

# Optimization of the method for preconcentration and separation of lead from aqueous systems using flotation by cobalt (III) heptyldithiocarbamate

Katarina ČUNDEVA, Trajče STAFILOV and Gorica PAVLOVSKA

*Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Republic of Macedonia*

**Abstract.** A fast method for preconcentration and separation of lead in nanogram quantities from fresh drinking waters (source, well, tap) and waters for irrigation using coflotation is described. Cobalt(III) heptyldithiocarbamate,  $\text{Co}(\text{HpDTC})_3$ , is applied as a collector. The experimental conditions for a successful remove of analyte are optimized. After flotation separation from the mother liquor, the solid sublimate containing trace of Pb was dissolved and the determination was performed by Zeeman electrothermal atomic absorption spectrometry (ZETAAS). The ZETAAS limit of detection for Pb is  $0.274 \mu\text{g/l}$ .

**Key words:** lead, water, determination, flotation, ETAAS

## 1. Introduction

Lead toxicity is very well known [1], but this pollutant is practically everywhere in today's environment. It enters in human bodies mainly by food, air and water polluted by many different sources (auto exhaust, ammunition, batteries, containers for corrosives, contaminated soil, cosmetics, fertilizers, hair dyes, insecticides, lead based paint, lead-glazed pottery, pesticides, solder, tobacco smoke *etc.*). Even in traces Pb can be dangerous. It accumulated in some part of organisms, and the harmful consequences of that poisoning can manifested by the times. Therefore, lead monitoring is an imperative of environmental chemistry.

There are many methods for determination lead in environmental waters. but each new developed procedure for its detection, quantification and removing is always useful. The aim of this report is to present a new fast method for preconcentration and separation of Pb in nanogram quantities from fresh drinking waters (source, well, tap) and waters for irrigation using flotation. Flotation is technique for separation of species from liquid systems by air bubbles. The most frequently used one is the method of precipitate colloid flotation called coflotation [2-10]. That procedure depends of many factors, but the main role to perform a proper flotation separation of trace elements from water matrix has the collector

with its colloid nature [2, 3]. This work is the attempts to present cobalt(III) heptyldithiocarbamate,  $\text{Co}(\text{HpDTC})_3$ , as a new possible reagent for Pb separation and preconcentration from fresh water matrices. Coflotation methods are commonly coupled by atomic absorption (AAS) or emission spectroscopic methods. This work is the example of flotation separation of Pb in combination with Zeeman electrothermal atomic absorption spectrometry (ETAAS).

## 2. Experimental

### *Instrumentation*

The ETAAS of Pb was made by Varian SpectrAA 640Z. All pH readings were carried out with Iskra pH-Meter MA 5705. The flotation cell was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom.

### *Reagents*

All chemicals used were of the highest analytical grade except for surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC) and cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX-100). 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, serves for preparation of 0.1 mol/L solution of HpDTC in 96 % ethanol. For optimization of the general procedure stock solution of 1 g/l Pb(II), as well as stock solution 10 g/l of Co(II) were daily diluted and series of standards were freshly prepared. The 0.5 % solutions of surfactants were prepared in water (TX-100), in 95 % ethanol (NaDDS, NaOL) and in 99.7 % propan-2-ol (NaPL, NaST). The pH was regulated by HNO<sub>3</sub> (0.1 mol/l) and of KOH (10 %) solutions. Ionic strength ( $I_c$ ) was adjusted by a saturated solution of KNO<sub>3</sub>.

Table 1. Instrumental parameters for Zeeman ETAAS of Pb

Wavelength	283.3 nm
Spectral slit	0.5 nm
Lamp current	5.0 mA
Drying temperature	85, 95, 120 °C
Time of drying	5, 40, 10 s
Pyrolysis temperature	400 °C
Time of pyrolysis	5, 1, 2 s
Atomization temperature	2100 °C
Time of atomization	1, 2 s

### Procedure

A pH electrode was immersed into a 1l of acidified water sample. After adding 6 ml of saturated KNO<sub>3</sub> 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)<sub>3</sub> occurs [11]. After stirring 15 min, 1

ml NaDDS solution was added and the content of the beaker was transferred into the flotation cell. Then an air stream (50 ml/min) raises the precipitate to the water surface. The glass pipette-tube was immersed into the cell through the froth layer and the processed water phase was sucked off. The solid phase in the cell was decomposed with 2.5 ml of hot conc. HNO<sub>3</sub> and the solution was sucked off through the porous bottom of the cell and collected in 25-ml bottle. The cell and the pipette-tube were washed four times with 4 mol/l HNO<sub>3</sub>. The flask was filled up to the mark redistilled water and the sample was ready for AAS measurements.

## 3. Results and Discussions

### Effect of pH

The influence of pH on Pb(II) flotation recovery was studied within pH range of 6.5 to 10.5 floating series of solutions containing 25 mg Pb per 1l. Mass of Co (10 mg) was kept constant, amount of HpDTC<sup>-</sup> (0.3 mmol) and ionic strength (0.02 mol/l) were kept constant. The highest recoveries for Pb (95.0 %) were reached at pH range 9.0 (Fig. 1). So pH 9.0 was selected for the next investigations.

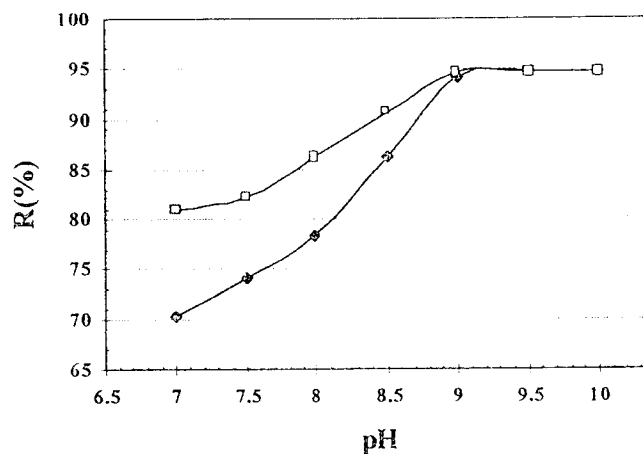


Fig. 1 Effect of pH on Pb flotation

### Influence of Co mass

This influence was investigated performing series of flotation by addition of different amounts of Co (1.0-30.0 mg) to the working solutions containing 25 mg Pb per 1 l at pH 9. The ionic strength and amount of HpDTC were kept constant ( $I_c = 0.02$  mol/l, 0.3 mmol HpDTC). The data show

that the increasing of Co mass influences on Pb flotation efficiency. Satisfactory recoveries for all three were reached by 10 mg Co (Fig. 2).

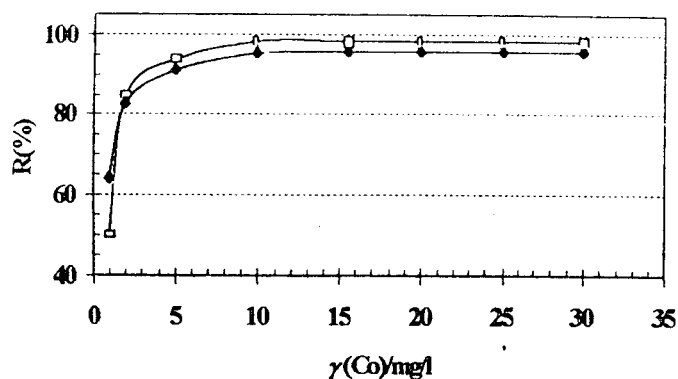


Fig. 2. Influence of  $m(\text{Co})$  on Pb flotation

#### Influence of $n(\text{HMDTC}^-)$

Four series of flotations were performed by addition of different amounts of HpDTC (0.13-0.90 mmol) added to 1L solutions containing 25 mg Pb at a constant pH (9.0) and  $I_c$  (0.02 mol/l). The first series contained 5 mg, the second 10 mg, the third 15 mg and the fourth 20 mg Co. The data show that the using of 10 mg Co together with 0.3 mmol HMDTC<sup>-</sup> is the most satisfactory for all three analytes (Fig. 3).

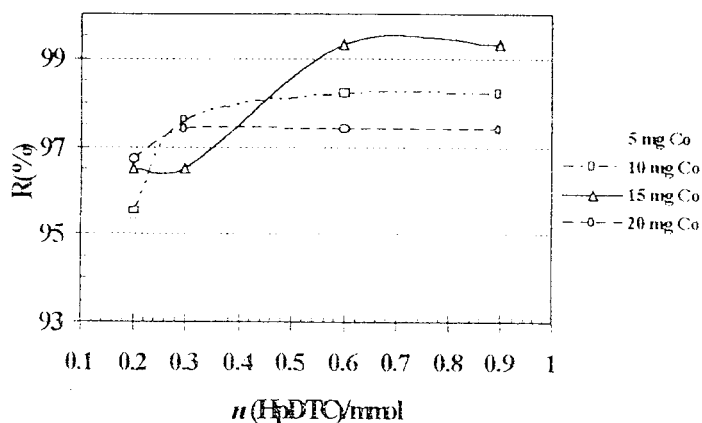


Fig. 3. Influence of  $n(\text{HpDTC})$  on Pb flotation

#### Selection of surfactant

Several anionic (NaDDS, NaOL, NaPL and NaST), cationic surfactants (BTC and CTAB) and one non-ionic tenside (TX100), were investigated at pH 9.0. To each tested solution 1 ml of 0.5 % solution of surfactant was added. Mass of Co (10

mg), amount of HpDTC (3 mmol) and ionic strength (0.02 mol/L) were kept constant. BTC, CTAB and TX100 frothed very well, but there was no flotation (Table 2). These investigations suggest that the surface of  $\text{Co}(\text{HpDTC})_3$  particles might be the same charge as the cationic surfactants. The investigation by NaDDS, NaOL, NaPL and NaST verified that pH 9.0 is the optimal value for Pb flotation preconcentration by  $\text{Co}(\text{HpDTC})_3$  (Table 1). Among anionic surfactant NaDDS has been shown as the most appropriate for flotation reaching 100.0 % recoveries of Pb.

Table 2. Selection of surfactant for flotation Pb(II) (pH = 9.0,  $I_c = 0.02$  mol/L, 20 mg/L Co, 3 mmol/l HpDTC<sup>-</sup>)

Surfactant	Pb recovery, %
Cationic BTC CTAB	Foam, No flotation
Non-ionic, TX-100	Foam, No flotation
Anionic NaDDS	100
NaOL	95.1
NaPL	91.0
NaST	92.4

#### Induction time

The flotation by  $\text{Co}(\text{HpDTC})_3$  needs only one induction time, because at pH 6 any precipitate of the collector can not occur. The experiment showed that Pb can be collected quantitatively by the precipitate of  $\text{Co}(\text{HpDTC})_3$  for 10 min of stirring under conditions optimised in the previous sections.

#### Interferences of cobalt mass on analyte absorbance

To check if cobalt quantity in the final 40-fold concentrated by flotation test solutions is enough to interfere on Pb absorbance, series of solutions with the constant concentration of analyte and different concentration of cobalt were prepared. The masses of Pb, as well as the mass ratio Co/Pb, were similar to those in the natural water sample investigating. Then, analyte was tested by AAS. The results show there are no interferences up to 20 mg of cobalt, added to 1 l of water sample.

#### Applicability of the method

To verify the method, tap and well waters were analyzed. Standard addition method was used. After flotation waters were 40-fold concentrated and then Pb was determined by ETAAS. The recoveries of Pb obtained by the proposed method with  $\text{Co}(\text{HpDTC})_3$  (95.0-101.2 %) evidence that its preconcentration and separation was satisfactory (Tables 1). Standard deviation by  $\text{Co}(\text{HpDTC})_2$  as collector was 0.0913  $\mu\text{g/L}$  Pb, limit of detection 0,2740  $\mu\text{g/L}$  Pb, while relative standard deviation 4.7 %.

Table 4. ETAAS determinations of Pb preconcentrated by  $\text{Co}(\text{HpDTC})_2$  (in mg/L)

Sample	Added	Estimated	Found	R, %
Pantelejmon	-	-	0.540	-
	0.625	1.165	1.153	98.9
	1.25	1.79	1.71	95.5
	2.50	3.04	3.05	100.3
	6.25	6.79	6.76	99.5
Sreden Izvor	-	-	0.625	-
	0.625	1.250	1.230	98.4
	1.25	1.875	1.825	97.3
	2.50	3.125	3.063	98.0
	6.25	6.675	6.667	99.9
Rašče	-	-	0.570	-
	0.625	1.195	1.21	101.2
	1.25	1.82	1.73	95.0
	2.50	3.07	2.97	98.3
	6.25	6.82	6.76	96.3
Demir Kapija	-	-	0.530	-
	0.625	1.155	1.143	98.9
	1.25	1.78	1.711	96.1
	2.50	3.03	2.980	98.3
	6.25	6.78	6.533	96.3
Veles	-	-	0.650	-
	0.625	1.275	1.255	98.4
	1.25	1.90	1.830	96.3
	2.50	3.15	3.070	97.5
	6.25	6.90	6.804	98.6

<sup>a</sup> Results of comparative ICP-AES determination of Pb. The samples for ICP-AES were enriched by evaporation.

<sup>b</sup> dH (*Deutsche Härte*) German degree of water hardness.

#### 4. Conclusion

The present paper proved that Pb can be preconcentrated and successfully separated by flotation using  $\text{Co}(\text{HpDTC})_3$ , prior to ZETAAS. The pH of the media, as well as the amounts of Co and

HpDTC, as the constituents of the collector investigated, have the effect on flotation recoveries of Pb.  $\text{Co}(\text{HpDTC})_3$  was shown as a collector with a significant hydrophobicity, which is an important criterion for a successful flotation. The recommended preconcentration procedures are rapid (about 25-30 min), extends the range of conventional AAS determination of Pb, and 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.

#### 5. Acknowledgments

The authors gratefully acknowledge the financial support provided by the Ministry of Education and Science of the Republic of Macedonia.

#### 6. References

- \*E-mail address: kcundeva@iunona.pmf.ukim.edu.mk
- [1] \*\*\**Casarett and Doull's Toxicology*, Fifth Edition, C. D. Klaassen, ed., McGraw-Hill, Health Professions Division, New York, 1995.
  - [2] A. Mizuike, *Enrichment Techniques for Inorganic Trace Analysis*, Springer-Verlag, Heidelberg, 1983.
  - [3] M. Caballero, R. Cela, J. A. Pérez-Bustamante, *Talanta*, **3**, 275 (1990).
  - [4] T. Stafilov, K. Čundeva, *Talanta*, **46**, 1321 (1998).
  - [5] K. Čundeva, T. Stafilov, G. Pavlovska, *Microchem. J.*, **65**, 165 (2000).
  - [6] G. Pavlovska, T. Stafilov, K. Čundeva, *Fresenius' J. Anal. Chem.*, **360**, 670 (2001).
  - [7] G. Pavlovska, K. Čundeva, T. Stafilov, *Anal. Lett.*, **35**, 2347 (2002).
  - [8] K. Čundeva, T. Stafilov, G. Pavlovska, I. Karadjova, S. Arpadjan, *Int. J. Environ. Anal. Chem.*, **83**, 1009 (2003).
  - [9] U. Ay, K. Čundeva, G. Akçin, T. Stafilov, V. Paneva Zajkova, G. Pavlovska, *Anal. Lett.*, **37**, 695-710 (2004).
  - [10] I. Koyuncu, J. M. Bundaleska, Ü. Ay, K. Čundeva, T. Stafilov, G. Akçin, *Sep. Sci. Technol.*, **39**, 2751 (2004).
  - [11] K. Glen, R. Schwab, *Angew. Chem.*, **62** (1950) 320.