

COBALT(III) DITHIOCARBAMATE AS COLLECTOR FOR FLOTATION PRECONCENTRATION OF Tl(I) AND Tl(III) FOR WATER ANALYSIS BY ETAAS

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Abstract

An accurate, fast and simple method for determination of thallium in environmental water samples with Zeeman electrothermal atomic absorption spectrometry (ZETAAS) by previous flotation preconcentration is given. The possibility of using Co(III) dithiocarbamates as colloidal precipitate collectors for simultaneously flotation separation of Tl(I) and Tl(III) from water matrices was studied. The experiments showed that Co(HMDTC)₃ as a collector for flotation of both Tl species is far more effective than Co(HpDTC)₃. The limit of detection of Tl is 0.031 µg/l.

Introduction

Thallium compounds are well known as very toxic substances [1]. Because of the health of live beings, the monitoring of Tl in environmental water systems is very important. Since concentration of Tl in natural waters is very low a preconcentration is necessary. In our earlier works we used cobalt(III) hexamethylenedithiocarbamate, Co(HMDTC)₃ [2-5], and cobalt(III) heptyldithiocarbamate, Co(HpDTC)₃ [4, 6], as collectors for flotation preconcentration of several metals from fresh and sea waters. The scope of this paper is to test the same dithiocarbamates as new possible reagents for flotation of both Tl ions prior to ZETAAS. The method was applied for total Tl determination in some water samples from Republic of Macedonia and Republic of Turkey.

Experimental

Apparatus

The ETAAS determinations of Tl were made by Varian SpectrAA 640Z, while the ICP-AES measurements by Varian Liberty 110. The flotation cell was a glass cylinder (4x105 cm) with a sintered glass disc (porosity No. 4) at the bottom.

Reagents

Stock solutions of Tl(I) and Tl(III) were prepared of chemicals of the highest grade (Solution Plus Inc.). Stock solution of Co(II) (10g/l) was made of Co(NO₃)₂·6H₂O (Merck). Hexamethylenammonium hexamethylenedithiocarbamate, HMA-HMDTC, and Na hethylthiocarbamate, NaHpDTC, were made as 0.1 mol/l solutions in 96 % ethanol. Sodium dodecylsulfate, NaDDS was used as surfactant.

Procedure

Six ml of saturated KNO_3 solution was added to 1 l of acidified water sample. Then, 1 mL of 1.5 g/l solution of Co(II) was introduced. The pH was adjusted to 6.0. A volume of 3 ml 0.1 mol/L solution of HMA-HMDTC was added. Under continuous stirring Co(II) was oxidized in Co(III) and a green bulky precipitate of $\text{Co}(\text{HMDTC})_3$ was occurred. After 15 min stirring, 1 ml of NaDDS solution was added. The content was transferred into the flotation cell and air stream raises the precipitate to the water surface. The processed water phase was sucked off and the solid phase in the cell was dissolved using 5 ml hot conc. HNO_3 . Then by means vacuum the red solution passed through the sintered bottom of the cell in volumetric bottle of 25 ml. The flask was filled up to the mark and the sample was ready for measurements.

Results and discussion

pH, formation of sublimate and separation of Tl from matrix

The processes occurring in both steps of flotation (formation of the sublimate and flotation separation) depend of medium pH. Therefore, the optimization of pH must be performed by the special carefulness. For that purpose series of 25 $\mu\text{g/l}$ solutions of Tl(I) and Tl(III), were prepared. They were separately floated by $\text{Co}(\text{HMDTC})_3$, as well as $\text{Co}(\text{HpDTC})_3$ varying pH from 3.0 to 10.0. The results show that Tl(I) can be floated successfully by $\text{Co}(\text{HMDTC})_3$ within pH range 5.0-6.5 (recoveries of 95.8 %). Tl(III) reaches quantitative recoveries (94.6–100.0 %) within a pH interval from 4.0 to 9.5. So pH 6.0 was selected as optimal value for the simultaneous flotation of Tl(I) and Tl(III) by $\text{Co}(\text{HMDTC})_3$. Considering the results of flotations obtained by $\text{Co}(\text{HpDTC})_3$, show that there is no flotation within pH range 3–7.

Influence of Co mass

This influence was studied by performing series of flotations with $\text{Co}(\text{HMDTC})_3$ using different mass of Co (0.5-10.0 mg). The working solutions contained 25 μl Tl(I) and Tl(III), consequently. The pH 6 was kept constant, as well as the other parameters. The data show that satisfactory recoveries for both Tl species (97.1 %) were reached by 1.5 mg Co added to 1 l sample.

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

Four series of flotations (contained 0.5, 1.0, 1.5 mg and 2.0 mg Co) were performed by addition of different amounts of HMDTC^- (0.13-0.60 mmol) to 1 l solutions at a constant pH (6.0). The data show that the using of 1.5 mg Co and 0.3 mmol HMDTC^- is the most satisfactory for Tl(I) flotation, as well as Tl(III) flotation. The results for Tl(I) and Tl(III) recoveries using HpDTC^- evidence that they are not quantitative.

Application of the method

To confirm the developed method for simultaneous preconcentration of Tl(I) and Tl(III) by $\text{Co}(\text{HMDTC})_3$, waters samples taken from the Republic of Macedonia and Republic of Turkey were analyzed. Standard addition method was used. The recoveries of Tl obtained by the proposed method (94.8-100.4 %) evidence that its preconcentration with $\text{Co}(\text{HPDTC})_3$ was satisfactory (Tables 1). The data show that ZETAAS results agree with those obtained by ICP-AES (concentrated 40-fold by evaporation).

Table 1. Results of determination of Tl in environmental water samples by ZETAAS following flotation by Co(HMDTC)_3 compared with AES-ISP results

Sample environmental water	ETAAS			AES-ISP	
	Added $\mu\text{g/L Tl}$	Estimated $\mu\text{g/L Tl}$	Find $\mu\text{g/L Tl}$	R (%)	Find $\mu\text{g/L Tl}$
Pantelejmon 15.17 dH° ** pH = 7.45	- 1.25 2.50	- 1.37 2.62	0.12 1.35 2.62	- 98.5 100.0	- <0.1
Sreden Izvor 20.23 dH° pH = 7.2	- 1.25 2.50	- 1.37 2.62	0.12 1.35 2.63	- 98.5 100.4	- <0.1
Rašče 12.25 dH° pH = 7.17	- 1.25 2.50	- 1.35 2.60	0.10 1.28 2.55	- 94.8 98.1	- <0.1
Demir Kapija 8.79 dH° pH = 7.47	- 1.25 2.50	- 1.35 2.60	0.10 1.29 2.57	- 95.5 98.8	- <0.1
Veles 1.86 dH° pH = 6.56	- 1.25 2.50	- 1.36 2.61	0.11 1.35 2.59	- 99.3 99.2	- <0.4
Iski Kagithane, dam water			0.035		-
Iski Kagithane, refined tap water			0.05		-
Iski Buyuk Çekmece, dam water			0.054		-
Iski Buyuk Çekmece, refined tap water			0.051		-
River Topolka			0.054		0.053
Veles, tap water (new system)			0.027		0.037
Accumulation lake Mavrovica			0.055		0.051
Sv. Nikole tap water			0.073		0.066

Conclusion

The present paper proved that Tl(I), as well as Tl(III) can be preconcentrated successfully using flotation with Co(HMDTC)_3 , prior to ZETAAS. Co(HMDTC)_3 was shown as a collector with a significant hydrophobicity, which is an important criterion for a successful flotation. That can be evidenced by the excellent recoveries of Tl. The ETAAS detection limit of Tl is $0.031 \mu\text{g/L}$.

References

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