XIII_1728

Cobalt(III) Tetramethylenedithiocarbamate as a New Flotation Collector for Preconcentration and Separation of Lead Determinated by Zeeman ETAAS

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Abstract

A fast method for the preconcentration of lead in fresh water samples using colloidal precipitate flotation is described. Co(III) tetramethylenedithiocarbamate, $Co(TMDTC)_3$, was used as a flotation collector formed of Co(II) and $TMDTC^-$ anion. During the reaction, Co(II) oxidizes in Co(III) and as a product of the reaction green amorphous precipitate of $Co(TMDTC)_3$ is obtained, which coprecipitates lead traces from the water matrix. A successful separation of lead was attained at the correct optimized pH of the system, mass of Co, amount of $TMDTC^-$, type of tenside and other important experimental parameters. After flotation separation from the liquor, the solid sublate containing traces of lead was dissolved by nitric acid and the determination was performed by using Zeeman electrothermal atomic absorption spectrometry (ZETAAS). The results of the ZETAAS analysis are validated with the method of standard additions and by the application of the method to the water reference material.

Key words: Lead, fresh water, flotation, cobalt(III) tetramethylenedithiocarbamate, ZETAAS

Introduction

Lead has no biological role and is very toxic to humans and other organisms (Klassen *et al*., 1996; Hayes A.W. (ed.), 2001; WHO, 2003). This heavy metal affects the gut, central nervous system and causes anaemia. It can damage nervous connections (especially in young children) and cause blood and brain disorders. Long term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can cause nephropathy and colic-like abdominal pains. Lead has many anthropogenic sources. It was once commonly used in automobile fuels, paint and plumbing. Although these uses have decreased, lead is still used in batteries and alloys, and it is found in sewage wastes and in fossil fuel combustion products. Therefore this highly toxic element is an important chemical of concern in the environment and it is very important to follow its concentration in fresh water (drinking, river or lake).

The most used method for lead determination in water matrices is atomic absorption spectrometry (AAS). However, if the level of lead in water samples is very low, their direct determination is impossible without any previous step of preconcentration (Mizuike & Hiraide, 1982; Mizuike, 1983; Zolotov & Kuzmin, 1990; Caballero *et al*., 1999). Recently, significant attention has been paid to flotation techniques as enrichment methods for heavy metals before their AAS. Among several flotation techniques colloid precipitate flotation, so called coflotation, is the most useful. Coflotation has the advantages in relation to the other conventional carrier precipitation techniques, as coprecipitation, liquid-liquid extraction, ion-exchange etc. (Mizuike & Hiraide, 1982; Mizuike, 1983; Zolotov & Kuzmin, 1990; Caballero *et al*., 1999). Many factors influence the performance of a proper flotation. During the performance of the most frequently used precipitate flotation, the primary condition is the selection of the suitable collector. The bulky hydrated metal oxides, as hydrated iron(III) oxide, hydrated aluminium(III) oxide etc., were the first reagents used for those purposes. Our experience has shown that the addition of dithiocarbamate anions to water systems containing metal cations, yield metal dithiocarbamate salts, which could play a role of precipitate collector with very high flotation effectiveness (Čundeva & Stafilov, 1997; Čundeva *et al*., 2000; Pavlovska *et al*., 2001; Stafilov *et al*., 2001; Pavlovska *et al*., 2000; Bundalevska *et al*., 2005; Zajkova Paneva *et al*., 2005; Paneva *et al*., 2007; Čundeva *et al*., 2007; Bakreska Kormušoska *et al*., 2009). During the precipitation of these dithiocarbamate salts metal traces present in the aqueous solution incorporate in their structure forming hydrophobic solid phase surface that is the most important criterion for the successful flotation by air bubbles. The aim of this work is to present cobalt(III) tetramethylenedithiocarbamate, $Co(TMDTC)_3$, as a new flotation collector of lead traces. Establishing previously the experimental conditions of separation procedure, this work gives a clear insight into the degree of lead recoveries by $Co(TMDTC)_3$.

UDK: 628.161.2:546.815

Materials and Methods

Apparatus

The flotation was performed in a flotation cell, consisting of a glass cylinder (4 x 105 cm) with a sintered glass disk (porosity No.4) (Stafilov *et al*., 2001). The pH measurements of the solutions during the coprecipitation were carried out with a digital Iskra pH-meter MA 5705 using a combined glass electrode (Iskra M 0101). The atomic absorption spectrometric (AAS) measurements were performed with a Zeeman atomic absorption spectrophotometer Varian SpectrAA 640Z. A lead hollow cathode lamp was used as a primary source. Optimal instrumental parameters for ETAAS determination are given in Table 1.

Table 1: Instrumental parameters for lead determination by Zeeman ETAAS

Parameter	Pb
Wavelength	283.3 nm
Spectral width slit	0.5 nm
Lamp current	5.0 mA
Calibration mode	Peak area
Background correction	Zeeman
Dry	
Temperature	120 °C
Increasing time	30 s
Holding time	10 s
Pyrolysis	
Temperature	500 °C
Increasing time	5 s
Holding time	3 s
Atomising	
Temperature	2100 °C
Increasing time	1 s
Holding time	2 s
Cleaning	
Temperature	2300 °C
Increasing time	1 s
Holding time	2 s
Gas	Argon

Reagents and Standards

Stock solution of Co(II) (1 mg/mL) was prepared by dissolving an appropriate amount of $Co(NO_3)_2x6H_2O$ in redistilled water. Stock solution of Pb(II) was delivered by Solution Plus Inc. (USA) with the concentration of 1 mg mL^{-1}. From these solutions other diluted solutions were prepared. Ammonium tetramethylenedithiocarbamate, NH_4-TMDTC, was prepared as 0.1 mol/L solutions in redistilled water.

Foaming reagents tested for the procedure were: sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC) and triton X-100 (TX-100). They were prepared as 0.5 % solutions in appropriate solvents as follows: TX-100 in water, NaDDS and NaOL in 95 % ethanol, NaPL and NaST in 99.7 % propan-2-ol. The pH of media was regulated by a HNO_3 solution (0.1 mol/L) and solutions of KOH (1.25 %, 2.5 % and 10 %). A saturated solution of KNO_3 was used to adjust the ionic strength of the system. To transfer the content of the beaker into the flotation cell a 0.1 mol/L solution of NH_4NO_3 was used.

Flotation Procedure

The first step of the recommended procedures is the coprecipitation of lead traces present in 0.5 L acidified water sample in the solid precipitate of cobalt(III) tetramethylenedithiocarbamate solid precipitation. The second step is the flotation separation of the solid phase of Co(III) dithiocarbamate salt from the aqueous system. The coprecipitation was performed in a beaker, while the flotation separation in a flotation cell:

Coprecipitation: After adding 3 mL of saturated KNO_3 solution into 0.5 L of the water sample analysed, 3 mg of Co(II) [3 mL of 1 mg/mL $Co(NO_3)_2$ stock solution] was added.. For this procedure the medium pH was adjusted to 6.0 by KOH solution. Then 0.3 mmol $TMDTC^-$ (3 mL of 0.1 mol/L solution of NH_4-TMDTC) was introduced. Co(II) oxidized to Co(III) and a green precipitate of $Co(TMDTC)_3$ was formed (Pavlovska *et al*., 2001; Bundalevska *et al*., 2005; Zajkova Paneva *et al*., 2005). After 15 min of stirring, 1 ml of NaDDS solution was added and the content of the beaker was transferred into the flotation cell by using a small amount of the electrolyte solution (0.1 mol/L solution of NH_4NO_3) to avoid dissolution and change the ionic strength of the system.

Flotation: When the investigated system was placed in the flotation cell a stream of fine air bubbles (which effluxes from the bottom of the cell at a rate of 50 mL/min) was passed through the solution for 1 min. The foamy layer was formed at the surface of the liquid phase and the processed solution in the cell was cleared up. The liquid phase was vacuum extracted through pipette immersed into the cell. The solid phase left in the cell was dissolved by 4 mL hot 65 % HNO_3. The cell and the pipette-tube were washed by 3 mL of 4 mol/L HNO_3 and 2 mL hot 65 % HNO_3. The solution created was sucked off through the bottom of the cell and collected in a 25 mL volumetric flask. The flask was filled up to the mark with redistilled water and the sample was ready for ETAAS measurements.

Results and Discussion

The values of pH, mass of Co, amount of TMDTC$^-$ and type of surfactant were optimised for procedures by using the new collector, Co(TMDTC)$_3$. During all optimisation steps the solutions tested contained 0.8 mg/L lead.

Determination of Optimal pH Value

To find an optimal pH value for Pb recovery by Co(TMDTC)$_3$, the pH value was varied in range from 4.0 to 8.0 (Figure 1), while the cobalt mass (3.5 mg) and amount of dithiocarbamate (0.3 mmol TMDTC$^-$) were kept constant. The percentage of recovered Pb over 95 % were obtained within pH values from 5.0 to 8.0. For further investigations by this collector pH 6.0 was chosen as appropriate, because the highest recovery of Pb (101.87 %) was reached at that pH value (Figure 1).

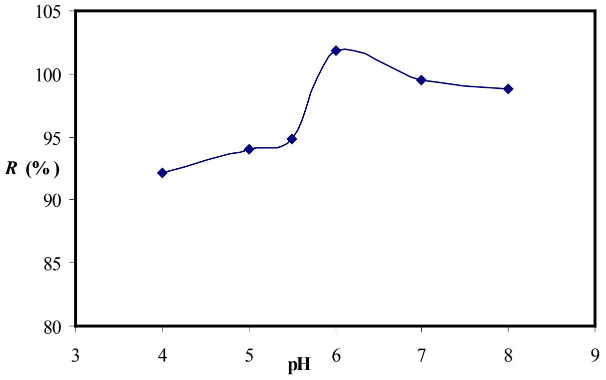

Figure 1: Influence of pH on lead recoveries with Co(TMDTC)$_3$(3.5 mg Co, 0.3 mmol TMDTC$^-$)

Determination of Optimal Co mass

The investigations for determination of optimal Co mass, as Co(HMDTC)$_3$, were performed at a pH value optimised in the previous section (pH = 6.0). The mass of Co was changed from 2 to 4.5 mg. The flotation by this collector could not be performed by using mass of Co larger than 4.5 mg, because of the formation of a dark-pink precipitate in the final concentration by flotation solutions, which made the system inappropriate for AAS measurement. The obtained results are presented in Figure 2. As it can be seen, the optimal lead recovery by Co(TMDTC)$_3$ was 98.0% using 3.5 mg cobalt. Therefore, the amounts of 0.3 mmol TMDTC$^-$ and 3.5 mg Co were selected as optimal.

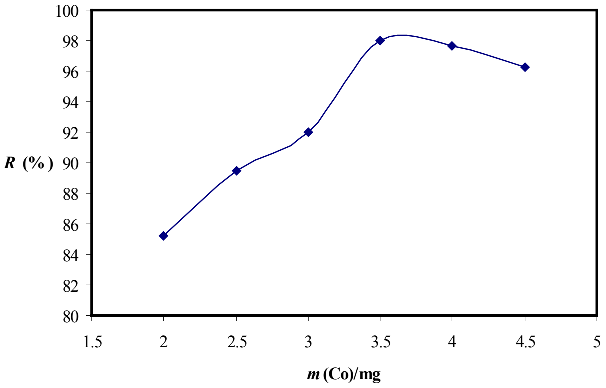

Figure 2: Influence of cobalt mass on lead recovery with Co(TMDTC)$_3$, (pH 6.0, 0.3 mmol TMDTC$^-$)

Determination of Optimal Amount of Dithiocarbamate

To investigate the influence of TMDTC$^-$ amount on lead separation from investigated media, two series of flotation tests were performed at pH 6.0. The first series of standard solutions contains 3.5 mg Co and the second 4.0 mg of Co. The amounts of TMDTC$^-$ were changed from 0.2 to 0.45 mmol. Data of these investigations for both collectors are presented in Figure 3. The highest recovery rate was achieved by 3.5 mg Co and 0.4 mmol TMDTC$^-$ (97.9 % of Pb recovery). Because no significant differences in recovery rates between the two different series were detected, subsequent investigations were performed by using smaller amounts of cobalt and TMDTC$^-$ (3.5 mg Co and 0.4 mmol TMDTC$^-$).

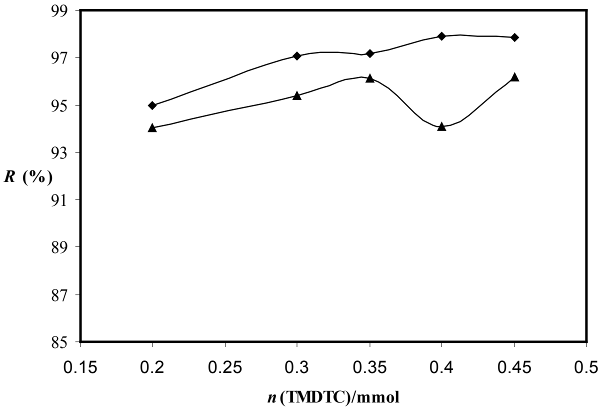

Figure 3: Influence of TMDTC$^-$ amount and cobalt mass on lead recovery with Co(TMDTC)$_3$ at pH 6.0

Selection of Surfactant

To select the most suitable surfactant for separation of lead ions, different foaming reagents were tested by flotation of a series of standard solutions under conditions previously determined as optimal. The cationic surfactant (BTC), as well as non-ionic surfactant (TX-100) foam very well, but no flotation occurred. The anionic surfactants floated with different recovery efficiencies. NaDDS and NaOL were the most successful surfactants for lead flotation with $Co(TMDTC)_3$ (Table 2). Several anionic surfactants (NaDDS, NaOL, NaPL and NaST) and the pair of NaDDS /NaOL were also used. The detergent NaDDS shows the highest recovery rate of lead ions by flotation (98.44 %) and therefore was selected as a reagent for this method (Table 2).

Table 2: The influence of several cationic, non-ionic and anionic surfactants on lead flotation recoveries

Surfactant	R (%)
Cationic surfactants	
BTC	foam, no flotation
Anionic surfactants	
NaDDS	98.44
NaOL	93.48
NaPL	93.60
NaST	90.02
Non-ionic surfactants	
TX-100	foam, no flotation
Pairs of anionic surfactants	
NaDDS/NaOL	97.27

Influence of Ionic Strength and Induction Time

The ionic strength (I_c) of the floating reaction mixture must be $I_c = 0.02$ mol/L regulated by saturated solution of KNO_3. That value was chosen from previous work (Čundeva & Stafilov, 1997; Čundeva *et al.*, 2000; Pavlovska *et al.*, 2001; Stafilov *et al.*, 2001; Pavlovska *et al.*, 2000; Bundalevska *et al.*, 2005; Zajkova Paneva *et al.*, 2005; Paneva *et al.*, 2007; Čundeva *et al.*, 2007).

The induction time (τ) is the time necessary for the incorporation of metal traces in the collector precipitate. For this procedure by $Co(TMDTC)_3$ performed at pH 6.0, the optimal induction time was 15 min.

Detection Limit

To determine the standard deviation of the method ten blanks were floated by the recommended procedure and then the concentration of lead was determined by Zeeman ETAAS. The limit of detection (LOD) of the method was estimated as three values of the standard deviation (s) of the blank. The precision of the method was expressed by means of the relative standard deviation (s_r).

The standard deviation (s) of ETAAS method for lead was 0.59 mg/L, the detection limits 0.18 mg/L, while the relative standard deviation 1.55 %.

Application of the Method

The developed method was successfully applied for Pb flotation preconcentration for natural water samples. For those purposes four samples in two series of fresh and tap waters from Strumica (the city tap water and fountains Kalinka, Topuska and Sofilari) were analysed by ETAAS. Each water sample (0.5 L) was preserved by acidification with a few milliliters of nitric acid (pH<3). The proposed procedure with $Co(TMDTC)_3$ was applied. After flotation lead was 20-fold concentrated and determined with ETAAS using calibration curves and the methods of standards additions (Table 3). The recovery value (98.44 %) shows that the preconcentration and separation of lead by the recommended procedure is satisfactory.

Table 3: Results of the flotation/ETAAS determination of lead in fresh water samples using $Co(TMDTC)_3$

Water sample	Added, ng/L Pb	Estimated, ng/L Pb	Found, ng/L Pb	R (%)
Tap water -1			1.63	
	1.95	3.58	3.01	84.0
	3.86	5.49	5.50	100.1
Tap water - 2			1.69	
	1.95	3.64	3.55	97.5
	3.86	5.55	5.68	102.3
Kalinka -1			1.15	
	1.95	3.1	3.41	110.0
	3.86	5.01	5.35	106.7
Kalinka -2			1.12	
	1.95	3.07	3.24	105.5
	3.86	4.98	5.23	105.0
Topuska -1			2.44	
	1,95	4.39	4.32	98.4
	3.86	6.30	5.47	86.8
Topuska -2			2.07	
	1.95	4.02	3.81	94.8
	3.86	5.93	5.47	92.2
Sofilari -1			2.53	
	1.95	4.48	4.18	93.3
	3.86	6.39	6.10	95.5
Sofilari -2			2.99	
	1.95	4.94	4.18	84.6
	3.86	6.85	6.10	89.1

As for confirmation, this method was verified by determination of lead in the surface water reference materials SPS-SW1 Batch 107 (Spectra pure Standards AS) and LGC-6019 River Thames Water (LGC Standards). Before the application of the method with the reference standard materials they were diluted 10 times. The data in Table 4 shows that the results of the reference materials analysis agreed well with the certified values (Student's t-test, 95 %).

Table 4: Determination of Pb in the certified reference material sample SPS-SW1 Batch 107 by the proposed method (given in µg L^{-1} Pb), n=5

	SPS-SW1 Batch 107 [mean±SD]	LGC-6019 [mean±SD]
Certified	5.1±0.1	4.9±0.3
Found	4.9±0.2	4.7±0.4
$t_{calc., n=5}$	2.5	2.4

$t_{tab., n=5}$ = 2.72

Conclusion

The investigations prove that cobalt(III) tetramethylenedithiocarbamate can be used successfully for precipitation and separation of lead traces from water matrices. Lead was determined with recovery of 98.44 %. Optimal experimental parameters were pH 6.0, mass of cobalt 3.5 mg, amount of 0.4 mmol TMDTC$^-$. NaDDS was used as a foaming reagent. The proposed flotation procedure by using Co(TMDTC)$_3$ as a collector has the advantage because the use of only one surfactant requires a smaller amount of acid and consequently the matrix of the final solution is less complex.

The excellent recoveries of lead, as well as the validation by the method of standard adition, evidence the successfulness of the method recommended. The procedure is rapid (about 25–30 min) and extends the range of conventional ETAAS determination. The necessary equipment for flotation is simple and low cost. The use of a small amount of surfactant and fine air bubbles necessary to perform the proper flotation does not allow for any serious contamination risks which could result in high blank values.

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