) into the THADOSS and TBADOSS ionic liquids formed *in situ* on pH are shown in Fig. 1. In the case of THADOSS IL, in the presence of  $5 \times 10^{-4}$  M PAR of Cd(II) and Ni(II) are extracted quantitatively from slightly acidic solutions at pH 4.9; for Cu(II) and Co(II) at this pH value, the extraction is close to quantitative, reaching more than 90%. Zn(II) and Pb(II) are extracted worse, with extraction efficiency of 80 and 73%, respectively. In TBADOSS IL, the extraction of Ni(II) is quantitative, Cd(II) extraction is close to quantitative – at least 92% at pH 4.9; at the same pH, the maximum degree of extraction of Co(II) (93%), Pb(II) (77%) and Zn(II) (70%) is achieved. For both extraction systems, the maximum extraction of metal-PAR complexes is achieved from slightly acidic or close to neutral solutions, in contrast to the optimal pH range of complexation in aqueous solutions: pH 9.5–11.0 for Cu(II), Cd(II) and Zn(II), pH 8.5–10.5 for Ni(II), pH 6.0–9.7 for Co(II) [22]. It is known that in aqueous-organic media, the optimal pH range of complexation can expand due to a weakening of the acidic properties of the reagent and, accordingly, an increase in the area of existence of a single dissociated form of the reagent by the hydroxy group in the *para* position. As a result, the metal-PAR complexes are extracted from more acidic solutions, apparently mainly in the form of singly charged partially protonated anion complexes  $\text{MeHR}_2^-$  (where R is a doubly charged PAR anion), the counterion to which is the tetraalkylammonium cation of an ionic liquid; from acidic solutions at pH < 5 – in the form of  $\text{Me}(\text{HR})_2$ . Extraction of  $\text{MeR}_2^{2-}$  compounds can be assumed in an alkaline medium. For THADOSS IL with a more hydrophobic tetrahexylammonium cation, the pH range of effective extraction is wider. It is obvious that the tetrabutylammonium cation does not provide sufficient hydrophobicity of the extracted double-charged complex,

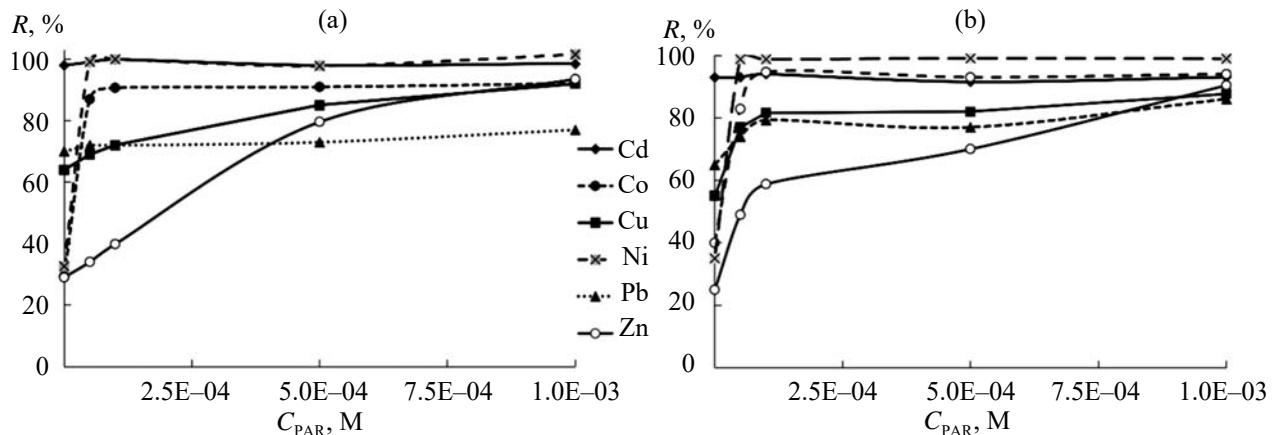
which leads to a faster decrease in the degree of extraction with increasing pH. For almost all the studied metal ions, the maximum values of the extraction efficiency were reached at pH 4.9, at which further studies were carried out.

In order to achieve quantitative extraction of all the metals studied, the effect of reagent concentration on the extraction efficiency was studied. The PAR concentration was varied in the range of  $5 \times 10^{-5}$ – $1 \times 10^{-3}$  M. In the absence of PAR, high extraction efficiency was observed only for Cd(II); in IL THADOSS, the extraction efficiency was 98%, in TBADOSS – 93%. The dependence of the metal extraction on the PAR concentration is shown in Fig. 2. Extraction close to quantitative for all metals was achieved at a PAR concentration of  $1 \times 10^{-3}$  M.

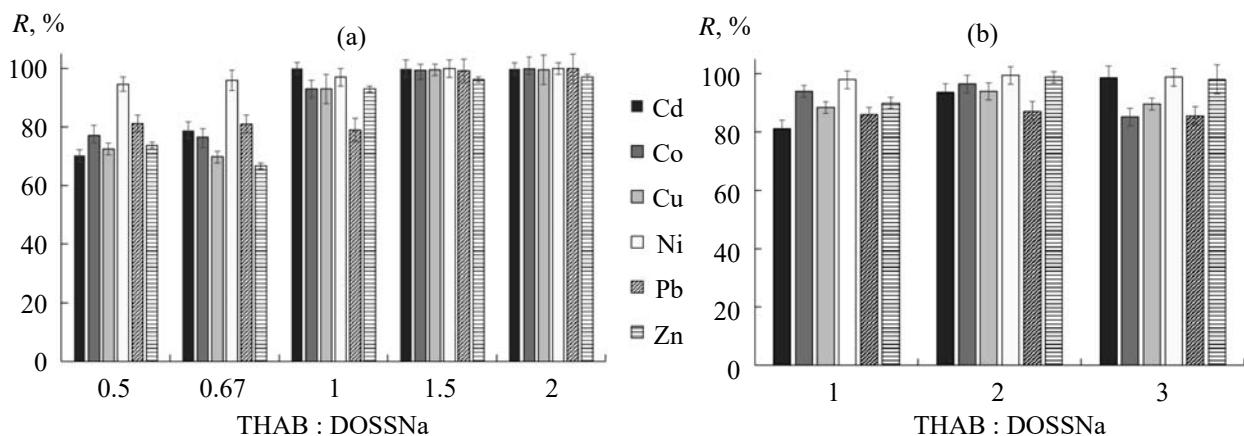
When an excess of DOSSNa was introduced in relation to the cationic component of IL – THAB, effective dispersion of the resulting IL THADOSS was noted, while its aggregation into a separate phase was weak, and prolonged centrifugation was required to separate the phases (at least 30 min at 10,000 rpm). All the studied metals were extracted quantitatively with a twofold excess of THAB in relation to DOSSNa. The dependence of the extraction efficiency of metal extraction (in the combined presence) into the THADOSS and TBADOSS ionic liquids formed *in situ* on the ratio of the amounts of the cationic (THAB or TBAB) and anionic (DOSSNa) components of the ILs taken for their preparation is shown in Fig. 3. When *in situ* IL TBADOSS is obtained under conditions of an excess of the anionic component relative to the cationic one, the dispersion of the resulting TBADOSS is so effective that there is no aggregation of IL into a separate phase (even during centrifugation at 14,000 rpm). This is possibly due to the surface-active properties of DOSSNa and the greater hydrophilicity of TBAB compared to THAB. For this reason, extraction with an excess of the anionic component (DOSSNa) in TBADOSS was not investigated. Metals are extracted most efficiently when the cationic component of IL



**Fig. 1.** Dependence of the extraction efficiency of 200  $\mu\text{g}/\text{ml}$  of metals into (a) THADOSS and (b) TBADOSS formed *in situ* in the presence of  $5 \times 10^{-4}$  M PAR on pH.  $V_o : V_w = 1 : 20$ , THAB : DOSSNa = TBAB : DOSSNa = 1 : 1.



**Fig. 2.** Dependence of the extraction efficiency of 200 µg/l of metals into (a) THADOSS and (b) TBADOSS formed *in situ* on the PAR concentration. pH 4.9,  $V_o : V_w = 1 : 20$ , THAB : DOSSNa = TBAB : DOSSNa = 1 : 1.



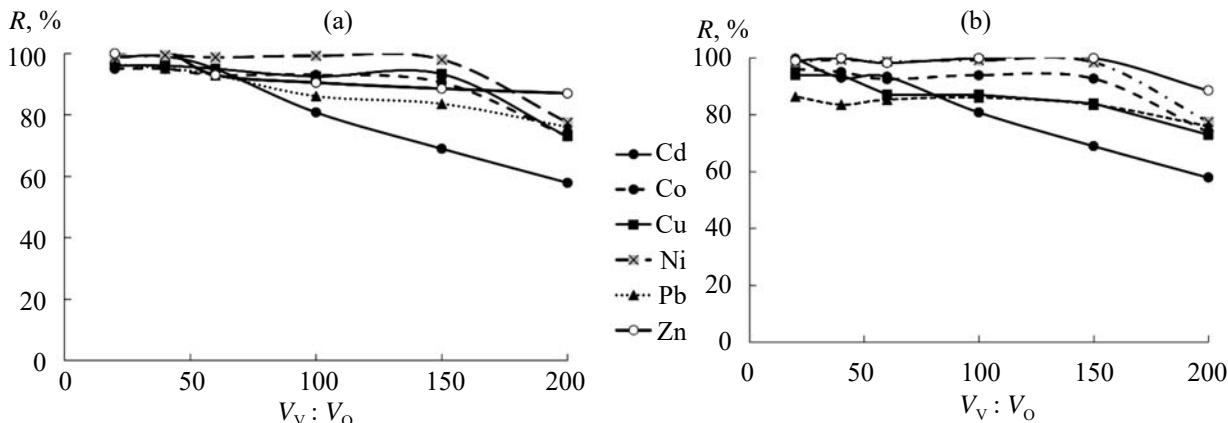
**Fig. 3.** Dependence of the extraction efficiency of 200 µg/l of metals into (a) THADOSS and (b) TBADOSS formed *in situ* in the presence of  $1 \times 10^{-3}$  M PAR on the concentrations ratio THAB : DOSSNa and TBAB : DOSSNa.  $V_w : V_o = 40:1$ ,  $c_{PAR} = 1 \times 10^{-3}$  M, pH 4.9.

(TBAB) is twice as much as the anionic component (DOSSNa). Quantitative recovery was achieved for three metals: Co(II), Ni(II), and Zn(II). Recovery close to quantitative recovery was observed for Cd(II), Cu(II), and Pb(II) (94, 94, 87%, respectively).

The results of the elemental analysis of *in situ* ionic liquids formed under conditions of a twofold excess of the cationic component of THAB showed that a liquid salt of the composition  $\text{THA}(\text{DOSS}_x)(\text{Br}_{1-x})$ , immiscible with water, is formed, where  $x = 0.5$ . In the case of an excess of TBAB, the formed ionic liquid was  $\text{TBA}(\text{DOSS}_x)(\text{Br}_{1-x})$ , where  $x = 1$ , i.e. TBADOSS. According to the elemental analysis data, the content of C, N, S and H was 66.8, 2.6, 2.9 and 12.5 wt.% for THADOSS; experimental values for the ratios were: C/N 25.7, C/S 23.0 and N/S 0.90. For TBADOSS, the content of C, N, S and H according to the elemental analysis data was 63.9, 2.25, 5.0 and 11.8 wt.%; the ratios of C/N, C/S, N/S are 28.4, 12.8 and 0.45, respectively, which is in good agreement with the calculated values.

The formation of the mixed salt  $\text{THA}(\text{DOSS}_x)(\text{Br}_{1-x})$  is apparently due to the fact that tetrahexylammonium bromide can form a liquid–liquid system when a solid salt is added to water [13]. When two salts THAB and DOSSNa are mixed, the bromide in tetrahexylammonium bromide released from water is partially replaced by a more hydrophobic anion, dioctyl sulfosuccinate. The release of tetrabutylammonium bromide from water as a separate hydrophobic phase can occur only in the presence of high concentrations of salting agents [14], therefore, when DOSSNa is added in quantities comparable to those of TBAB, only immiscible with water liquid TBADOSS can be released from water.

The study of the dependence of the metal ions extraction on the ratio of volumes of aqueous and organic phases showed that quantitative extraction of all metals is achieved with a ratio of volumes of aqueous and organic phases of 40 : 1 and 20 : 1 (Fig. 4). The volume of the aqueous phase was 4.0 ml, and the volume of the organic



**Fig. 4.** Dependence of the extraction efficiency of 200 µg/l of metals into (a) THADOSS and (b) TBADOSS formed *in situ* in the presence of  $1 \times 10^{-3}$  M PAR on the volume ratio of the aqueous and organic phases. pH 4.9, THAB : DOSSNa = TBAB : DOSSNa = 2 : 1.

phase varied from 20 to 200 µl. A further decrease in the volume of formed IL only leads to a decrease in the extraction efficiency. The ratio of  $V_w : V_o = 40 : 1$  was chosen for the work.

A study of the time required to establish extraction equilibrium during the group extraction of metals into THADOSS and TBADOSS formed *in situ* showed that extraction equilibrium is achieved in less than 1 min. With a twofold excess of tetralkylammonium bromide relative to DOSSNa, centrifugation for 3 min at 6000 rpm is sufficient to separate the phases.

Thus, Cd(II), Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) ions are extracted into THADOSS and TBADOSS ionic liquids formed *in situ* in the presence of  $1 \times 10^{-3}$  M PAR by mixing aqueous solution of salts supplying the cation and anion components of the ionic liquid. Quantitative extraction of metal ions into THADOSS formed *in situ* (pH 4.9,  $V_w : V_o = 40 : 1$ ) can be used for the group preconcentration of metal ions from aqueous solutions. The THADOSS ionic liquid has a lower solubility in water compared to TBADOSS, which avoids losses of IL due to partial solubility in water.

**Determination of metals by atomic emission spectrometry with microwave plasma after extraction preconcentration.** The selected conditions for the extraction and preconcentration of metal ions into THADOSS ionic liquid formed *in situ* were used for their determination by MP-AES. Metal ions were extracted from aqueous solutions with a volume of 8.0 ml in the presence of  $1 \times 10^{-3}$  M PAR at pH 4.9. The total concentration of the initial THAB and DOSSNa salts for the preparation of THADOSS was 0.095 M with a molar ratio of THAB : DOSSNa = 2 : 1. Under these conditions, the volume of the separating organic phase was  $200 \pm 50$  µl.

The high viscosity of the extract did not allow it to be directly injected into the plasma of the spectrometer. To reduce the viscosity, the extract was diluted with an organic solvent, similar to the approach proposed

in the [13, 23], this allowed ICP-AES and MP-AES determination to be carried out directly in the extract. The use of an organic solvent, as well as the transition from an aqueous to an organic matrix, usually reduces the sensitivity of the determination of elements. This is due to changes in the physical properties of the sample, such as viscosity, density, and surface tension, which affect the efficiency of its supply to the plasma and evaporation. The introduction of carbon into the plasma has a much greater effect on the intensity of the lines, and it can also cause damage to the burner due to contamination or overheating. Nevertheless, spraying and evaporation of the sample with the addition of an organic diluent may be more effective compared to aqueous solutions. When choosing a solvent, the determining factor is the volatility and viscosity of the introduced sample. It is shown that the introduction of mixtures of extractant and diluent into the spectrometer at volume ratios of no more than 1 : 3 does not affect the plasma temperature, and the use of volatile diluents leads to more intense signals [24].

Isopropanol was used as a diluent: 300 µl of isopropanol was added to 75 µl of the extract. This amount of organic solvent was chosen to obtain a sample volume sufficient to be injected into the spectrometer. Since the registration of the emission signal in MP-AES occurs sequentially, at least 350 µl of dilute extract was required to determine all the elements.

An inert polymer nebulizer One Neb was used to spray the sample, which provides more efficient spraying due to the formation of a finely dispersed aerosol with a narrow droplet size distribution and reduces sample consumption compared to a glass nebulizer. In this case, high spray efficiency is also achieved at low sample feed rates used for the introduction of non-aqueous solutions. A low sample feed rate of 7 rpm was chosen in order to minimize sample consumption, as well as to reduce contamination of the atomizer (burner) with combustion/decomposition

products of the matrix. For all elements, the maximum intensity of the lines was observed at a gas flow rate of 0.4 l/min in the nebulizer. Moderate gas consumption in the nebulizer (<0.5 l/min) is recommended to reduce matrix effects [25]. In addition, to eliminate carbon and soot emissions accumulating on the burner, an external gas flow control module (EGCM) was used to continuously supply air to the plasma. The minimum possible air consumption proved to be sufficient to prevent the deposition of combustion/decomposition products in the burner and to obtain a reliable and stable signal when determining the elements in dilute extracts. The wavelengths of the emission lines of the elements were selected based on the following conditions: the least influence of the background signal from the organic matrix, the maximum distance from the emission lines of iron, the maximum intensity and shape close to the Gaussian distribution (Table 1).

Table 2 shows the performance characteristics of the determination of metals in the extract by the MP-AES. The detection limits (LOD) were calculated as a ratio of  $3s/S$  for 20 measurements of blank samples, where  $s$  is the standard deviation and  $S$  is the slope of the calibration curve. The blank sample was an extract diluted with isopropanol obtained from a sample containing all the components of the system, except for the metals being determined, prior to extraction. The calculated detection limits for Co, Cu, Ni, and Pb are comparable to the detection limits of these elements achieved by the FAAS and MP-AES for direct detection in light matrices [15, 26]; for Cd and Zn, the calculated detection limits are 3-20 times higher. An increase in the detection limits of elements in the presence of significant amounts of inorganic acids, salts, or organic substances may be associated with the appearance of emission bands of molecular ions. In addition, there are a number of elements (Zn, Pb, etc.), the detection limits of which are quite high even when detected in relatively light matrices. So, for lead, the detection limit in deionized water is 4.4  $\mu\text{g/l}$  [16], in a solution of nitric acid – 10  $\mu\text{g/l}$ , and in a microemulsion of kerosene with propanol – 60  $\mu\text{g/l}$  [27]. When using plasma sources with nitrogen, the

detection limit for zinc is always relatively high due to the overlap of the NO bands with and the analytical Zn line at 213.837 nm [28]. For all elements, the detection limits after extraction preconcentration into the THADOSS ionic liquid formed *in situ* turned out to be lower than in the direct determination of these elements by the MP-AES in seawater [13]. Optimization of the instrumental parameters (spray chamber pressure, sample stabilization time in the plasma, variation of the sample volume supplied, viewing position) and the selection of a diluent can help to reduce the detection limits [13]. The accuracy and reproducibility of the proposed approach were confirmed using the standard addition method by analyzing artificial seawater with a mineralization of 33 g/l [21] (Table 2).

\* \* \*

Thus, the possibility of the multi-element determination of metal ions by the MP-AES method after extraction into ionic liquids has been demonstrated. Extraction preconcentration reduced the effect of matrix components, the detection limits of the studied metals compared with determination in seawater, and expand the capabilities of the MP-AES for analyzing solutions with high salinity.

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## CONFLICT OF INTEREST

The authors of this paper declare that they have no conflict of interest.

**Table 2.** Analytical characteristics of metal determination by atomic emission spectrometry with microwave plasma after extraction<sup>a</sup> into THADOSS

Element	Range of detectable contents, $\mu\text{g/l}$	LOD, $\mu\text{g/l}$	Added, $\mu\text{g/l}$	Found <sup>b</sup> , $\mu\text{g/l}$	RSD, %
Cd	10–200	3	50	47 $\pm$ 4	8
Co	15–200	5	50	47 $\pm$ 1	2
Cu	7–200	2	50	51 $\pm$ 3	7
Ni	15–150	5	50	50 $\pm$ 3	6
Pb	40–150	12	50	48 $\pm$ 3	8
Zn	75–150	25	50	50 $\pm$ 4	8

*Note:* a Extraction conditions: pH 4.9, cPAR = 1  $\times$  10<sup>-3</sup> M, THAB : DOSSNa = 2 : 1, Vo : Vw = 1 : 40; b artificial seawater (mineralization 33 g/l [21]; n = 3, P = 0.95).

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