Determination of the Ions of Copper (II), Cadmium (II), Lead (II), Zinc (II) in Snow and Water Samples after Extraction with Thiopyrinium Salicylate

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Abstract

For the purpose of analytical application of thiopyrine in the analysis of the natural samples − the solid components of snow and the filtrate of surface river water, an equimolar melt of thiopyrinium salicylate with the melting point 145 ˚C was obtained, and its physicochemical properites were studied. The melt was used to extract the sorbed inorganic forms of copper, cadmium, lead, and zinc from the solid particles of snow cores sampled at the territory of Barnaul. The resulting extracts and acid mineralizates were analyzed by means of flame atomic absorption spectrometry. Analysis of the concentrations of chalcophilic metals under investigation allowed us to determine the total content of the sorbed forms and the mass concentration of inorganic forms of copper, cadmium, lead, and zinc in the solid particles from snow at the stage of sample preparation. The variation ranges for the mass concentrations of the inorganic forms were 50−94 % for copper, 58−95 % for cadmium, 68−89 % for lead, 74−89 % for zinc. The mass concentrations of organic forms were calculated from the difference between the amounts of Cu, Cd, Pb, Zn in the acid mineralizate and the extract. The filtrates of river water were preserved with hydrochloric acid and studied separately with the help of layering *in situ* in the system of water ($\geq$ 0.01M HCl) − thiopyrinium salicylate − modifier to form two liquid phases. The lower and upper phases were analyzed for concentrations of Cu, Cd, Pb, Zn by means of stripping voltammetry. The degree of extraction of the ionic forms of copper (II), cadmium (II), lead (II) and zinc (II) from the samples of river water filtrate after single extraction was 92±2, 90±3, 94±2, 97±1 %, respectively.

Keywords: thiopyrine, salicylic acid, melt, extraction

INTRODUCTION

The analytical application of low-melting melt of acetylsalicylate antipyrinium $[\text{AntH}^+]\cdot[\text{AcSal}^-]$ (ρ = 1.2 g/cm^3, T_m = 85 °C) for individual and group concentrating or the ions of elements from acid solutions for subsequent analysis of the elements in the concentrate was studied previously [1−4]. Thiopyrine is an efficient thio-containing photometric reagent [5], 2,3-dimethyl-1-phenylpyrazoline-3-thione-5 with a sextet of π electrons in the heterocycle and the excessive negative charge on the sulphur atom, which means

electron-donor properties [6]. The constant of thiopyrine protonation is about 30 times smaller than that of antipyrine. The nucleophilic sulphur atom renders the properties of a soft base to thiopyrine, making it able to enter the coordination interaction with soft Pearson acids M^{m+} with the formation of intercalation complexes $\text{M(R)}_n\text{X}_z$ and ion associates of the cations of thiopyrinium $(\text{RH})^+_{m-z}[\text{M}^{m+}\text{X}_z]^{(m-z)}$ [7, 8] with anion partners X^-. Molecular spectrometry of the extracts of the ions of chalcophilic elements was used previously [6] in the systems water − thiopyrine − organic acid, but the electrochemical properties of

the reagent in extraction have not been studied yet. The isolation of Zn (II), Cd (II), Pb (II), Cu (II) with the hydrophobic melt of thiopyrinium salicylate through extracting, and the *in situ* extraction of the listed ions from acid chloride filtrates of snow and river waters provides unification of the extraction-based method of the preparation of analytical samples to one-element and group analyses. The ions of Zn (II), Cd (II), Pb (II), Cu (II) are determined in various complicated matrices by means of stripping voltammetry. The method described in [9] demonstrated in model systems a principal possibility to be used in the practice of extraction voltammetry. The necessity to study real samples arose. The concentrations of copper, cadmium, lead and zinc in the samples of snow cover in the area affected by Barnaul were determined previously [10].

The goal of the work was to demonstrate the analytical possibilities of thiopyrinium salicylate in the analysis of solid particles in snow (solid samples) and filtrates of the surface river water (liquid samples) by means of extraction-absorption and extraction-electrochemical methods using thiopyrinium salicylate as an efficient low-melting extragent. To study the extraction possibilities of the new low-melting melt, it is first of all necessary to

determine its physicochemical properties: melting temperature, density, electroconductivity at the melting temperature, solubility at 25 °C in distilled water and the solution of 0.1 M HCl. It is also necessary to extract the inorganic ion forms of Zn (II), Cd (II), Pb (II), Cu (II) into the melt of thiopyrinium salicylate at the stage of preparation of the solid samples of snow mass and to analyze the inorganic ion forms.

EXPERIMENTAL

Replacement of oxygen-containing antipyrine by the sulphur-containing reagent thiopyrine provides the coordination interaction of the inorganic ion forms of zinc, cadmium and copper with sulphur as a chalcophilic reaction centre of the reagent molecule − thiopyrine. Thiopyrine has a higher melting point 167 °C [11], that antipyrine (113 °C). For extraction, we used thiopyrine as a melt ($T_m \approx 145$ °C) with salicylic acid ($T_m = 159$ °C). To study the solubility of thiopyrinium salicylate melt in distilled water and the solution of 0.1 M HCl, two series of exact weighted portions (0.3000−0.8000 g) of the melt were prepared, placed in tubes, thermostated for 30 min with
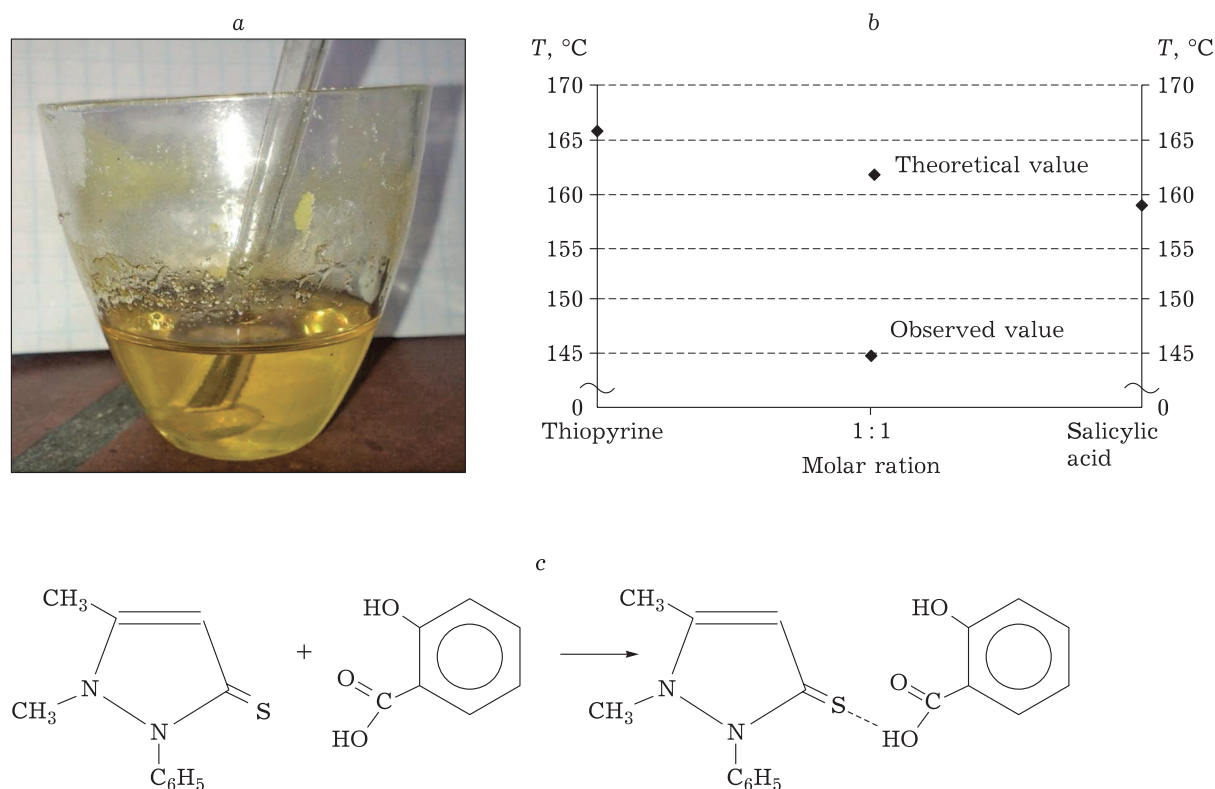

Fig. 1. General view of the melt of thiopyrinium salicylate (*a*), depression of the melting temperature of thiopyrinium salicylate melt from the additive calculated value (*b*), a scheme of the protolytic interaction of thiopyrine with salicylic acid (*c*).

10 mL of distilled water (acid), and the refractive index was determined with the help of refractometer IRF-454B. The equilibrium state of saturation was determined from the plots exhibiting the dependences of the refractive index n of the solution on the amount of matter (1 mmol of thiopyrinium salicylate in 10 mL) and from the attainment of the plateau of the graphic dependence of solution n on the amount of the substance at 25 °C.

The general view of the melt is shown in Fig. 1. Extraction of the inorganic forms of mercury and selenium from the solid samples of natural objects was previously realized [12] with the help of the hydrophilic liquid organic phase of the system water − antipyrine − sulphosalicylic acid, which was prepared by mixing the aqueous solutions of antipyrine (2 mol/L) and sulphosalicylic acid (2 mol/L) with the volume ratio of 2 : 1. In the case of thiopyrinium salicylate, the equimolar ratio of reagents in the reaction melt was used: thiopyrinium/salicylic acid = 1 : 1. The melt of thiopyrinium salicylate may be heated to its melting point thus increasing the efficiency of extrac-

TABLE 1

Results of the determination of zinc and cadmium in mineralizates (AE) and extracts (E)
of solid snow particles (SP) by means of flame AAS

Sample	Zn, g/g		Cd, µm/g	
	AE (Σ)	E (IP, %)	AE (Σ)	E (IP, %)
1	98	73 (74)	1.9	1.1 (58)
2	89	70 (79)	7.9	5.5 (70)
3	107	95 (89)	5.7	3.4 (60)
4	137	108 (79)	1.7	1.0 (59)
5	178	150 (84)	6.1	5.3 (87)
6	126	106 (84)	9.0	5.6 (62)
7	101	87 (86)	2.0	1.5 (75)
8	82	70 (85)	1.1	1.0 (91)
9	192	170 (89)	2.0	1.9 (95)
10	66	54 (82)	1.4	1.2 (86)
Variation range	66−192	54−170 (74−89)	1.1−9.0	1.0−5.6 (58−95)
$C_a \pm \varepsilon\alpha$	118±9	98±5 (83±3)	3.9±0.2	2±0.3 (74±10)

Note. Here and in Tables 2−7: C_a − arithmetic mean of the results of snow sample analyses; $\varepsilon\alpha$ − confidence interval; IP − inorganic phase.

TABLE 2

Results of lead and copper determination in mineralizates (AE) and extracts (E) of solid snow particles (SP)
by means of flame AAS

Sample	Pb, g /g		Cu, µm/g	
	AE (Σ)	E (IP, %)	AE (Σ)	E (IP, %)
1	54	37 (69)	13	10 (77)
2	50	34 (68)	22	11 (50)
3	78	66 (85)	16	11 (69)
4	73	61 (84)	18	13 (72)
5	90	70 (78)	57	38 (67)
6	43	33 (77)	25	19 (76)
7	73	64 (88)	28	18 (64)
8	58	48 (83)	18	16 (89)
9	65	58 (89)	71	67 (94)
10	79	63 (80)	100	76 (76)
Variation range	43−90	33−70 (68−89)	13−100	10−76 (50−94)
$C_a \pm \varepsilon\alpha$	67±7	53±5 (80±5)	37±2	28±2 (73±9)

Note. For designations, see Table 1.

tion with lower reagent consumption in comparison with the ionic liquid [12].

Ethyl alcohol was added as a modifying agent for the analysis of the filtrate of river water.

Sampling procedure

Snow cores were collected at the urban territory of Barnaul using a tubular sampler by means of an envelope, with 5 cores in the sites with natural snow accumulation (10 sampling sites). The united cores were placed in plastic containers and mixed. The total mass of the collected snow was determined by technical weighting in the laboratory. Then the snow samples were melted at room temperature, and the resulting snow water was filtered through track membranes in the atmosphere of argon. The filtrates were acidified with hydrochloric acid of Kh. Ch. reagent grade (chemically pure) to pH ≤ 2.00 and analyzed separately. The collected precipitates of solid particles from snow (SP) were dried to the constant mass under the IR lamp. Each filter with the SP precipitate was weighted with the analytical balance and cut into two equal parts.

Analysis of solid samples

One half of the precipitate in the form of a precisely weighted portion (0.1000−0.2000 g) was treated in a mixture of sulphuric, nitric and hydrochloric acids (2 mL H_2SO_4 + 4 mL HNO_3 + 2 mL HCl) in the mineralizer evaporating till humid salts. Thus obtained acid extract (AE) was transferred quantitatively into a volumetric flask 25 mL in volume, then distilled water was added to the volume mark, and analysis was carried out by means of atomization in air-acetylene flame to determine the general (Σ) content of zinc, cadmium, lead, and copper (see Tables 1 and 2). Then the contents of zinc (213.9 nm), cadmium (228.8 nm), lead (283.3 nm) and copper (324.8 nm) were calculated using the linear regression calibration equations of the dependence of absorption intensity (peak height h, mm) on the concentration of Zn (II), Cd (II), Pb (II), Cu (II) in the working solution (in μg/mL):

$h = 1.6 + 9.5C_{Zn}$, analytical λ = 213.9 nm,
   $r = 0.999$
$h = 0.43 + 22.3C_{Cd}$, analytical λ = 228.8 nm,
   $r = 0.997$
$h = 1.8 + 2.8C_{Pb}$, analytical λ = 283.3 nm,
   $r = 0.981$
$h = 0.82 + 9.6C_{Cu}$, analytical λ = 324.8 nm,
   $r = 0.978$

Results of the analysis of SP samples (10 sampling points, two parallel analyses per each point) are presented in Tables 1 and 2.

The second half of the precipitate in the form of the exact weighted portion (0.1000−0.2000 g) was also placed in dry weighing bottles, then 1.000 g of the equimolar melt of thiopyrinium salicylate was added to the exact weighted portion, the melt was mixed with a glass stick. After solidification of the melt with SP, 1.0 mL of ethanol was added as the modifying agent, mixing with a glass stick was thoroughly carried out, and heating to 40−50 °C for 15−20 min with periodic mixing with the glass stick. Then the bottles were cooled for 10 min, 2.0 mL of ethanol was added, under mixing with the glass stick. After the natural precipitation of SP to the bottom of the bottle, the extract (E) was sprayed into the air-acetylene flame of the atomic absorption spectrometer (AAS) AAS 1N (Germany).

Analysis of the liquid samples of river water filtrate

The filtrates of river water samples were obtained by filtering through track membranes and acidification with hydrochloric acid to pH ≤ 2.0. The melt of thiopyrinium salicylate in the amount of 1.000 g was placed in dry tubes made of polyethyleneterephthalate together with 1 ml of ethanol as a modifier, then 4.00 mL of the acidic chloride solution of the filtrate of natural surface water under analysis, the tubes were closed with caps, stirred up intensively for 2−3 min and placed in the tube holder. Layering (Fig. 2) to the

Fig. 2. General view of the samples of river water filtrates (pH ≤ 2.0) after layering in the system water − thiopyrine − salicylic acid modified with ethanol.

aqueous phase (upper) and the organic (lower) phases proceeded *in situ* as a result of the protolytic interaction of the acid chloride solution of the filtrate of natural surface water with the melt of thiopyrinium salicylate and the modifier. The ratio of the volumes of the lower target organic phase (OP) and the rendering upper aqueous phase (AP) is presented in Table 3. The organic phase and AP were analyzed separately by means of stripping voltammetry (SVA) with the help of Ekotest-VA analyzer. A three-electrode system was used in the procedure: the working

TABLE 3

The phase volumes in the tubes with the samples of river water filtrates (the total volume is 6 mL)

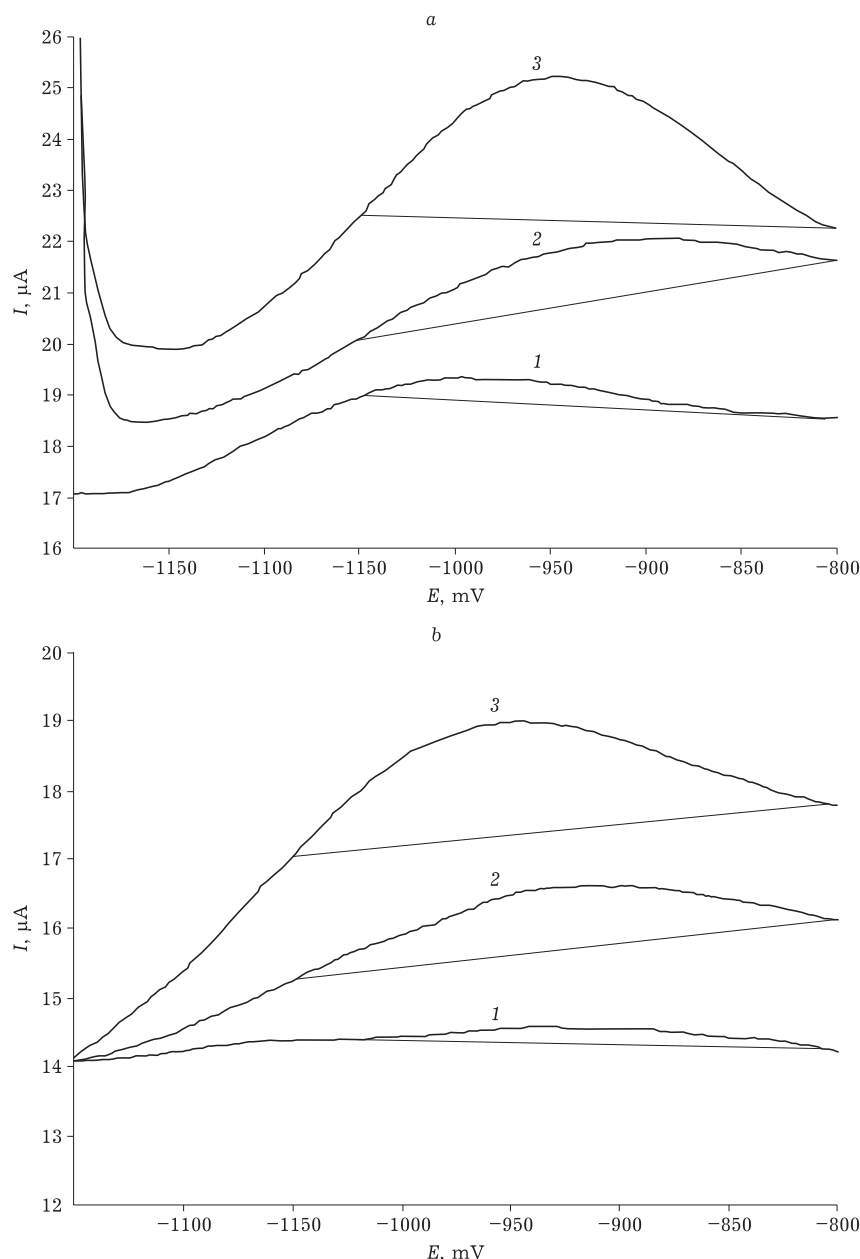| Tube No.	Volume, mL	
	OP (the lower phase of concentrate)	AP (the rendering upper phase of raphinate)
1	1.80	4.20
2	1.80	4.20
3	1.70	4.30
4	1.80	4.20
5	1.70	4.30

Fig. 3. Voltammograms of the ion forms of zinc in OP (*a*) and AP (*b*): *1* − background (melt + 4 mL 0.1 M HCl); *2* − melt + 4 mL of the filtrate of river water; *3* − melt + 4 mL of the filtrate of river water + 3 µg Zn (II).

solid carbon macroelectrode KTZhG 414324.005 No. 169, reference electrode − silver chloride laboratory EVL-1M4 and auxiliary platinum laboratory electrode EPL-02. Before the start of the series of determinations, the working surface of the electrode was polished with filtering paper wetted in ethanol, then activated with atomic hydrogen and washed in 0.1 M HCl. After that, 5 μL of the OP sample were deposited on the dry working surface using a microsyringe for gas chromatography (10 μL) and placed into the electrochemical cell of the Ekotest-VA analyzer with the solution of 4 mL of 0.1 M HCl. Electroaccumula-

tion of the ion forms was carried out at −1400 mV for 60 s. Then the square-wave voltammogram was recorded with the sweep amplitude from −1200 to 200 mV. The current range was 2−200 μA. The sweep rate was 50 mV/s. Typical voltammograms of the micro-amounts of OP and AP are shown in Fig. 3−6. One can see that the analytical signals of the ion forms of metals are characterized by the maxima of the limiting diffusion current of the graphite working macro-electrode KTZhG 414324.005 No. 169 at the corresponding potential. The calculations of the efficiency of the isolation of ion forms of elements are presented in
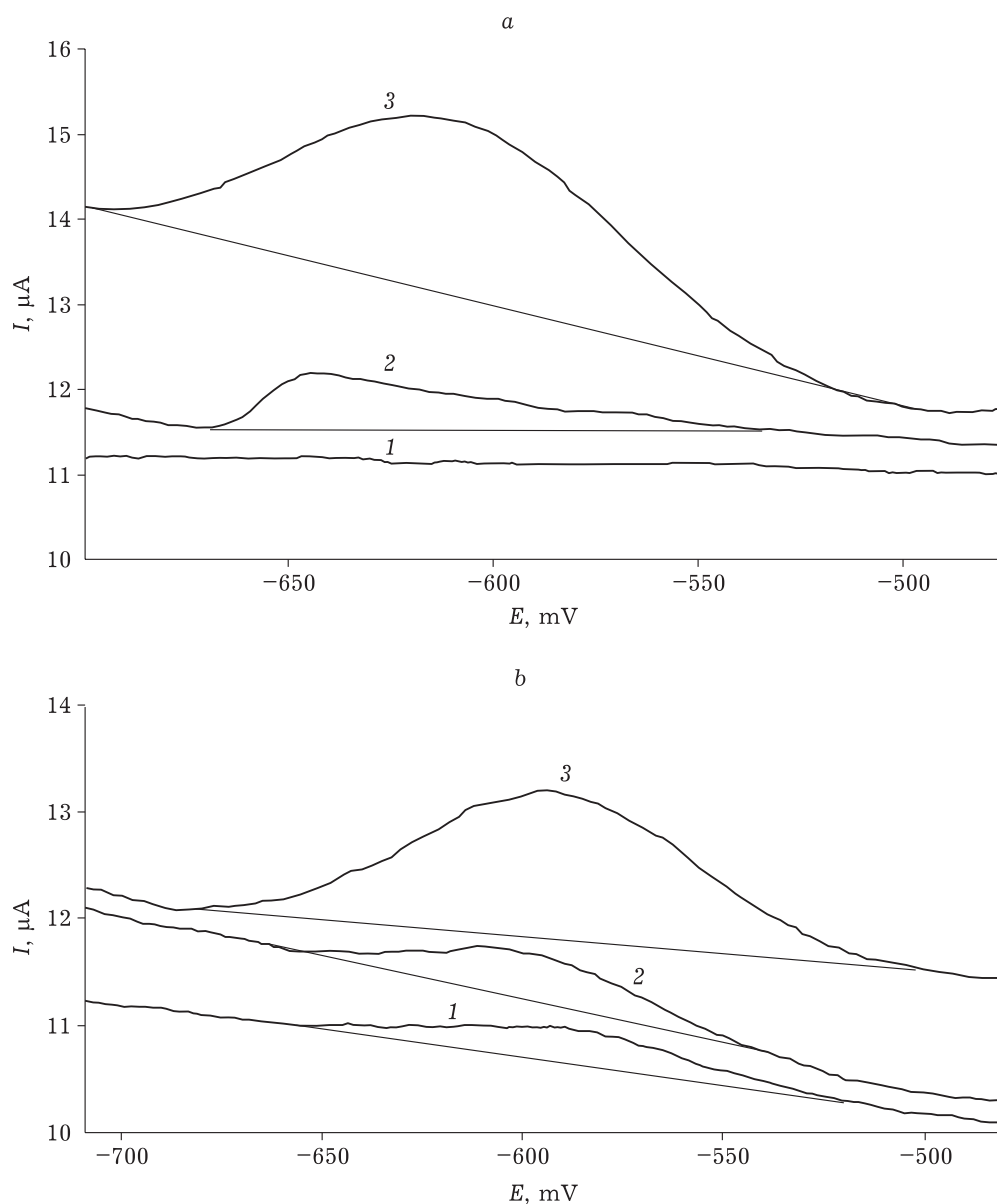

Fig. 4. Voltammograms of the ion forms of cadmium in the OP (*a*) and AP (*b*): *1* − background 5 μL of the OP (melt + 4 mL of 0.1 M HCl); *2* − melt + 4 mL of the filtrate of river water; *3* − melt + 4 mL of river water filtrate + 0.1 μg Cd (II).
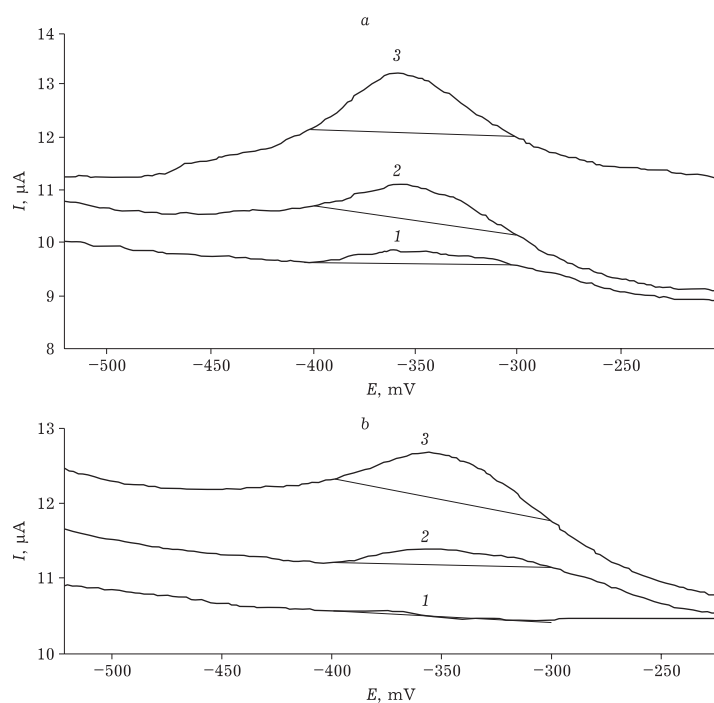
Fig. 5. Voltammograms of the ion forms of lead in the OP (*a*) and AP (*b*):
1 − background (melt + 4 mL 0.1 M HCl); *2* − melt + 4 mL of river water
filtrate; *3* − melt + 5 mL of river water filtrate + 0.1 µg of Pb (II).

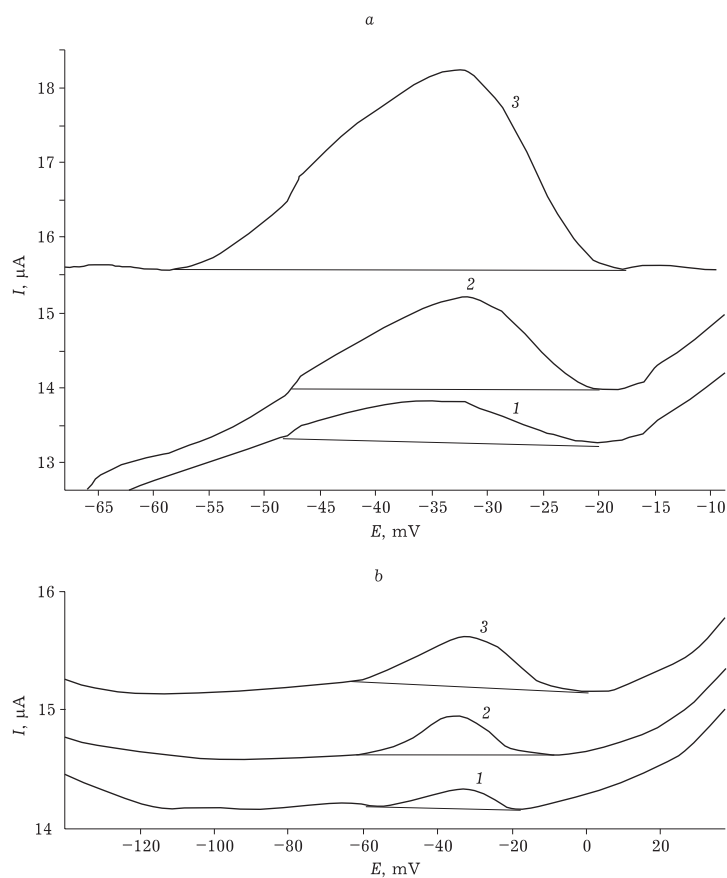Fig. 6. Voltammograms of the ion forms of copper in the OP (*a*) and AP (*b*):
1 − background 5 µL of the OP (melt + 4 mL 0.1 M HCl); *2* − melt + 5 mL of
river water filtrate; *3* − melt + 4 mL of river water filtrate + 1 µg of Cu (II).

TABLE 4

Results of the determination of Zn (II) in the filtrates
of river water by means of stripping voltammetry

Analysis No.	Zinc content, μkg/L		D	R, %
	OP	AP		
1	146.0±0.3	1.96±0.05	75	97
2	145.9±0.3	1.90±0.05	77	97
3	146.5±0.3	1.92±0.05	76	97
4	145.8±0.3	2.00±0.05	73	97
5	146.2±0.3	1.98±0.05	74	97
Average (n = 5)	146.1	1.95	74±2	97±1

Note. Here and in Tables 5−7: 1. Analysis Nos. correspond to extraction tubes 1−5 in Table 3. 2. D is the distribution coefficient which is equal to the ratio of the concentrations of target component in the organic (OP) and aqueous (AP) phases: $D = C(OP)/C(AP)$.

TABLE 5

Results of the determination of Cd (II) in the filtrates
of river water by means of stripping voltammetry

Analysis No.	Cd content, μkg/L		D	R, %
	OP	AP		
1	2.24	0.086	26	92
2	1.90	0.079	24	91
3	1.79	0.094	19	88
4	2.15	0.090	24	91
5	1.66	0.11	15	86
Average (n = 5)	1.95±0.3	0.092±0.01	22±5	90±3

TABLE 6

Results of the determination of Pb (II) in the filtrates
of river water by means of stripping voltammetry

Analysis No.	Lead content, μkg/L		D	R, %
	OP	AP		
1	14.0±0.4	0.38±0.05	37	94
2	13.5±0.4	0.32±0.05	42	95
3	14.1±0.4	0.42±0.05	34	93
4	13.5±0.4	0.34±0.05	40	94
5	13.8±0.4	0.37±0.05	37	94
Average (n = 5)	13.8	0.37	38±4	94±2

TABLE 7

Results of the determination of Cu (II) in river water
filtrates by means of stripping voltammetry

Analysis No.	Cu content, μkg/L		D	R, %
	OP	AP		
1	4.78	0.19	25	91
2	5.73	0.20	28	92
3	4.83	0.16	30	89
4	6.21	0.21	29	93
5	5.64	0.19	30	92
Average (n = 5)	5.44±0.8	0.19±0.02	28±3	92±2

Tables 4−7. The numbers in Tables 4−7 correspond to extraction tubes 1−5 in Table 3.

RESULTS AND DISCUSSION

The electrical conduction of the melt of thiopyrinium salicylate determined with the help of a conductivity meter with plate-like electrodes was approximately 90 mS/m with the melting point of $T_m \approx 145$ °C. The melt conduction was determined within the range of conduction of ion liquids with imidazolinium cations [13]. The solubility of the melt of thiopyrinium salicylate was 1.50 mmol in 10 mL of distilled water and 2.05 mmol in 10 mL of 0.1 M HCl.

Unlike thiopyrine, which is soluble in hot water [8], the hydrophobic melt of thiopyrinium salicylate modified with ethanol efficiently extracts the inorganic forms of elements: zinc, cadmium, lead and copper. The inorganic forms (sulphates, oxides, chlorides, nitrates, *etc.*) are more significant as sorbed by the snow particles of the solid component of snow mass. However, organometallic compounds MR_4 in which the ligands are methyl, alkyl, aryl and others, coordinationally bound with the central complex-forming metal atom, form organometallic forms more toxic than the inorganic forms, mainly determined in the extracts (E). The amounts of organic forms were calculated as the difference between the total contents of the element Σ in the acid mineralizate of SP and element content in the inorganic phase (IP, see Tables 1, 2). This value is of critical importance in chemical monitoring of the components of natural systems under the conditions of chemical pollution of components (aerosol, soil, bottom sediments).

In spite of the broad ranges of variation of sorbed forms (Σ) (see Tables 1 and 2), the metals under investigation may be arranged as a sequence with respect to the average total metal content in solid SP, μg/g: Zn (118±9) > Pb (67±7) > Cu (37±2) > Cd (3.9±0.2).

If the average content of the inorganic metal forms is subtracted from the total content Σ, we obtain the average content of the organic metal forms. The contribution from the organic forms of metals (mass fraction, %) into the total metal content in snow samples increases in the sequence of elements:

Zn (27 %) ≈ Cu (27 %) > Cd (26 %) > Pb (20 %).

In spite of substantial errors connected with the variability of chemical load on the atmospheric aerosol in Barnaul in 2015, the contribution from the organic forms should be considered to be representative and essential because of the higher toxicity of organometallic forms compared to the inorganic forms of metals.

It follows from the data shown in Tables 4–7 that the concentrate of the OP is representative with respect to the content of Zn (II), Cd (II), Pb (II), Cu (II) in the parallel samples of river water, and the amount of Zn (II), Cd (II), Pb (II), Cu (II) ions in the rendering phase (AP) was determined within the limits of random errors of the parallel determinations of average content.

Depression of melting temperature (see Fig. 1) is the evidence of the chemical protolytic interaction of thiopyrine and salicylic acid in the melt of thiopyrinium salicylate at the molar ratio of 1 : 1. This product in the form of the melt with $T_m \approx 145$ °C and $\rho \approx 2.2$ g/cm^3 was introduced in the amount of 1.000 g into each tube, 1 mL of ethanol was added, and then 4 mL of the filtrate of river water under analysis (pH ≤ 2.0); then the mixture was stirred up intensively (see Table 3). A two-fold decrease [12] in the molar fraction of the higher-melting component thiopyrine and an increase in the molar fraction of less water-soluble component salicylic acid in the melt, in combination with the modifier, allowed creating the conditions for system layering into two liquid transparent phases at room temperature (see Fig. 1, 2). The lower phase is coloured in yellow, and according to [14], this corresponds to the transmitted basic blue light. Extraction photometric procedures of the determination of a broad list of chalcophilic elements with thiopyrine under the optimal conditions of molecular absorption of light within the range 330–735 nm are presented in a review [8]. Extraction with thiopyrinium salicylate in combination with photometry is also promising in the analysis of acid chloride solutions, for example, waste and surface waters. Extraction degree (R) of the ion forms of copper (II), cadmium (II), lead (II) and zinc (II) from the samples of river water filtrates after single extraction

was 92±2, 90±3, 94±2, and 97±1 %, respectively (see Tables 4–7).

CONCLUSION

It was established that the equimolar melt of thiopyrinium salicylate and the organic phase is a conducting ion associate which is poorly soluble even in hydrochloric acid; it is promising as an extractant in the instrumental methods of the determination of the ins of chalcophilic elements and was tested with real samples of river water.

In the case of modification with ethanol, the ion associate of thiopyrinium salicylate efficiently concentrates *in situ* by single extraction the ion forms of copper, cadmium, lead and zinc from acid chloride solutions (*e.g.*, filtrates of natural surface waters) and is combined with stripping voltammetry.

The low-melting melt of thiopyrinium salicylate efficiently extracts the inorganic forms of zinc, cadmium, lead and copper from the solid aerosols of snow, is odourless, corresponds to the requirements of green analytical chemistry and is efficient as the extractant of the ions of elements in combination with atomic spectrometry.

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