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LEAD(II) AND COBALT(III) HEPTHYLDITHIOCARBAMATES AS NEW COFLOTATION REAGENTS FOR PRECONCENTRATION OF CADMIUM BEFORE ITS ETAAS DETERMINATION

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Abstract.

Two collectors, lead(II) hepthyldithiocarbamate, $Pb(HPDTC)_2$, and cobalt(III) hepthyldithiocarbamate, $Co(HPDTC)_3$, for colloidal precipitate flotation of Cd in traces from water matrices were proposed. After flotation Cd was determined by electrothermal atomic absorption spectrometry (ETAAS). The optimal conditions for effective Cd flotation performed separately by each collector were established. The results of ETAAS analyses are compared with those obtained by the method of inductively coupled plasma-atomic emission spectrometry. The ETAAS limit detection of Cd by $Pb(HPDTC)_2$ is 0.0048 μg/l, while by $Co(HPDTC)_3$ is 0.003 μg/l.

Keywords: Cadmium, water, determination, electrothermal atomic absorption spectrometry, coflotation, lead(II) hepthyldithiocarbamate, cobalt(III) hepthyldithiocarbamate

1. Introduction

Because the level of Cd in uncontaminated fresh water is very low, its determination has to be performed by analytical methods with very low detection limits. Atomic absorption spectrometry (AAS) is very useful for this purpose, but in the case when the Cd concentration is extremely low, a previous preconcentration step is necessary. Recently much attention has been paid to the preconcentration of heavy metals from water matrices by flotation techniques based on adsorptive bubbles [1-3]. Among them the method of colloid precipitate flotation, called coflotation, has show as the most advantageous and helpful due to its rapidity and excellent recoveries of analytes. Many factors influence to perform a proper coflotation, but an important role has the collector with its colloid nature. In this work, we present two dithiocarbamate salts, $Pb(HPDTC)_2$ and $Co(HPDTC)_3$, as new possible reagents for coflotation of Cd traces prior to ETAAS determination.

2. Experimental

Apparatus and reagents. AAS determinations were made with Varian SpectrAA 640Z Zeeman atomic absorption spectrometer and Cd hollow cathode lamp (Table 1). All pH readings were carried out with Iskra pH−Meter MA 5705 with combined glass electrode (Iskra Model 0101). Inductively coupled plasma-atomic emission spectrometric (ICP-AES) measurements were made by Varian Liberty 110. The flotation cell, which served to separate the solid precipitate from water phase by means the air bubbles was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate gas bubbling. Stock solutions of Cd (1 g/l), Pb (10 g/l) and Co (10 g/l) were nitrates. By diluting these stock solutions before each investigation series of standards were freshly prepared. Sodium hepthyldithiocarbamate, NaHPDTC, was made as 0.1 mol/l in 96 % ethanol. The surfactant sodium dodecylsulfate, NaDDS, was made as 0.5 % alcoholic solution. The pH was regulated by HNO_3 (0.1 mol/l) and of KOH (10 %) solutions. Ionic strength (I_c) was adjusted by a saturated solution of KNO_3.

Table 1. Instrumental parameters for AAS determination of cadmium

Wavelength	228.8 nm
Spectral slit	0.5 nm
Lamp current	4 mA
Dry	120 °C; 20 s
Pyrolysis	250 °C; 8 s
Atomize	1800 °C; 2 s

Procedure by $Pb(HPDTC)_2$. A combined glass electrode was dipped into 1-l acidified water sample. After adding 6 ml of saturated KNO_3 solution, 15 mg of Pb(II) was put into the beaker. The medium pH was adjusted to 6.5 by KOH solutions and 6 ml 0.01 mol/l solution of $HPDTC^-$ was added to the system. A white precipitate of $Pb(HPDTC)_2$ was formed. After stirring for 15 min, 1 ml NaDDS was added. Then, the content of the beaker was transferred quantitatively into the flotation cell with small portions of 0.1 mol/l NH_4NO_3.The following coflotation procedure is the same as previously described [4-7].

Procedure by $Co(HPDTC)_3$. After adding 6 ml of saturated KNO_3 solution into 1-l water sample, 10 mg of Co(II) was introduced into the system. Monitoring the pH value on the pH–Meter display the medium pH was carefully adjusted to 9.0 by KOH solutions and the blue colloid precipitate was formed. After stirring 5 min, 6 ml 0.01 mol/l solution of $HPDTC^-$ was added to the system. During the formation and growing of product particles, Co(II) oxidizes to Co(III) and a green precipitate of $Co(HPDTC)_3$ occurs [8]. After stirring 15 min, 1 ml NaDDS solution was added and the content of the beaker was transferred into the flotation cell. The following coflotation procedure is the same as previously described [4-7].

3. Results and discussion

Effect of pH. The medium pH influences on flotation recovery of each analyte and so this effect on Cd flotability was studied within pH range of 3 to 10 at constant I_c = 0.02 mol/l, floating series of solutions containing 25 μg Cd per 1 l. The mass of Pb *i.e.* Co (10 mg) was kept constant, as well as the amount of $HPDTC^-$ (0.3 mmol). The highest Cd recoveries using $Pb(HPDTC)_2$ (93.5 %) were reached at pH 6.5 (Fig. 1). The flotation by $Co(HPDTC)_3$ could not be performed at pH's below 7, because there was not any precipitate within pH range of 3 to 7. The highest Cd recoveries using $Co(HPDTC)_3$ (94.2 %) was obtained at pH 9.0 (Fig. 1).

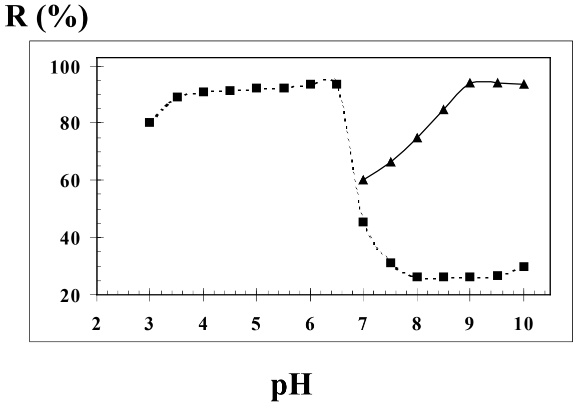

Fig. 1 Cd flotation recovery dependence on pH; ---■--- $Pb(HPDTC)_2$ —●— $Co(HPDTC)_3$

Influence of Pb and Co mass. This influence was investigated by performing series of flotations by addition of different amounts of Pb (2.5–30.0 mg) *i.e.* Co (1.0–20.0 mg) to the working solutions containing 25 μg Cd per 1 l at pH's ascertained in the previous section. The ionic strength and amount of $HPDTC^-$ was kept constant (I_c = 0.02 mol/l, 0.3 mmol $HPDTC^-$). The data show that the increasing of Pb *i.e.* Co mass, influences on Cd flotation efficiency. Satisfactory Cd recoveries were reached applying 15 mg Pb (91.8 %) *i.e.* 10 mg Co (94.7 %) (Table 2).

Table 2. Influence of Pb and Co mass on Cd flotation

γ(Pb) mg/l	R (%)	γ(Co) mg/l	R (%)
	γ(Cd)/1μg/ml		γ(Cd)/1μg/ml
2.5	47.5	1.0	63.0
5.0	83.8	2.0	66.0
10.0	91.8	5.0	89.1
15.0	91.9	10.0	94.7
20.0	15.2	15.0	94.5
30.0	5.8	20.0	94.5

Influence of n(HPDTC⁻). Eight series of flotations were performed by addition of different amounts of HPDTC⁻ (0.13-0.60 mmol) to 1-l solutions containing 25 μg Cd. The first four series of standard solutions, floated by $Pb(HPDTC)_2$ at a constant pH (6.5) and I_c (0.02 mol/l), contained 2.5 mg, 5 mg, 10 mg and 15 mg of Pb. The second four series of standard solutions, floated by $Co(HPDTC)_3$ at a constant pH (9.0) and I_c (0.02 mol/l), contained 5 mg, 10 mg, 15 mg and 20 mg of Co. The data show that if 15 mg Pb together with 0.6 mmol HPDTC⁻ per 1 l were applied, the flotation recoveries of Cd could be 93.1 % (Fig. 2). In the case $Co(HPDTC)_3$, 10 mg of Co and 0.6 mmol HPDTC⁻ per 1 l (Fig. 3) were necessary for Cd flotation recoveries of 96.9 %.

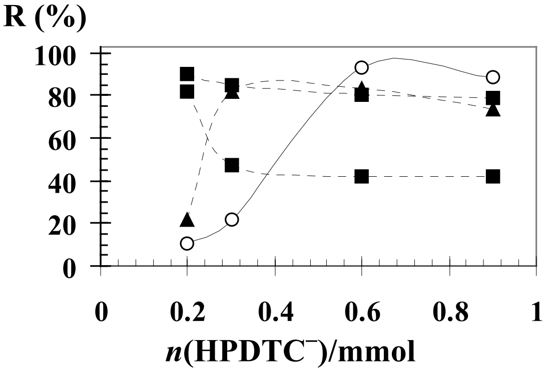

Fig. 2. Cd recoveries dependence on *n*(HPDTC⁻) during the flotation with $Pb(HPDTC)_2$; *m*(Pb): --◆-- 2.5 mg; --■-- 5 mg; --▲-- 10 mg; —○— 15 mg Pb

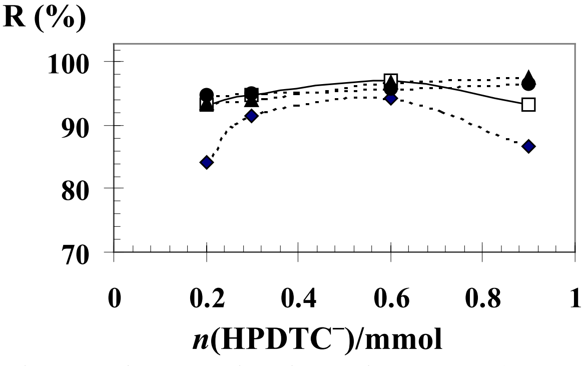

Fig. 3. Cd recoveries dependence on *n*(HPDTC⁻) during the flotation with $Co(HPDTC)_3$ *m*(Co): --◆-- 5 mg; —— 10 mg; --▲-- 15 mg; --●-- 20 mg Pb

Applicability of the methods. To verify the methods, tap and well waters with divers water hardness from the city of Skopje were analyzed. Standard addition method was used. To prevent the possible hydrolytic precipitation of some mineral salts, each 1-l water sample was acidified by few ml conc. HNO_3 at pH 2.7-3. After flotation waters were 40-fold concentrated and then Cd was determined by ETAAS. The recoveries of Cd obtained by the proposed method with $Pb(HPDTC)_2$ (94.4−102.7 %), as well as by $Co(HPDTC)_3$ (94.1−101.7 %) evidence that its preconcentration and separation was satisfactory (Tables 2,3). Standard deviation by $Pb(HPDTC)_2$ as collector was 0.0016 μg/l Cd, limit of detection 0.0048 μg/l Cd, while relative standard deviation 2.4 %. Standard deviation applying $Co(HPDTC)_3$ was 0.001 μg/l Cd, limit of detection 0.003 μg/l Cd and relative standard deviation 1.31 %. The data show that ETAAS results agree with those obtained by the independent method of ICP-AES.

4. Conclusion

The present paper proved that Cd can be preconcentrated successfully by coflotation using $Pb(HPDTC)_3$, as well as $Co(HPDTC)_3$ prior to ETAAS. The pH of the media, as well as the amounts of Pb, Co and $HPDTC^-$, as the constituents of the collectors investigated, have the effect on Cd flotation recoveries. $Pb(HPDTC)_3$ and $Co(HPDTC)_3$ were shown as collectors with a significant hydrophobility, which is an important criterion for a successful coflotation. That can be evidenced by the excellent recoveries of Cd obtained by means of each collector. The recommended preconcentration procedures are rapid (about 25-30 min). They extend the range of conventional AAS determination of Cd. The necessary equipment for flotation is simple and inexpensive. The use of a little amount of surfactant and tiny air bubbles necessary to perform the proper coflotation cannot permit some serious contamination risks, which could be manifested by the high blank values.

Table 2. The ETAAS results of Cd determinations preconcentrated by $Pb(HPDTC)_2$

Sample of water	ETAAS				ICP-AES[a]
	Added μg l^{-1} Cd	Estimated μg l^{-1} Cd	Found μg l^{-1} Cd	R (%)	Found μg l^{-1} Cd
Pantelejmon	-	-	0.025	-	0.024
15.17 DH^{o}[b]	0.0250	0.0500	0.048	96.0	
pH = 7.45	0.0625	0.0875	0.088	100.6	
Sreden Izvor	-	-	0.028	-	0.030
17.65 DH^{o}	0.0250	0.0530	0.050	94.4	
pH = 7.2	0.0625	0.0905	0.093	102.7	
Rašče	-	-	0.046		0.043
12.25 DH^{o}	0.0250	0.0710	0.071	100.0	
pH = 7.17	0.0625	0.1085	0.108	99.5	

[a] Results of comparative ICP–AES determination of Cd. The samples for ICP–AES were enriched by evaporation.

[b] DH (*Deutsche Härte*) German degree of water hardness.

Table 3. The ETAAS results of Cd determinations preconcentrated by $Co(HPDTC)_3$

Sample of water	ETAAS				ICP-AES
	Added μg l^{-1} Cd	Estimated μg l^{-1} Cd	Found μg l^{-1} Cd	R (%)	Found μg l^{-1} Cd
Pantelejmon	-	-	0.021	-	0.024
15.17 DH^{o}	0.0625	0.0835	0.079	94.6	
pH = 7.45	0.1250	0.1460	0.139	101.7	
Sreden Izvor	-	-	0.020	-	0.030
17.65 DH^{o}	0.0625	0.0825	0.080	97.0	
pH = 7.2	0.1250	0.1450	0.139	95.9	
Rašče	-	-	0.044		0.043
12.25 DH^{o}	0.0625	0.1065	0.101	94.8	
pH = 7.17	0.1250	0.1690	0.159	94.1	

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