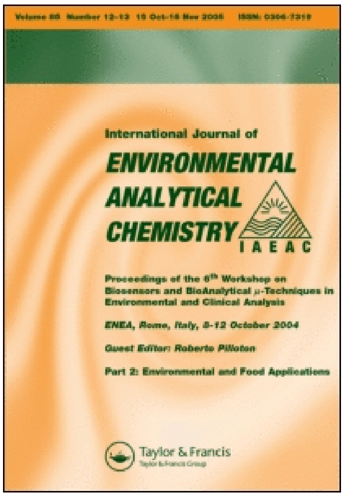

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PRECONCENTRATION PROCEDURES FOR TRACE CADMIUM DETERMINATION IN NATURAL AQUEOUS SYSTEMS PRIOR TO ZEEMAN ETAAS

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Nanotrace Cd determination in natural waters using two new flotation collectors, lead(II) heptyldithiocarbamate, $Pb(HpDTC)_2$, and cobalt(III) heptyldithiocarbamate, $Co(HpDTC)_3$, are presented. The optimization of the most important experimental parameters for flotation is given. Zeeman electrothermal atomic absorption spectrometry (ZETAAS) is used as an instrumental technique for Cd measurement. The results are compared with those obtained by other preconcentration procedures as independent methods. The limit of detection of ZETAAS using $Pb(HpDTC)_2$ as collector is 4.8 ng/L, while using $Co(HpDTC)_3$ it is 3.0 ng/L.

Keywords: Cadmium; Preconcentration; Flotation; Zeeman ETAAS

INTRODUCTION

Cadmium is a toxic element and as a result of world-wide accumulation (electroplating, galvanizing, preparation of some low-melting alloys, cathode material for rechargeable batteries, colour pigment for paint and plastics, etc.), it presents a serious environmental hazard. In natural waters Cd concentrations often range from 5 to 100 ng/L. The detection power of mass spectrometry with inductively coupled plasma (ICP-MS) has the sensitivity to determine Cd in this concentration range. However, in natural waters with high hardness, this modern and very expensive instrumental technique suffers from problems with isobaric polyatomic interferences and signal suppression. Therefore, improvements, modifications, and the development of new methods for separation and preconcentration of this analyte are of practical value.

Recently significant attention has been paid to colloid precipitate flotation as a method for heavy metal preconcentration prior to atomic absorption spectrometry (AAS) [1–5]. This bubble technique has advantages relative to other conventional

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carrier preconcentration techniques, such as coprecipitation, ion-exchange, etc., because of shorter analysis times, the high enrichment factor achieved, low detection limits, good reproducibility and repeatability and also because it uses very cheap reagents and simple equipment [1–12].

Proper flotation depends on many factors but the most important is the nature of the collector used. The collector is a bulk precipitate in which the colligends – the microelements investigated – are incorporated. Experience has shown that dithiocarbamate salts can be successfully applied as collectors [6–12]. After separation by flotation with small gas bubbles with the help of surfactants, the collector precipitate containing the colligends is dissolved and the microelements are determined by an instrumental method.

The aim of this work is to present for the first time two dithiocarbamate salts, lead(II) heptyldithiocarbamate, $Pb(HpDTC)_2$ and cobalt(III) heptyldithiocarbamate, $Co(HpDTC)_3$, as new potential reagents for flotation procedures. The optimization of the experimental parameters is presented in detail. Zeeman electrothermal atomic absorption spectrometry (ZETAAS) is used as an instrumental technique for Cd measurement.

The possibilities of these two new flotation methods used as preconcentration procedures prior to Cd determination by ETAAS are compared with three other preconcentration techniques: solid-phase extraction using Empore disks, solid-phase extraction using home-made polyurethane foams loaded with hexamethyleneammonium hexamethylenedithiocarbamate, HMA-HMDTC [13,14] and liquid–liquid extraction by ammonium tetramethylenedithiocarbamate, NH_4TMDTC [15].

The developed flotation methods, as well as the comparative extraction methods, were applied for Cd analyses in spring, well and tap freshwater samples.

EXPERIMENTAL

Apparatus

ETAAS measurements of Cd were made using a Varian SpectraAA 640Z spectrometer equipped with a GTA 100 graphite furnace and a Perkin-Elmer Zeeman 3030 spectrometer equipped with an HGA-600 graphite furnace. A hollow cathode lamp was used as light source and the spectral bandpass and wavelength were as recommended by Varian and Perkin-Elmer, respectively. Pyrolytically coated graphite tubes with standard pyrolytic platforms were used as atomizers. Sample solutions (10–20 μL) were introduced into the graphite furnaces using PSD-100 Varian (USA) and AS-60 Perkin-Elmer (USA) autosamplers. The graphite furnace operating parameters are presented in Table I for both instruments. Only peak areas were used for quantification.

The pH readings were carried out on an Iskra pH-Meter M 5705 supplied with a combined glass electrode M 0101. The flotation cell was a glass cylinder (4 × 105 cm) with a sintered glass disk (porosity No. 4) at the bottom to generate air bubbling (scheme presented in [11]). The 3 M Company's Empore disk for extraction (diameter 47 mm, thickness 0.5 mm) is made of 90 ± 2% adsorbent particle (sodium salt of iminodiacetic acid) and 10 ± 2% polytetrafluoroethylene as an inert carrier. It is situated in a special device for filtration (3 M Company) connected by a peristaltic pump Barrington, Illinois 6.

TABLE I Temperature program for GTA-100 (Varian SpectrAA-640Z) and for HGA-600 (Perkin-Elmer Zeeman 3030)

Step	*Varian 640Z*	*Perkin Elmer 3030*	
		Aqueous phase	*Organic extracts*
Drying			
Temperature (°C)	100	120	120
Ramp time (s)	45	10	15
Hold time (s)	10	10	15
Internal gas flow (mL $\min^{-1}$)	3000	300	300
Pre-treatment			
Temperature (°C)	250	250	400
Ramp time (s)	15	5	10
Hold time (s)	2	10	10
Internal gas flow (mL $\min^{-1}$)	3000	300	300
Atomization			
Temperature (°C)	1800	1200	1100
Ramp time (s)	1	0	0
Hold time (s)	2	3	3
Internal gas flow (mL $\min^{-1}$)	0	0	0
Cleaning			
Temperature (°C)	2500	2300	2300
Ramp time (s)	2	2	2
Hold time (s)	2	3	3
Internal gas flow (mL $\min^{-1}$)	3000	300	300

Reagents and Standards

All chemicals used were of the highest analytical grade except for the surfactants: sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC) and cetyltrimethylammonium bromide (CTAB). Deionized redistilled water was used throughout. Standard solutions were prepared from Titrisol (Merck) solution (1 g/L). Intermediate standard solutions were prepared daily by appropriate dilution. Crystalline home-synthesized sodium heptyldithiocarbamate, NaHpDTC, served for preparation of a 0.1 mol/L solution of heptyldithiocarbamate, $HpDTC^-$, in 96% ethanol. A 2% (w/w) solution of tetramethylenedithiocarbamate, $TMDTC^-$, was made by dissolving crystalline NH_4TMDTC (Merck) in water. Surfactants were prepared as 0.5% solutions in 95% ethanol (NaDDS, NaOL, BTC, CTAB) and in 99.7% propan-2-ol (NaPL, NaST). pH values were adjusted by using acetate buffer (pH 5.5–5.7), KOH solutions (2.5 and 10%, w/w) and HNO_3 solution (0.1 mol/L). Ionic strength (I_c) for flotation was regulated with a saturated solution of KNO_3. A 0.1 mol/L NH_4NO_3 solution served to transfer the contents of the beaker into the flotation cell.

Flotation Procedures

The flotation procedures for the two recommended collectors differ in some details.

Flotation using $Pb(HpDTC)_2$

A saturated solution of KNO_3 (10 mL) and 15 mg of Pb(II) were added to a 1-L aliquot of acidified water sample. The pH was adjusted to 6.5 using KOH solutions.

Next, a solution of $HpDTC^-$ (0.1 mol/L; 6 mL) was introduced. A white precipitate of $Pb(HpDTC)_2$ was formed. After 15-min stirring (induction time [19]), NaDDS (1 mL) was added and the contents of the beaker were transferred quantitatively into the flotation cell with the aid of a small portion of NH_4NO_3 solution. A stream of air bubbles (50 mL/min) was passed through the system for 1 min, lifting the precipitate particles to the top of the liquid column. The glass pipette-tube was immersed into the cell through the froth layer. The liquid phase in the cell was removed via the pipette-tube by vacuum. Then, the solid phase was decomposed by 2.5 mL hot conc. HNO_3. The clear colourless solution was drawn out through the porous bottom into a 25-mL volumetric bottle. The cell and pipette-tube were washed with three portions of 5 mL 4 mol/L HNO_3, the flask was filled to the mark with redistilled water, and the sample was ready for ETAAS.

Flotation using $Co(HMDTC)_3$

Saturated KNO_3 solution (6 mL) and 10 mg of Co(II) were introduced into the system. The pH was carefully adjusted to 9.0 using KOH solutions and a blue colloidal precipitate of hydrated cobalt(II) oxide, $CoO \cdot xH_2O$, was formed. After 5-min stirring, a 0.1 mol/L solution of $HpDTC^-$ (6 mL) was introduced. During the formation and growth of the product particles, Co(II) oxidized to Co(III) and a green precipitate of $Co(HpDTC)_3$ occurred [16,17]. After 15-min stirring, NaDDS (1 mL) was added and the contents of the beaker were transferred quantitatively into the flotation cell. The subsequent procedure was the same as for $Pb(HpDTC)_2$, except that, because the chelate complex $Co(HpDTC)_3$ is slightly stronger than $Pb(HpDTC)_2$, more hot conc. HNO_3 (5 mL) is used for decomposition of the solid phase.

Extraction Procedures

Solid-phase Extraction with Empore Disk

The new disk was washed with 20 mL redistilled water, followed by 20 mL 3 mol/L solution of HNO_3 and again by 50 mL redistilled water. To convert it to its more active ammonia form, 50 mL 0.1 mol/L acetate buffer (pH 5.5–5.7) were passed. Finally the disk was washed again with 20 mL of redistilled water and it was ready for sorption.

A 1-L sample of natural water buffered to pH 5.5–5.7 was introduced in the glass funnel. When the whole sample had passed (rate 20 mL/min) through the disk, 20 mL of redistilled water were added and the disk was washed and dried by vacuum. The subsequent elution was performed by 20 mL of 3 mol/L HNO_3 (rate 2 mL/min). The eluate was collected and Cd was determined by ETAAS.

Sorption in Column with Home-made Sorbent

The HMDTC-loaded polyurethane (PU) foam pieces (approx. 0.3 g), prepared according to the method of Arpadjan *et al.* [18], was transferred into a disposable syringe after packing a small wad of cotton-wool at the end of the column and covering it with a disk of filter paper. A sample of 150 mL natural water buffered to pH 5.0–6.0 was passed through the sorbent column using a peristaltic pump at a rate of 2 mL/min. Elution was performed with 3 mL methylisobutilketone (MIBK). The atomic absorption signals of Cd in this solution were measured against organic calibration standards. A new column was prepared for each experiment.

Liquid–Liquid Extraction Procedure

To 20 mL of water sample, 2 mL acetate buffer (pH 5.0–6.0), 2 mL 2% (w/w) solution of $TMDC^-$ and 2 mL MIBK were added. Extraction was performed for 2 min. Then, 10 μL of the organic phase obtained were introduced in to the graphite atomizer and measured against organic calibration standards.

Water Sampling

The new flotation methods were used for cadmium determination in several spring, well and tap waters with high hardness. Sampling was performed according to the European Commission Guidelines. Water samples were conserved with 2 mL conc. HNO_3 per litre (final pH around 2).

RESULTS AND DISCUSSION

Effect of pH on Flotation Separation

This parameter must be performed with special care, because variation of the solution pH can induce coagulation, precipitation or hydrolysis of ionic species involved in the separation process.

The effect of pH on cadmium flotation was studied within the pH range 3.0–10.0 at constant $I_c = 0.02$ mol/L. For this purpose a series of 1-L solutions containing 25 ng cadmium were floated by $Pb(HpDTC)_2$ and $Co(HpDTC)_3$ separately. The mass of lead and cobalt, respectively, was kept constant (10 mg), as well as the amount of $HpDTC^-$ (0.3 mmol). NaDDS was added as surfactant.

The highest cadmium recoveries using $Pb(HpDTC)_2$ were reached at pH 6.0–6.5, where the recoveries are 93.5%. The R/pH curves in Fig. 1 show that the flotation by $Co(HpDTC)_3$ could not be carried at $pH < 7$, because there was no precipitate within the pH range 3–7. The highest recoveries of analyte (94.2%) reached by this collector were within the pH range 9.0–9.5, Therefore, pH 6.5 was selected for further investigations using $Pb(HpDTC)_2$ and pH 9.0 for $Co(HpDTC)_3$.

Influence of $Pb(HpDTC)_2$ and $Co(HpDTC)_3$ on the Flotation Process

During the flotation process Cd^{2+} ions are removed from the aqueous system by incorporation in the collector precipitate mass. There are two mechanisms of incorporation of trace metal ions into the precipitate. The first is the adsorption on the surface of the collector particles, including ion exchange of Pb^{2+} or Co^{3+} with Cd^{2+}, and the second is the occlusion of Cd^{2+} into the structure of the collector particles during their formation and growth. The amounts of Pb^{2+} or Co^{3+} and $HpDTC^-$ influence the rate of formation of $Pb(HpDTC)_2$ and $Co(HpDTC)_3$, the formation of collector particles, and as a consequence the collection of Cd^{2+}. In order to investigate the influence of lead and cobalt mass, and the amount of dithiocarbamate on the flotation

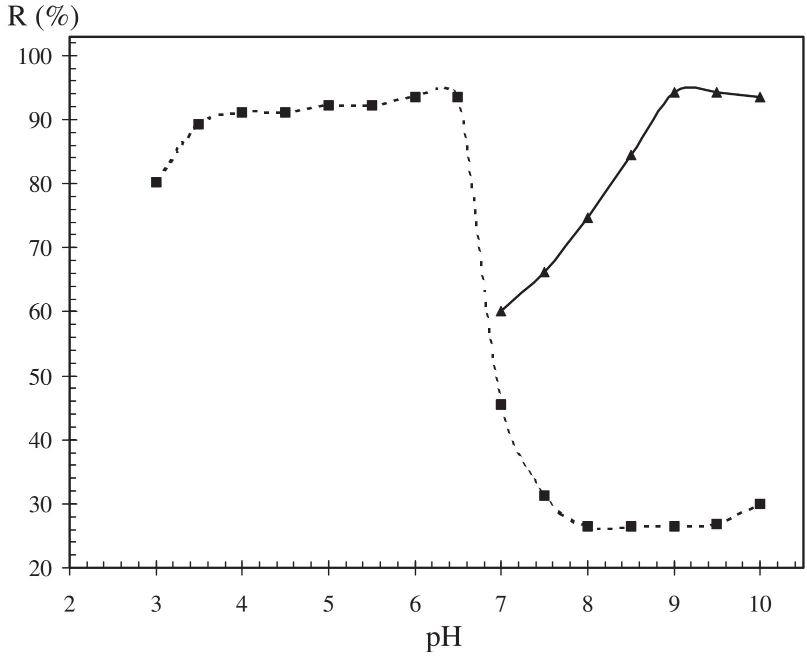

FIGURE 1 Effect of solution pH on cadmium recoveries, *R* (%), during flotation by $Pb(HpDTC)_2$ (---■---) and by $Co(HpDTC)_2$ (—▲—).

process, 1-L redistilled water samples were spiked with 25 ng of Cd and were floated at the previously determined optimum pH values [6.5 for $Pb(HpDTC)_2$ and 9.0 for $Co(HpDTC)_3$]. To each solution different quantities of lead and cobalt (5.0–15.0 mg) were added. The amount of $HpDTC^-$ varied from 0.2 to 0.9 mmol. The ionic strength I_c (0.02 mol/L) was kept constant. The data for these investigations are displayed in Fig. 2 for $Pb(HpDTC)_2$ and in Fig. 3 for $Co(HpDTC)_3$. Cd reaches greatest flotation recoveries (93.1%), if the lead mass is 15 mg together with 0.6 mmol $HpDTC^-$ per 1 L. In the case of $Co(HpDTC)_3$ 10 mg of cobalt and 0.6 mmol $HpDTC^-$ per 1 L (Fig. 3) were necessary for the highest Cd recoveries of 96.5%.

Selection of Surfactant

Several foaming reagents were tested under conditions optimized as described in previous sections. The cationic surfactants (BCT and CTAB) foamed very well, but no flotation occurred. The anionic surfactants, having the opposite charge of $Pb(HMDTC)_2$ and $Co(HMDTC)_3$ particles, were shown to be more effective (Table II). Since the recoveries obtained by NaDDS were the highest with both collectors, it was selected as the most appropriate surfactant for both procedures.

Interferences of Matrix Elements on ETAAS Measurement of Cd

The interferences of matrix elements Co and Pb on ETAAS measurement of Cd were checked. The experiments performed indicated that masses of lead and cobalt up to

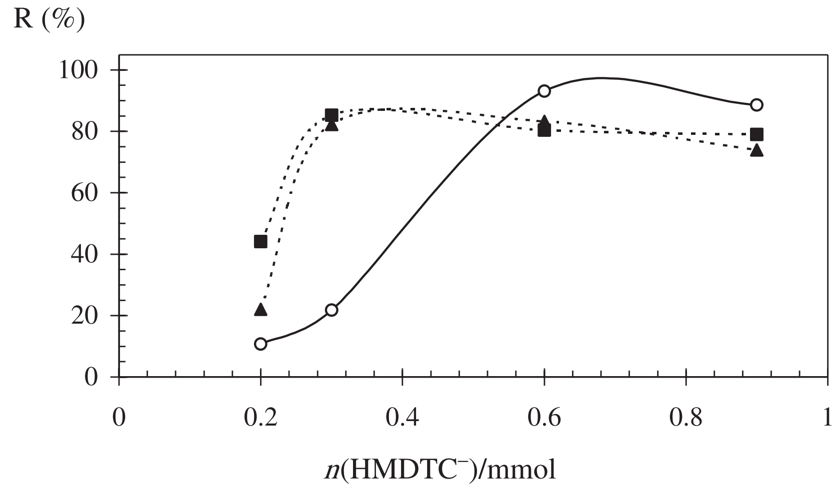

FIGURE 2 Influence of $n(\mathrm{HMDTC}^-)$ on cadmium flotation recoveries during flotation by $\mathrm{Pb(HMDTC)_2}$. (- - -■- - - 5.0 mg Pb; - - - ▲ - - - 10.0 mg Pb; —○—15.0 mg Pb).

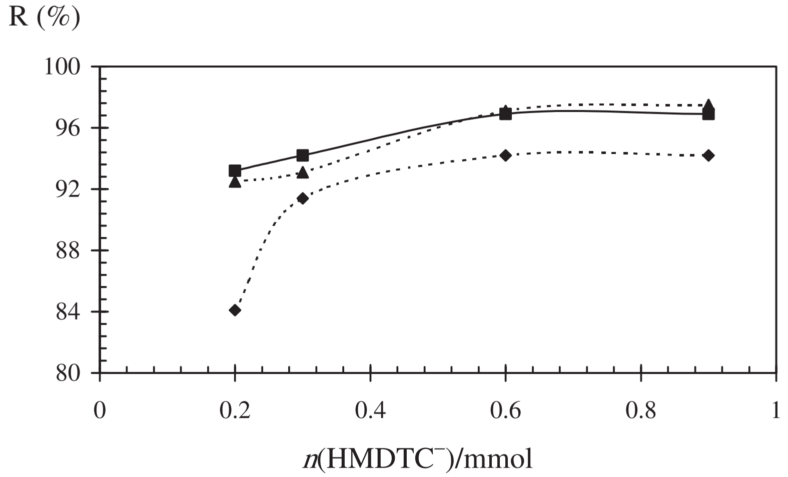

FIGURE 3 Influence of $n(\mathrm{HMDTC}^-)$ on cadmium flotation recoveries during flotation by $\mathrm{Co(HMDTC)_3}$. (- - - ◆- - -5 mg Co; —■—10.0 mg Co; - - - ▲ - - - 15.0 mg Co).

50 mg present in the final solutions preconcentrated by flotation did not influence ETAAS measurements of Cd.

Optimization of the Conditions for Column Solid-phase Extraction with Empore Disks

The processes of sorption and elution were studied separately in order to define optimal conditions for each of them. The concentration of Cd was measured in the effluents obtained after sorption and in the eluates after desorption. Redistilled water was enriched with 25 ng/L Cd and used as the model solution.

TABLE II Selection of surfactant

γ (*Cd*)[b] ng/L	*R* (%)					
	BCT[c]	*CTAB*[c]	*NaDDS*[d]	*NaOL*[d]	*NaPL*[d]	*NaST*[d]
Flotation with $Pb(HpDTC)_2$[a]						
25	Foam, no	Foam, no	93.3	88.3	48.3	60.0
50	Flotation	Flotation	92.4	86.6	65.0	75.0
Flotation with $Co(HpDTC)_3$[e]						
25	Foam, no	Foam, no	98.2	94.6	98.2	93.8
50	Flotation	Flotation	96.4	96.4	95.2	94.6

[a] pH = 6.5, $I_c = 0.02$ mol/L, 15 mg Pb, 0.6 mmol $HpDTC^-$.

[b] Mass concentration of cadmium in final solution concentrated by flotation.

[c] Cationic surfactant.

[d] Anionic surfactant.

[e] pH = 9.0, $I_c = 0.02$ mol/L, 10 mg Co, 0.6 mmol $HpDTC^-$.

The most important parameter for the process of sorption is pH. At pH 2 the degree of sorption is 80 ± 5%, at pH 4.5 degree of sorption is 94 ± 4%, while at pH 5.5–5.7 the degree of sorption is 98 ± 2%. Quantitative sorption of Cd could be obtained even if the sample solution was passed through the disk at a rate of 20 mL/min and the degree of sorption did not depend on the volume of sample solution up to 2 L.

Solutions of HNO_3 (3 mol/L), as well as EDTA (free acid, 0.2 mol/L) were tested as possible eluents for Cd. It was observed that in this case the rate at which the eluent passes through the disk is a very important parameter for quantitative elution of Cd and should not exceed 4 mL/min. Quantitative elution of sorbed Cd is achieved with 20 mL HNO_3 or 15 mL EDTA as eluents with elution rates in the range 2–2.5 mL/min. Calibration against an aqueous standard calibration curve is proposed.

Water Analysis

The accuracy of the two newly developed procedures using $Pb(HpDTC)_2$ and $Co(HpDTC)_3$ was checked by the added/found method and by analyzing certified reference material. Results from the added/found method (applied to the real samples) for flotation procedures are presented in Table III. As can be seen recoveries between 93 and 100% were achieved. Therefore calibration against an aqueous standard calibration curve is proposed. Results achieved proved that Cd could be preconcentrated successfully by flotation, using two new flotation reagents, prior to ETAAS measurement.

The limit of detection (LOD) of ZETAAS was estimated as three times the standard deviations of the blanks. It was found that LOD using $Pb(HpDTC)_2$ as collector is 4.8 ng/L while precision (expressed as relative standard deviation, s_r) of the method was in the range 2–5% for Cd concentrations up to 100 ng/L. LOD for $Co(HpDTC)_3$ is 3.0 ng/L and the precision ranges from 3 to 6%.

The results of water analysis obtained by flotation and independent comparative extraction methods are presented in Table III. In all cases very good agreement was achieved.

Cadmium in SRLS-3 reference material was determined using all the proposed procedures (Table IV) and results obtained agree well with the certified value (Student's t-test, 95%).

TABLE III Results from ETAAS determination of Cd (ng/L) in tap and well water samples obtained by using different separation and preconcentration procedures

Water samples	*Flotation*							*Solid-phase extraction*		*Liquid–liquid extraction*
	Determined, (mean ± s)		*Added* (μg/L)	*Found, (mean ± s)*		*Recovery* (%)		*Empore disks*	*Home-made sorbents*	
	$Pb(HpDTC)_2$	$Co(HpDTC)_2$		$Pb(HpDTC)_2$	$Co(HpDTC)_2$	$Pb(HpDTC)_2$	$Co(HpDTC)_2$	(*mean* ± *s*)	(*mean* ± *s*)	(*mean* ± *s*)
Pantelejmon 15.2 DH°, pH 7.45	25 ± 2	21 ± 3	25	48 ± 3	47 ± 3	96 ± 3	102 ± 2	28 ± 2	20 ± 6	30 ± 3
Sreden Izvor 17.7 DH°, pH 7.20	28 ± 3	26 ± 2	25	50 ± 3	49 ± 3	94 ± 3	96 ± 4	30 ± 2	26 ± 4	30 ± 2
Rašče 12.3 DH°, pH 7.17	46 ± 3	51 ± 2	25	70 ± 3	73 ± 4	99 ± 3	96 ± 3	50 ± 2	42 ± 6	55 ± 5
Demir Kapija 8.8 DH°, pH 7.47	–	11 ± 1	25	–	35 ± 2	–	97 ± 3	12 ± 1	13 ± 2	14 ± 3
Veles 1.9 DH°, pH 6.56	66 ± 3	64 ± 3	25	90 ± 3	90 ± 2	99 ± 2	101 ± 2	50 ± 2	40 ± 6	56 ± 5

DH° (Deutsche Häarte) – water hardness in German degrees.

TABLE IV Analysis of certified reference material SRLS-3[a]

Preconcentration procedure	*Cd* [*mean* ± *s*] (μg/*L*)	*RSD* (%)	$t_{calc, n=5}$
Flotation with $Pb(HpDTC)_2$	0.011 ± 0.002	6.5	2.4
Flotation with $Co(HpDTC)_3$	0.012 ± 0.001	5.2	1.9
Empore disks	0.012 ± 0.001	8.3	1.3
Home-made sorbent	0.014 ± 0.002	14.2	1.0
Liquid–liquid extraction	0.011 ± 0.001	7.6	2.6

$t_{\mathrm{tabl}, n=5} - 2.72$

[a] Certified value: Cd, 0.013 ± 0.002 μg/L.

CONCLUSION

The main conclusion from the investigations performed is that $Pb(HpDTC)_2$ and $Co(HpDTC)_3$ can be applied as flotation collectors for Cd separation and preconcentration. $Pb(HpDTC)_2$ and $Co(HMDTC)_3$ were shown as compounds with a significant hydrophobicity, which is an important criterion for successful flotation. That can be evidenced by the excellent recoveries of cadmium (higher than 95.0%) obtained by using each of them. The analytical procedure developed permits determination of nano concentrations of Cd in natural waters.

However, from the practical point of view, it is interesting to compare the reproducibility, preconcentration factor, analysis time and detection limits of the proposed flotation methods. Both flotation procedures require a high volume of water sample for analysis, but show good reproducibility and repeatability and a high preconcentration factor, using very cheap reagents and simple apparatus. With respect to analysis time the procedure using $Pb(HpDTC)_2$ is a little faster, because it needs only one induction time (15 min), while the procedure with $Co(HpDTC)_3$ needs two induction times (5 + 15 min). To achieve quantitative flotation of cadmium it is necessary to apply 15 mg of lead, while the mass of cobalt required is smaller (10 mg). However, the quantity of metal used is far lower than the critical mass of lead and cobalt that could interfere with cadmium absorbance during its ETAAS measurement. The procedure using $Co(HpDTC)_3$ has lower s, LOD and s_r than the procedure using $Pb(HpDTC)_2$. Comparing the performances of these two new flotation methods it can be concluded that the method with $Co(HpDTC)_3$ has some advantages for the determination of trace quantities of cadmium.

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