

## **ETAAS determination of thallium and silver from water matrix after colloidal precipitate flotation using lead(II) hexamethylenedithiocarbamate**

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A fast method for the preconcentration of thallium and silver in nanogram quantities in fresh drinking waters (source, well, tap) and waters for irrigation using colloidal precipitate flotation is described. Lead(II) hexamethylenedithiocarbamate,  $\text{Pb}(\text{HMDTC})_2$  played the role of flotation collector. The experimental conditions for the successful separation of thallium and silver (mass of Pb, amount of HMDTC<sup>-</sup>, pH of the system, induction time, type of surfactant *etc.*) were optimized. After flotation separation from the mother liquor, the solid sublimate containing traces of thallium and silver was dissolved and the analytes were determined by electrothermal atomic absorption spectrometry (ETAAS). The results of the ETAAS analysis are compared with those obtained by inductively coupled plasma-atomic emission spectrometry. The detection limit for thallium by this method is 0.027  $\mu\text{g/l}$ , and for silver 0.005  $\mu\text{g/l}$ .

*Keywords:* thallium, silver, determination, water, colloidal precipitate flotation, ETAAS, lead(II) hexamethylenedithiocarbamate.

### INTRODUCTION

Thallium is known as a very toxic element, which often occurs with silver in zinc and lead ores. Therefore, the presence of zinc and lead in natural waters, as a result of dissolved residues from zinc mining and smelting industries, always indicates the presence of thallium and silver in traces. Although, silver in lower concentrations does not have such a strong toxic effect on human beings as thallium, in higher levels this metal can still act harmfully on microorganisms in waters.<sup>1,2</sup> Consequently, the development of accurate and rapid determination methods for the monitoring of thallium and silver in natural waters is necessary.

Atomic absorption spectrometry (AAS) has been shown to be very useful for accurate and rapid determinations of thallium and silver in waters, but, commonly for extremely low concentrations, their direct determinations are not possible without previ-

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ous preconcentration.<sup>3,4</sup> Today in the analytical practice expensive separation instrumentation (*e.g.*, some chromatographic techniques) is used, but many labs around the world which cannot provide such instruments, can apply some of the classical preconcentration methods, such as liquid-liquid extraction, ion exchange, evaporation and coprecipitation.<sup>2,3</sup> Recently much attention has been given to preconcentration of heavy metals from water samples by adsorptive bubbles separation techniques, *i.e.*, flotations.<sup>3-6</sup> Many factors influence the performance of a proper flotation, on which this type of technique depends. In carrying out the most frequently used colloidal precipitate flotation, the collector, which is of colloidal nature, plays an important role. Among the diverse types of collectors proposed for this purpose, the bulky hydrated iron(III) oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , is the most widely applied.<sup>3-12</sup> Nevertheless, neither thallium nor silver can be floated by this collector without the addition of tetramethylenedithiocarbamate ( $\text{TMDTC}^-$ ) anions.<sup>13,14</sup> On addition of  $\text{TMDTC}^-$  to the system containing iron(III), the obtained amorphous bulky precipitate of iron(III) tetramethylenedithiocarbamate helps to carry out a proper and quick flotation of thallium and silver. This paper presents the application of another dithiocarbamate,  $\text{Pb}(\text{HMDTC})_2$ , as a possible collector for colloidal precipitate flotation of these colligends. This chelate has already been applied for the coprecipitation of silver and traces of other heavy metals in sea water prior to neutron activation.<sup>15</sup> This report is the first attempt to employ lead(II) hexamethylenedithiocarbamate,  $\text{Pb}(\text{HMDTC})_2$ , for flotation before ETAAS as a method for the determination of thallium and silver in fresh waters.

## EXPERIMENTAL

### *Instruments*

A Perkin-Elmer 1100 B atomic absorption spectrometer and HGA-700 graphite furnace were used for AAS measurements. Standard pyrolytically coated graphite tubes were utilized. All the parameters for AAS were established by extensive testing (Table I). Inductively coupled plasma-atomic emission spectrometric determinations (ICP-AES) were performed using a Varian Liberty 110. The flotation cell was a glass cylinder (diameter 4 cm, height 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate air bubbling. To monitor the pH of the media, a pH Meter (Iskra, M 5705) with a combined glass electrode (Iskra, M 0101) was used.

### *Chemicals*

All chemicals used were of the highest grade available (*p.a.*) except for sodium oleate ( $\text{NaOL}$ ), sodium palmitate ( $\text{NaPL}$ ) and sodium stearate ( $\text{NaST}$ ), which were synthesized from sodium hydroxide and the appropriate fatty acid. Deionized redistilled water was used throughout. A stock solution of silver (1 g/l) was made using  $\text{AgNO}_3$  (Merck). A stock solution of thallium(I) (1 g/l) was made by dissolving a commercial standard solution (Titrisol, Merck), containing 1 g of  $\text{Tl(I)}$  in the form of  $\text{TlNO}_3$ , in 1 l water. The same commercial standard solution served for the preparation of a thallium(III) stock solution. Thallium(I) of the commercial standard solution was oxidized to thallium(III) by the addition of several drops of bromine. After evaporation nearly to dryness (to remove excess of bromine), the residue was diluted to 1 l. Before each investigation these standard solutions were suitably diluted daily. A stock solution of the collector containing 10 g/l lead was made by dissolving an appropriate amount of  $\text{Pb}(\text{NO}_3)_2$  in water. By dilution of this stock solution, a series of standards within the concentration range 2.5 to 100 mg/l lead was obtained. A solution of hexamethylenediammonium hexamethylenedithiocarbamate (HMA-HMDTC) was synthesized from hexamethylenamine and  $\text{CS}_2$  according with the method of Busev *et al.*<sup>16</sup> HMA-HMDTC was prepared as a 0.1 mol/l solution in

96 % ethanol. The 0.5 % solutions of tensides were prepared in water, Triton X-100 (TX100), in 95 % ethanol, sodium dodecylsulfate (NaDDS), NaOL, benzethonium chloride (BTC), and cetyltrimethylammonium bromide (CTAB) or in 99.7 % propan-2-ol, (NaPL, NaST). The medium pH was adjusted by solutions of HNO<sub>3</sub> (0.1 mol/l) and KOH (2.5 % and 10 %). The ionic strength ( $I_c$ ) was regulated by a saturated solution of KNO<sub>3</sub>. A 0.1 mol/l solution of NH<sub>4</sub>NO<sub>3</sub> served to quantitatively transfer the content of the beaker to the flotation cell.

TABLE I. Optimal instrumental parameters for thallium and silver ETAAS determinations

Parameter	Tl	Ag
Wavelength	276.8 nm	328.1 nm
Spectral slit width	2.0 nm	0.7 nm
Lamp current	20 mA	10 mA
Background correction	D <sub>2</sub>	D <sub>2</sub>
Drying temperature	90 °C	100 °C
Time of drying	25 s	30 s
Pyrolysis temperature	400 °C	600 °C
Time of pyrolysis	30 s	20 s
Atomization temperature	2200 °C	2000 °C
Time of atomization	5 s	5 s
Cleaning temperature	2650 °C	2650 °C
Time of cleaning	5s	5 s
Carrier gas	Argon	Argon

#### Recommended procedure

Immediately after sampling, the waters were acidified (pH<3) with nitric acid. For ICP-AES analysis the acidified (pH<3) samples were concentrated by evaporation from 1 l to 25 ml.

The recommended preconcentration method in this work consisted of coprecipitation and flotation.

*Coprecipitation:* A combined glass electrode was immersed into a sample of acidified water (1.0 l). After adding 6 ml of saturated KNO<sub>3</sub> solution, 10 mg of Pb(II) was introduced. The pH was carefully adjusted to 6.0 with KOH solutions. The addition of 3 ml 0.1 mol/l HMA-HMDTC, under continuous stirring, produced a white precipitate of Pb(HMDTC)<sub>2</sub>. After 15 min of stirring, 1 ml of NaDDS solution was added. The content of the beaker was transferred into the flotation cell with small portions of 0.1 mol/l NH<sub>4</sub>NO<sub>3</sub>.

*Flotation:* The precipitate were flakes raised to the water surface with an air stream of 50 ml/min, for 1 min. A foamy layer was obtained and the aqueous solution in the cell became completely clear and cleaned of solid particles. A 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 using 2.5 ml of hot conc. HNO<sub>3</sub>. When the liquid in the cell become colorless and transparent, it was run off through the bottom of the cell and collected in a volumetric flask of 25 ml. The cell and the pipette-tube were washed with 4 mol/l HNO<sub>3</sub> solution. The flask was filled up to the mark with 4 mol/l HNO<sub>3</sub> and the sample was ready for ETAAS measurements.

## RESULTS AND DISCUSSION

*Selection of pH*

The value of the pH was shown to be the most critical variable for the two steps of the proposed method.<sup>3,5,6</sup> During the coprecipitation step variations in the pH influence the formation of complexes between the colligends and the ionic species present in the medium and their incorporation into the structure of the collector. The acidity of solutions can induce coagulation, precipitation or hydrolysis of the sublute. During the flotation step, the pH determines the sign and magnitude of the charge on the surface of the sublute particles and influences the stability of the foam.

The effect of pH on thallium (Fig. 1) and silver (Fig. 2) flotation recoveries ( $R$ ) was studied within the pH range of 3.0 to 10.0. A series of flotations of one litre of standard solutions, each containing either 25 or 50  $\mu\text{g}$  of thallium(I), thallium(III) or silver, were made. The final floated solutions had concentration of 1 and 2  $\mu\text{g}/\text{ml}$ . The mass of lead (20 mg), the amount of HMDTC<sup>-</sup> ( $3.0 \times 10^{-4}$  mol) and  $I_c$  (0.02 mol/l) were all kept constant. NaDDS was used as the surfactant.

The  $R/\text{pH}$  curves evidence that satisfactory recoveries between 96.6 – 100.0 % were achieved for thallium(I) within the pH range of 5.0 to 6.5. Thallium(III) floated quantitatively between pH 5.0 and 6.0 (99.0 – 100.0 %), while the recovery of silver was satisfactory between pH 5.5 and 6.5 (94.8 – 96.7 %). In more acidic media (pH < 5.0), all three colligends could not be properly floated and separated from the aqueous phase because of the protonation of the dodecylsulfate anions (DDS<sup>-</sup>). At pH values higher than 6.5, hydrolysis of  $\text{Pb}(\text{HMDTC})_2$  occurs and the recoveries of the colligends decrease. Due to the fact that the optimal pH range for the flotation of both thallium and silver ions was found to be between 5.5 and 6.0, for further investigations 6.0 was selected to be the working pH.

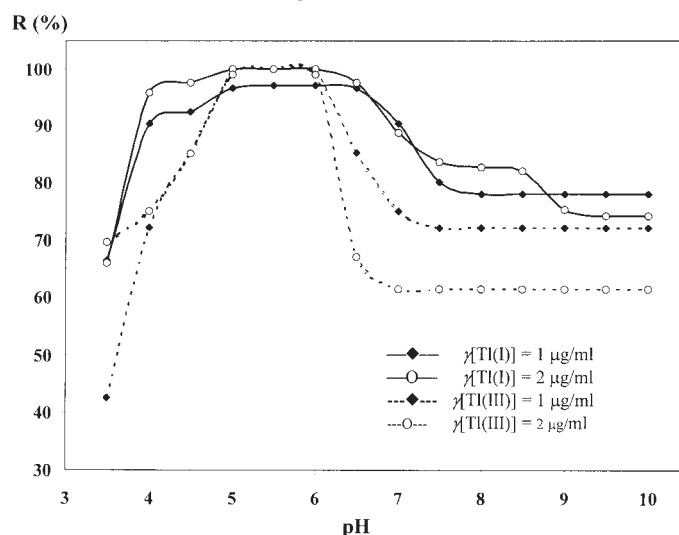


Fig. 1. Influence of pH on thallium(I) and thallium(III) flotability ( $R$ ) (20 mg Pb,  $3.0 \times 10^{-4}$  mol HMDTC<sup>-</sup>,  $I_c = 0.02$  mol/l, NaDDS as surfactant).

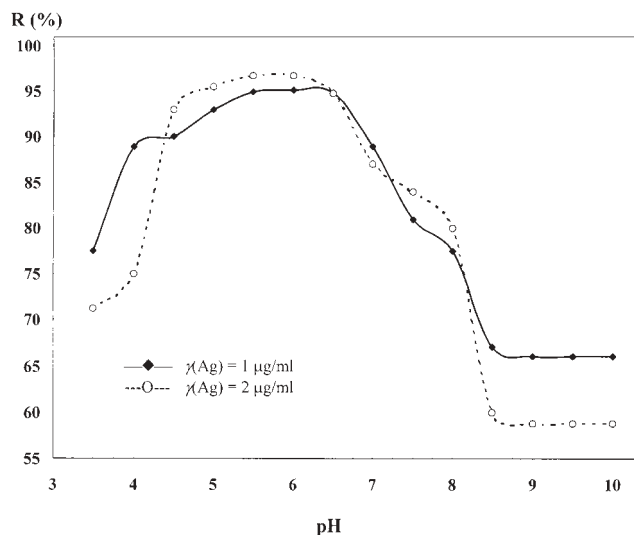


Fig. 2. Influence of pH on silver flotability ( $R$ ) (20 mg Pb,  $3.0 \times 10^{-4}$  mol HMDTC<sup>-</sup>mol,  $I_c = 0.02$  mol/l, NaDDS as surfactant).

#### *Coprecipitation of thallium and silver with Pb(HMDTC)<sub>2</sub>*

The incorporation of thallium and silver in the precipitate particles of Pb(HMDTC)<sub>2</sub> was studied by:

- changing the mass of lead added to reaction mixtures containing a given amount of HMDTC<sup>-</sup>;
- changing the amount of HMDTC<sup>-</sup> added to reaction mixtures containing a given mass of lead.

The examination under condition a) was performed by flotation of one litre of solutions each containing either 25 or 50 μg of thallium(I), thallium(III) or silver, at a constant pH (6.0),  $I_c$  (0.02 mol/l) and amount of HMDTC<sup>-</sup> ( $3.0 \times 10^{-4}$  mol). The flotations were carried out with masses of lead ranging from 2.5 to 100.0 mg. The surfactant used was NaDDS. The data from these investigations (Figs. 3 and 4) show that 10 mg lead is the appropriate mass for the flotation of all three colligends.

To perform the investigation under condition b), one litre of solutions containing 25 μg of thallium(I), thallium(III) or silver were floated by the addition of different amounts of HMDTC<sup>-</sup> ( $1.3 \times 10^{-4}$ – $6.0 \times 10^{-4}$  mol) at a constant pH (6.0) and  $I_c$  (0.02 mol/l). Four series of experiments were performed on each one litre of solutions containing a constant mass of lead (5, 10, 20 or 30 mg). The data of these investigations are given in Figs. 5, 6 and 7. The best recoveries of thallium(I) (100.0 %) and thallium(III) (97.6 %) were obtained with 10 mg lead and  $3.0 \times 10^{-4}$  mol HMDTC<sup>-</sup> per liter. The quantitative separation of silver (96.5 %) can occur with 10 mg lead with  $2.0 \times 10^{-4}$ – $3.0 \times 10^{-4}$  mol HMDTC<sup>-</sup> per liter. For the simultaneous flotation of thallium and silver, 10 mg of lead with  $3.0 \times 10^{-4}$  mol of HMDTC<sup>-</sup> were chosen as the most convenient.

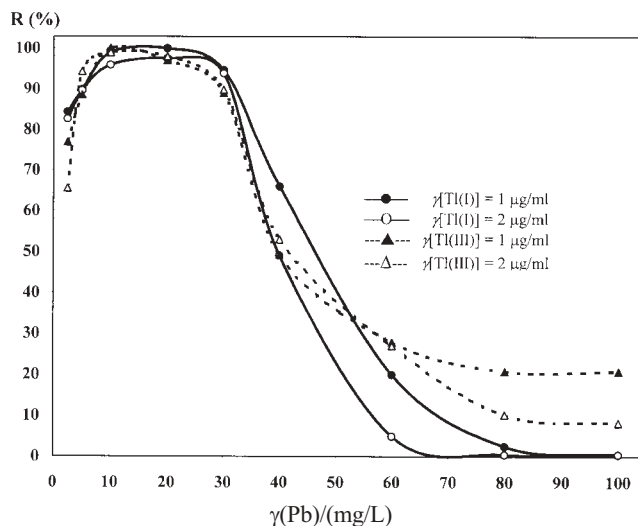


Fig. 3. Influence of the amount of lead on thallium(I) and thallium(III) flotability ( $R$ ) (pH 6.0,  $I_c = 0.02$  mol/l,  $c(\text{HMDTC}^-) = 3 \times 10^{-4}$  mol/l, NaDDS as surfactant).

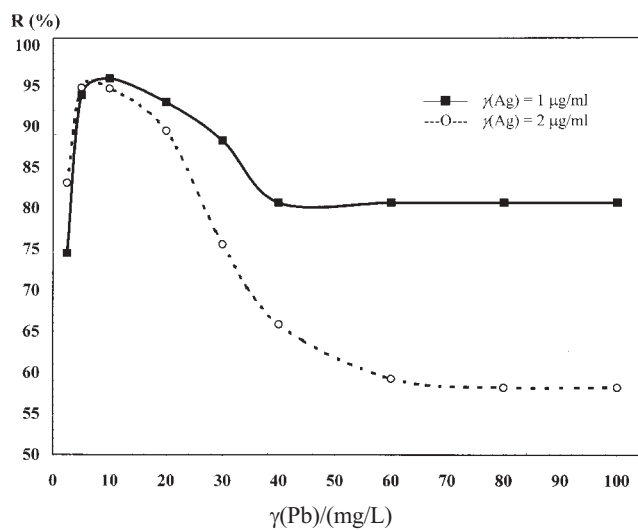


Fig. 4. Influence of the amount of lead on silver flotability ( $R$ ) (pH 6.0,  $I_c = 0.02$  mol/l,  $c(\text{HMDTC}^-) = 3 \times 10^{-4}$  mol/l, NaDDS as surfactant).

#### *Selection of the foaming reagent*

The proposed flotation procedure was performed using diverse foaming agents under the optimized conditions (Table II). Flotation of the analytes with BTC and CTAB were unsuccessful because of their positive charge, which is the same as the charge of the collector particle surface. TX100 is a non-ionic surfactant, *i.e.*, with uncharged species which explains its ineffectiveness. On the other hand, anionic surfac-

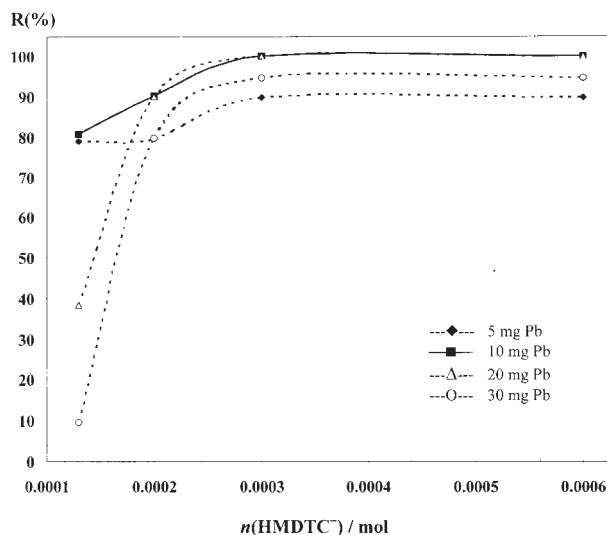


Fig. 5. Influence of the amount of HMDTC<sup>-</sup> on thallium(I) flotability (*R*) (pH 6.0,  $I_c = 0.02 \text{ mol/l}$ ,  $\gamma[\text{Tl(I)}] = 1 \text{ }\mu\text{g/ml}$ , NaDDS as surfactant).

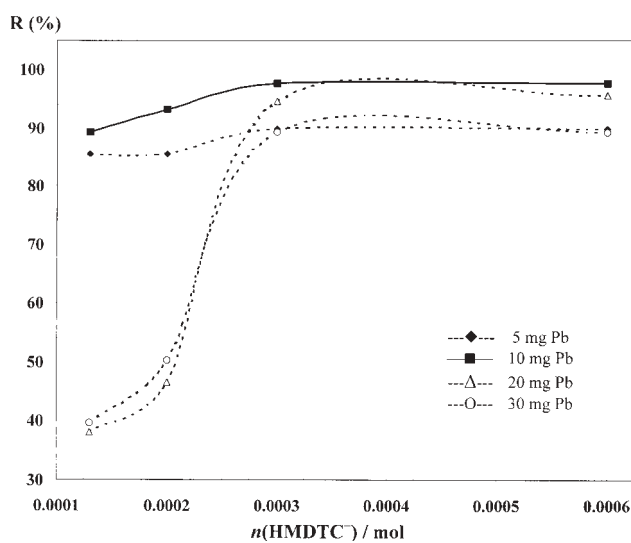


Fig. 6. Influence of the amount of HMDTC<sup>-</sup> on thallium(III) flotability (*R*) (pH 6.0,  $I_c = 0.02 \text{ mol/l}$ ,  $\gamma[\text{Tl(III)}] = 1 \text{ }\mu\text{g/ml}$ , NaDDS as surfactant).

tants having the opposite charge to  $\text{Pb}(\text{HMDTC})_2$  particles appeared to be more effective. Since the recoveries obtained by NaDDS were the highest for thallium and very good for silver, it was selected as the most appropriate foaming reagent for the procedure for the simultaneous flotation of both elements.

The role of the surface active agents (surfactants or tensides) added to the flotation system is to transform the hydrophilic substances into hydrophobic ones and to

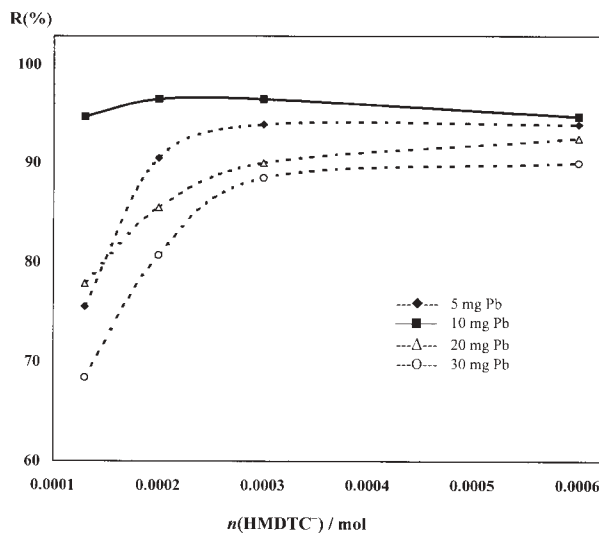


Fig. 7. Influence of the amount of  $\text{HMDTC}^-$  on silver flotability ( $R$ ) (pH 6.0,  $I_c = 0.02 \text{ mol/l}$ ,  $\gamma(\text{Ag}) = 1 \text{ }\mu\text{g/ml}$ , NaDDS as surfactant).

help bubble separation. Some substances that are hydrophobic enough do not need a surfactant.<sup>5</sup> To obtain information about the hydrophobicity of  $\text{Pb}(\text{HMDTC})_2$ , flotations under the previously optimized conditions were performed without the addition of any tenside (Table II). The results of these investigations show that  $\text{Pb}(\text{HMDTC})_2$  can not be applied without foaming reagent. However, the obtained recovery values of (70.9 – 90.6 %) indicate that a certain collection of the colligends occurs. This means that  $\text{Pb}(\text{HMDTC})_2$  itself possesses a significant hydrophobicity, which is illustrated by its  $\zeta$  potential.<sup>17</sup>

TABLE II. Selection of the foaming reagent for colloid precipitate flotation of thallium(I), thallium(III) and silver with  $\text{Pb}(\text{HMDTC})_2$  (pH 6.0,  $I_c = 0.02 \text{ mol/l}$ , 10 mg/l Pb,  $3 \times 10^{-4} \text{ mol/l HMDTC}^-$ )

Analyte	$R / \%$							
	Cationic surfactant		Anionic surfactant				Non-ionic Without surfactant	
	BTC	CTAB	NaDDS	NaOL	NaPL	NaST		TX100
$\gamma[\text{Tl(I)}]/$ (1 $\mu\text{g/ml}$ )	Foam, no flotation		97.75	93.3	79.0	69.3	Foam, no flotation	90.6
$\gamma[\text{Tl(III)}]/$ (1 $\mu\text{g/ml}$ )	Foam, no flotation		99.65	92.1	89.75	86.75	Foam, no flotation	70.9
$\gamma(\text{Ag})/$ (1 $\mu\text{g/ml}$ )	Foam, no flotation		95.35	96.2	84.8	77.0	Foam, no flotation	74.7



### Induction time

The induction time ( $\tau$ ) is the time necessary for the incorporation of the traces of the investigated elements into the collector during the coprecipitation. Based on the experimental data (Table III), thallium (I), thallium(III) and silver traces can be simultaneously quantitatively collected by  $\text{Pb}(\text{HMDTC})_2$  during 15 min.

TABLE III. Influence of the induction time on thallium(I), thallium(III) and silver flotation recoveries

$\gamma(\text{Ag})/$	$\tau/\text{min}$	3	5	10	15
(1 $\mu\text{g}/\text{ml}$ )	$R/\%$	65.2	66.7	67.0	96.5
(2 $\mu\text{g}/\text{ml}$ )		68.5	80.6	88.4	95.9
$\gamma[\text{Tl(I)} ]/$	$\tau/\text{min}$	3	5	10	15
(1 $\mu\text{g}/\text{ml}$ )	$R/\%$	89.9	86.2	92.9	100.0
(2 $\mu\text{g}/\text{ml}$ )		82.6	92.8	98.4	98.5
$\gamma[\text{Tl(III)}]/$	$\tau/\text{min}$	3	5	10	15
(1 $\mu\text{g}/\text{ml}$ )		89.9	94.6	94.7	100.0
(2 $\mu\text{g}/\text{ml}$ )	$R/\%$	82.6	92.8	98.4	100.0

### Detection limit

To determine the standard deviation of the method, ten blanks were floated by the recommended procedure and then the concentration of thallium or silver was determined by ETAAS. The detection limit of the method ( $L_d$ ) was estimated as three values of the standard deviation ( $s$ ) of the blank (Table IV).

TABLE IV. Standard deviation ( $s$ ), relative standard deviation ( $s_r$ ) and detection limit ( $L_d$ ) of thallium and silver determined by ETAAS

Element	$s/(\mu\text{g}/\text{l})$	$s_r/\%$	$L_d/(\mu\text{g}/\text{l})$
Tl	0.0090	3.95	0.027
Ag	0.0016	2.0	0.005

### Application of the method for fresh water analysis

The utility of the method with the new collector  $\text{Pb}(\text{HMDTC})_2$  was evaluated by examining the recovery of thallium and silver from six fresh water samples: source, well, tap and waters for irrigation. The analysis were performed using a calibration curve and the method of standard additions. For this purpose, known amounts of thallium (or silver) were added to 1–1 aliquots of water samples. Then they were floated, 40-fold concentrated and analysed by ETAAS. The results are showing Table V and VI. The obtained data for Tl and Ag concentrations are much lower than maximal permitted value (3  $\mu\text{g}/\text{l}$  for Tl and 2  $\mu\text{g}/\text{l}$  for Ag).<sup>18</sup> The data of the calibration and standard addition methods evidence that they are in good agreement. The recoveries of 94.1 – 103.7 % for thallium (Table V) and 94.8 – 104.3 % for silver (Table VI) show that the preconcentration and separation of these two analytes by the recommended procedure

is satisfactory. The results obtained by ETAAS were compared to ICP-AES results. As can be seen the data obtained by the two methods are in very good agreement.

TABLE V. Results of the ETAAS determination of thallium in natural water samples compared with ICP-AES results

Sample of water	ETAAS				ICP-AES <sup>a</sup>
	Added/( $\mu\text{g/l}$ ) Tl	Estimated/( $\mu\text{g/l}$ ) Tl	Found/( $\mu\text{g/l}$ ) Tl	Recovery/%	Found/( $\mu\text{g/l}$ ) Tl
Pantelejmon	–	–	0.20	–	0.21
15.05 DH <sup>o</sup> b	0.50	0.70	0.68	97.1	
pH 7.84	1.25	1.45	1.49	102.8	
	2.50	2.70	2.70	100.1	
Sreden izvor	–	–	0.49	–	0.50
17.65 DH <sup>o</sup>	0.50	0.99	0.96	97.0	
pH 7.36	1.25	1.74	1.68	96.5	
	2.50	2.99	3.10	103.7	
Raduša	–	–	0.28	–	0.3
25.57 DH <sup>o</sup>	0.50	0.78	0.74	96.1	
pH 8.50	1.25	1.53	1.52	99.3	
	2.50	2.78	2.70	97.1	
Kavadarci	–	–	0.50	–	–
5.71 DH <sup>o</sup>	1.25	1.75	1.67	95.4	
pH 7.58	2.50	3.00	2.90	96.6	
Rašče	–	–	0.43	–	–
16.49 DH <sup>o</sup>	0.50	0.93	0.91	97.8	
pH 7.18	1.25	1.68	1.63	97.0	
	2.50	2.93	2.93	100.0	
Kapištec	–	–	0.35	–	0.35
23.36 DH <sup>o</sup>	0.50	0.85	0.83	94.1	
pH 7.5	1.25	1.60	1.54	96.2	
	2.50	2.85	2.81	98.6	

<sup>a</sup>Results of comparative ICP-AES determination of thallium. Acidified ( $\text{pH} < 3$ ) samples were preconcentrated by evaporation

<sup>b</sup>DH<sup>o</sup> (Deutsche Harte) German degree of water hardness

#### *The possibility of the application of $\text{Pb}(\text{HMDTC})_2$ for sea water analysis*

Considering that thallium(I)<sup>13</sup> and silver,<sup>14</sup> as well as lead(II)<sup>16</sup> ions are predisposed to precipitation as chlorides, the possibility of the application of the proposed methods for sea water analysis was checked. For this purpose, a series of 1–1 solutions containing 25  $\mu\text{g}$  thallium(I), thallium(III) and silver, respectively, in the presence of different contents of NaCl (0.25, 0.50, 0.75, 1.0, 2.0 and 3.0 %) were floated. It was found that thallium(I) and silver cannot be floated in aqueous systems when the quan-

tity of NaCl exceeds 0.25 %. The flotations of thallium(III) could be performed up to 2.0 % NaCl. Thallium(III) suffers interferences indirectly *via* the influences of chlorides on lead(II).

TABLE VI. Results of the ETAAS determination of silver in natural water samples compared with ICP-AES results

Sample of water	ETAAS			ICP-AES <sup>a</sup>	
	Added/( $\mu\text{g/l}$ ) Ag	Estimated/( $\mu\text{g/l}$ ) Ag	Found/( $\mu\text{g/l}$ ) Ag	Recovery /%	Found/( $\mu\text{g/l}$ ) Ag
Pantelejmon	–	–	0.42	–	–
15.05 DH <sup>o</sup> b	0.50	0.92	0.90	97.8	
pH 7.84	1.25	1.67	1.69	101.2	
	2.50	2.92	2.52	99.3	
Sreden izvor	–	–	0.10	–	0.12
17.65 DH <sup>o</sup>	0.50	0.60	0.57	95.0	
pH 7.36	1.25	1.35	1.28	94.8	
	2.50	2.60	2.59	99.6	
Raduša	–	–	0.04	–	0.05
25.57 DH <sup>o</sup>	0.50	0.54	0.55	101.8	
pH 8.50	1.25	1.29	1.24	96.1	
	2.50	2.54	2.53	99.7	
Kavadarci	–	–	0.16	–	0.15
5.71 DH <sup>o</sup>	0.50	0.66	0.63	95.4	
pH 7.58	1.25	1.41	1.37	97.2	
	2.50	2.66	2.59	97.4	
Rašče	–	–	0.30	–	0.26
16.49 DH <sup>o</sup>	0.50	0.80	0.82	102.5	
pH 7.18	1.25	1.55	1.57	101.3	
	2.50	2.80	2.92	104.3	
Kapištec	–	–	0.12	–	0.12
23.36 DH <sup>o</sup>	0.50	0.62	0.61	98.4	
pH 7.5	1.25	1.37	1.31	96.4	
	2.50	2.62	2.59	98.9	

<sup>a</sup>Results of comparative ICP-AES determination of silver. Acidified (pH < 3) samples were preconcentrated by evaporation

<sup>b</sup>DH<sup>o</sup> (Deutsche Harte) German degree of water hardness

#### CONCLUSION

The present paper has proved that silver and thallium can be enriched and separated successfully from fresh waters by precipitate flotation using  $\text{Pb}(\text{HMDTC})_2$  prior to their ETAAS determination. The amounts of lead and  $\text{HMDTC}^-$ , as the constituents of the col-

lector, effect the colligend flotation recoveries. To obtain quantitative separation of both thallium and silver ions present in natural waters, the addition of 10 mg lead with  $3.0 \times 10^{-4}$  mol of HMDTC<sup>-</sup> to 1 l of sample is necessary. Pb(HMDTC)<sub>2</sub> was shown to be a collector with a significant hydrophobicity, which is an important criterion for successful flotation. The recommended preconcentration procedure is fast (about 25 min) and extends the range of conventional AAS determination of silver and thallium. The necessary equipment for flotation is simple and inexpensive. The use of a small amount of surfactant and tiny air bubbles necessary to perform a proper flotation cannot permit any serious contamination risks, which could be manifested by high blank values. One of the most important advantages of the recommended method is the ability to analyze a larger volume of sample solutions and to obtain a great preconcentration factor, as well as excellent recoveries of the trace elements investigated.

Hexamethylenedithiocarbamate compared with tetramethylenedithiocarbamate<sup>13,14</sup> has been shown to be a very appropriate reagent for flotation purposes. When this collector is used, the application of two surfactants (NaDDS and NaOL) is not necessary<sup>13,14</sup> and consequently the amount of conc. HNO<sub>3</sub> necessary to destroy the scum is lowered. The precision of the method, as a relative standard deviation, was found to be 3.95 % for Tl and 2.0 % for Ag and the detection limit was found to be 0.027 µg/l for Tl and 0.005 µg/l for Ag. Comparison of the obtained relative standard deviations, as well as detection limits with the method employing TMDTC<sup>-</sup> (5.02 % and 0.08 µg/l for Tl and 5.72 % and 0.01 µg/l for Ag),<sup>13,14</sup> show the advantage of the procedure with Pb(HMDTC)<sub>2</sub>.

#### ИЗВОД

##### ETAAS ОДРЕЂИВАЊЕ ТАЛИЈУМА И СРЕБРА ИЗ ВОДЕНИХ МАТРИЦА НАКОН КОЛОИДНЕ ТАЛОЖНЕ ФЛОТАЦИЈЕ ПРИМЕНОМ ОЛОВА(II) ХЕКСАМЕТИЛЕНДИТИОКАРБАМАТА

КАТАРИНА ЧУНДЕВА, ГОРИЦА ПАВЛОВСКА и ТРАЈЧЕ СТАФИЛОВ

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Описана је брза метода за преткоцентрисање талијума и сребра у нанограмским количинама из свежих пијаћих вода (изворске, бунарске, чесменске) и вода за наводњавање, помоћу колоидне таложне флотације. Као флотациони колектор примењен је олово(II) хексаметилендитиокарбамат, Pb(HMDTC)<sub>2</sub>. Оптимирани су експериментални услови за успешну сепарацију талијума и сребра (маса олова, количина HMDTC<sup>-</sup>, рН, индукционо време, избор сурфактанта и др. Након флотационе сепарације из матичног раствора, чврсте честице које садрже трагове талијума и сребра су биле растворене и анализи су били одређивани помоћу електротермичке атомске апсорпционе спектрометрије (ETAAS). Резултати добивени помоћу ETAAS упоређивани су са онима добивеним помоћу атомске емисионе спектрометрије са индуктивно спрегнутом плазмом. Граница детекције за одређивање талијума овом методом износи 0,027 µg/l, а за сребро 0,005 µg/l.

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