

**Determination of Thallium Traces  
from Aqueous Solutions  
Using Iron(III) Hexamethylenedithiocarbamate  
as a Flotation Collector and Subsequent  
Electrothermal Atomic Absorption Spectrometry**

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Hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDTC) was used as a new flotation reagent for enrichment and separation of thallium traces from aqueous solutions. HMA-HMDTC added to the first precipitate collector of hydrated iron(III) oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) gives the second precipitate collector of iron(III) hexamethylenedithiocarbamate ( $\text{Fe}(\text{HMDTC})_3$ ). During the coprecipitation step, thallium ions are incorporated in the structure of the collector particles forming a sublimate, which is separated from the processed water phase by flotation. After the preconcentration and separation step, a quantitative analysis is performed by electrothermal atomic absorption spectrometry (ETAAS). The diverse experimental parameters affecting the flotation efficiency were determined and optimized. It was ascertained by a proposed procedure that total thallium can be separated quantitatively by addition of 10 mg  $\text{Fe}^{\text{III}}$  and 3 mL 0.1 mol/L  $\text{HMDTC}^-$  to the sample at  $\text{pH} = 6.0$ . The applicability of the proposed new procedure has been verified by the analysis of natural water samples by the method of standard additions and by inductively coupled plasma - atomic emission spectrometry (ICP-AES), as an independent comparative method. The limit of detection for thallium in this method is  $0.024 \mu\text{g/L}$ .

*Key words:* thallium, enrichment, flotation, determination, electrothermal atomic absorption spectrometry.

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## INTRODUCTION

It is very important to know the concentration of trace heavy metals in natural waters because of their biological effects on the environment. The most commonly used methods for monitoring heavy metals are the AAS techniques. However, in many cases, when the heavy metal level in an uncontaminated natural water sample is very low, the enrichment step is necessary to improve the precision and accuracy. In recent years, there has been an increased interest in developing methods for preconcentration and separation of metal traces from large volumes of dilute aqueous solutions by flotation techniques.<sup>1-6</sup> Flotations were first used in mining industry for selective separation of minerals from ores. Gradually, these techniques began to be used in other fields of chemical engineering for separation and removal of toxic substances, suspended solid particles, microorganisms, *etc.* from residual, industrial, sea and drinking waters. In the middle of the 1970's, the flotation techniques began to be used in analytical chemistry. It was found that the flotation technique, compared with classical separation methods, such as liquid-liquid extraction, ion-exchange, coprecipitation, *etc.*, is much simpler. Flotation allows handling of large volumes of samples and considerable saving of reagents and time. Flotation used as an analytical procedure can be generally divided into two groups: precipitate flotation and ion flotation. Precipitate flotation has the advantage of many higher enrichment factors than ion flotation. In this technique, an important role is that of the collector with its colloid nature.

The scope of the present paper is to investigate the applicability of  $\text{Fe}(\text{HMDTC})_3$ , as a flotation collector for simultaneous collection of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  from natural fresh waters where these two ions are present in very low concentrations. Hexamethylenedithiocarbamate anion ( $\text{HMDTC}^-$ ) is a well known reagent for trace metal preconcentration and separation by classical enrichment methods, such as extraction, coprecipitation and sorption,<sup>4,7-17</sup> but this work is the first attempt to apply HMA-HMDTC as a flotation reagent for thallium preconcentration. Having previously established the experimental conditions of the separation procedure, this work gives a clear insight into the degree of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  recoveries by the proposed method.

## EXPERIMENTAL

### *Instrumentation*

A Perkin-Elmer atomic absorption spectrometer 1100 B with HGA-700 electrothermal atomizer was used for measurements. A thallium Perkin-Elmer hollow cathode lamp was applied as radiation source. For the ETAAS standard, pyrolytically

coated graphite tubes and platforms were used. High purity argon served to protect the graphite furnace during the atomization cycle. The same gas was used for ICP-AES measurements by Varian Liberty 110. Instrumental parameters (temperature and time) for ETAAS were established by extensive testing (Table I).

TABLE I  
Optimal instrumental parameters for thallium determination  
with ETAAS

Wavelength	276.8 nm
Spectral width slit	0.7 nm
Lamp current	20 mA
Background correction	D <sub>2</sub>
Drying	90 °C, 25 s
Charring	400 °C, 30 s
Atomizing	2200 °C, 5 s
Cleaning	2650 °C, 3 s
Sheath gas	Argon

All pH readings were performed using a digital Iskra pH-meter 5705 with a combined glass electrode (Iskra Model 0101). The flotation cell, which served to separate the solid precipitate from the processed water phase, was described previously.<sup>18-25</sup> The equipment for determination of the electrokinetic ( $\zeta$ ) potential of the collector particle surfaces was a device analogous to Chaikovskii's equipment.<sup>26-28</sup>

### *Reagents and Standards*

All reagents and standards were prepared of chemicals that were analytically pure, except for surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC), cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX100). Aqueous solutions were prepared with redistilled water. By dissolving a commercial standard solution (Titrisol, Merck) containing 1 g of Tl<sup>I</sup> in the form of TlNO<sub>3</sub> in 1 L water, the stock solution of Tl<sup>I</sup> was made as 1 mg/mL. The same commercial standard solution was used for preparation of Tl<sup>III</sup> stock solution. With the aid of several drops of bromine, the TlNO<sub>3</sub> solution was oxidized and Tl<sup>I</sup> was converted to Tl<sup>III</sup>. The solution was evaporated nearly to dryness (to eject the excess of bromine) and the residue was diluted to 1 L. Before each investigation series of Tl<sup>I</sup> and Tl<sup>III</sup>, standard solutions were freshly prepared by diluting these stock solutions. Stock solution of Fe<sup>III</sup> was prepared as 30 mg/mL solution of Fe(NO<sub>3</sub>)<sub>3</sub> by dissolving an appropriate mass of high-purity iron metal (Merck) in conc. HNO<sub>3</sub>. Diluting this Fe<sup>III</sup> stock solution, series of standards with the concentration of Fe ranging from 2.5 to 100 mg/mL were obtained. HMA-HMDTC solution was prepared as 0.1 mol/L in 96% ethanol. Solutions of foaming reagents were made as 0.5% by dissolving appropriate amounts of surfactants in water (TX-100), 95% ethanol (NaDDS, NaOL, BTC, CTAB) and 99.7%

propane-2-ol (NaPL, NaST). The pH of the medium was adjusted by a  $\text{HNO}_3$  solution (0.1 mol/L) and solutions of KOH (25% and 10%). A saturated solution of  $\text{KNO}_3$  ( $c = 2.78$  mol/L) at 20 °C was used to regulate the ionic strength. The solution of 0.1 mol/L  $\text{NH}_4\text{NO}_3$  served to transfer quantitatively the content of the beaker into the flotation cell.

### *Recommended Procedure*

The preconcentration procedure employed in this work consisted of coprecipitation and flotation. During the coprecipitation (which was carried out in the beaker) traces of thallium are incorporated in the collector particles and make a sublimate and then by flotation (which was performed in the flotation cell) the sublimate was separated from the water phase.

#### *Coprecipitation*

A combined glass electrode was immersed into 1 L of an acidified water sample. After adding 6 mL of saturated  $\text{KNO}_3$  solution, an appropriate amount of  $\text{Fe}^{\text{III}}$  was put into the beaker. Monitoring the pH value on the pH-Meter display, the medium pH was carefully adjusted to 6.0 by KOH solutions. The yellow-brown precipitate of hydrated iron(III) oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , was stirred for about 5 minutes (first induction time,  $\tau_1$ ) by means of a magnetic stirrer. Then, a suitable volume of  $\text{HMDTC}^-$  solution was added to the system. The precipitate gradually changed its colour from yellow-brown to black (colour of  $\text{Fe}(\text{HMDTC})_3$ ). After stirring for 10–15 minutes (second induction time,  $\tau_2$ ), 1 mL of the foamy reagent was added and the content of the beaker was transferred quantitatively into the flotation cell with small portions of 0.1 mol/L  $\text{NH}_4\text{NO}_3$ .

#### *Flotation*

When the investigated system was placed in the flotation cell, a stream of numerous air bubbles (which effluxes from the bottom of the cell at a speed of 50 mL/min) was passed through the solution for 1 min. Gas bubbles raised the precipitate flakes to the water phase surface. There, a foamy layer was formed and the water in the cell became completely clear and free of solid particles. Then, the glass pipette-tube was immersed into the cell through the foam layer on the liquid surface and the water phase was sucked off. By means of 2.5 mL of hot 65%  $\text{HNO}_3$ , the solid phase in the cell was decomposed and dissolved. When the liquid in the cell became clear yellow, the solution was sucked off by vacuum 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  $\text{HNO}_3$  solution. The flask was filled up to the mark with 4 mol/L  $\text{HNO}_3$  and the sample was ready for AAS measurements.

## RESULTS AND DISCUSSION

### *Effect of $\text{Fe}^{\text{III}}$ Mass on $\text{Tl}^{\text{I}}$ and $\text{Tl}^{\text{III}}$ Flotation*

To investigate the effect of  $\text{Fe}^{\text{III}}$  mass on  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  enrichment, a series of flotations of working solutions containing 25 and 50  $\mu\text{g}$  of  $\text{Tl}^{\text{I}}$  or  $\text{Tl}^{\text{III}}$

were carried out at constant pH (5.5) and ionic strength ( $I_c = 0.02$  mol/L). The mass of  $\text{Fe}^{\text{III}}$  added to each solution (1 L) was changed from 2.5 to 100.0 mg, while the amount of the chelating reagent  $\text{HMDTC}^-$  was kept constant ( $2 \times 10^{-4}$  mol). The experiment has proved that the increase of  $\text{Fe}^{\text{III}}$  mass did not influence enrichment of both thallium ions in the same way. The higher  $\text{Fe}^{\text{III}}$  mass caused an increase of  $\text{Tl}^{\text{I}}$  flotation efficiency, reaching quantitative recoveries of 99.3–98.5% with 30 mg  $\text{Fe}^{\text{III}}$ , while  $\text{Tl}^{\text{III}}$  recoveries, under the same conditions, are significantly lower (Figure 1). Use of 30 mg of  $\text{Fe}^{\text{III}}$  achieved maximal  $\text{Tl}^{\text{III}}$  flotation recoveries of 89.7–90.7%. A further addition of  $\text{Fe}^{\text{III}}$  ( $> 40$  mg Fe) produced a decrease of  $\text{Tl}^{\text{III}}$  flotation efficiency. Probably, a proper preconcentration of  $\text{Tl}^{\text{III}}$  might be carried out at some other pH or by using a different amount of  $\text{HMDTC}^-$ .

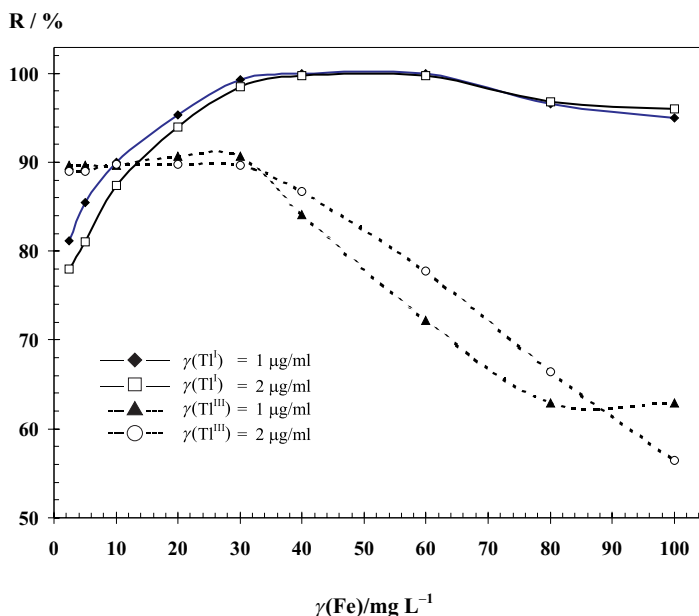


Figure 1. Influence of  $\text{Fe}^{\text{III}}$  mass on thallium recoveries ( $R$ ) at constant pH = 5.5,  $I_c = 0.02$  mol/L and  $c(\text{HMDTC}^-) = 2 \times 10^{-4}$  mol/L.

#### *Influence of Medium pH on $\text{Tl}^{\text{I}}$ and $\text{Tl}^{\text{III}}$ Floatability*

Because the variation of medium pH can induce coagulation, precipitation or hydrolysis of ionic species involved in the process, determination of this parameter must be performed with special care.

The influence of medium pH on thallium flotation efficiency was studied from the aspect of the incorporation of both thallium ions in the collector particles during the coprecipitation step. For this purpose, series of standard solutions of both thallium ions (with the same mass as in the previous section) were coprecipitated and floated using a constant  $\text{Fe}^{\text{III}}$  mass (30 mg) and amount of  $\text{HMDTC}^-$  ( $2 \times 10^{-4}$  mol) at constant ionic strength (0.02 mol/L) by consecutively varying the pH values (from 3.0 to 6.5). The experimental data of these investigations are presented as  $R/\text{pH}$  curves in Figures 2 and 3.

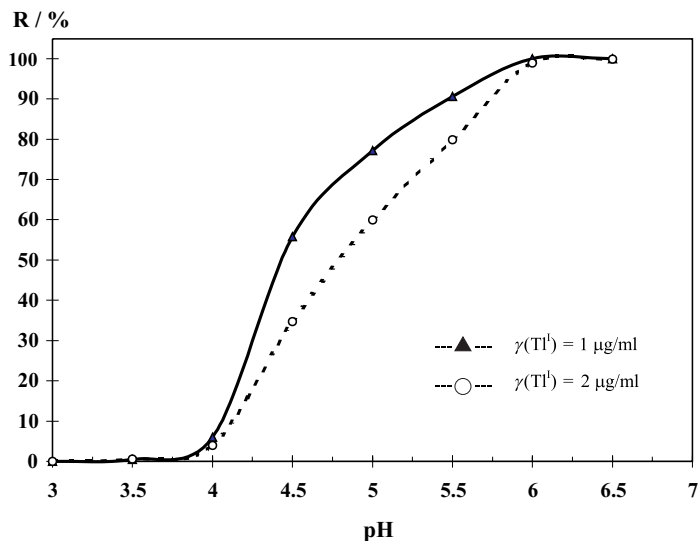


Figure 2. Influence of pH on  $\text{Tl}^{\text{I}}$  recoveries (30 mg Fe,  $2 \times 10^{-4}$  mol  $\text{HMADTC}^-$ , pH = 5.5,  $I_c = 0.02 \text{ mol L}^{-1}$  by  $\text{KNO}_3$ , NaDDS as surfactant).

The  $R/\text{pH}$  curves show that the flotation of both thallium ions at low pH's is ineffective. There is practically no foam in stronger acid media at pH's of 3.5 to 4.0, where the values of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  flotation recoveries are extremely poor. The optimal pH range for total Tl flotation is within the pH range 6.0–6.5, where the values of  $R$  for  $\text{Tl}^{\text{I}}$  are 99.9–100.0%, while  $\text{Tl}^{\text{III}}$  recoveries are 100.0%. For further investigations, a pH value of 6.0 was chosen as the working pH.

#### *Influence of the Amount of $\text{HMDTC}^-$*

To investigate the influence of the amount of  $\text{HMDTC}^-$  on  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  collection from investigated media, four series of solutions of both thallium

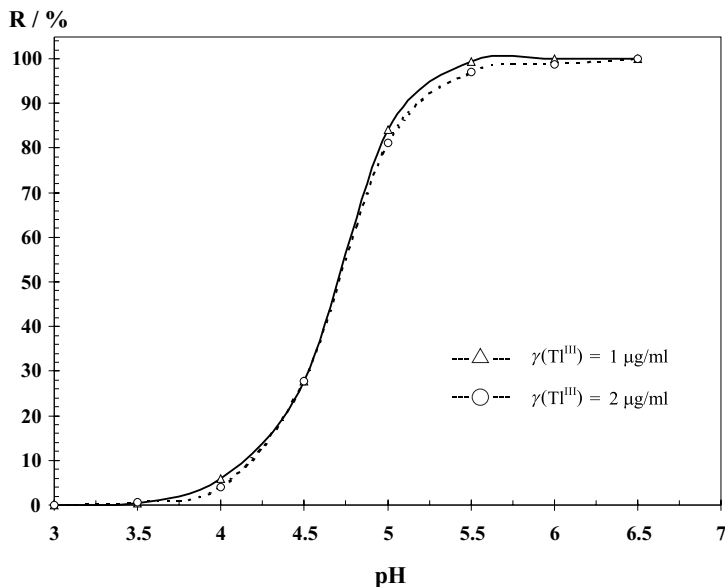


Figure 3. Influence of pH on  $\text{Tl}^{\text{III}}$  recoveries (30 mg Fe,  $2 \times 10^{-4}$  mol  $\text{HMADTC}^-$ , pH = 5.5,  $I_c = 0.02 \text{ mol L}^{-1}$  by  $\text{KNO}_3$ , NaDDS as surfactant).

ions were floated by addition of different amounts of  $\text{HMDTC}^-$  ( $(1.3\text{--}6) \times 10^{-4}$  mol to 1 L of solution) at a constant pH (6.0) and ionic strength (0.02 mol/L). All working solutions of 1 L contained  $25 \mu\text{g Tl}^{\text{I}}$  or  $\text{Tl}^{\text{III}}$ . The series of solutions contained 5.0, 10.0, 20.0 and 30.0 mg of  $\text{Fe}^{\text{III}}$ , respectively. As can be seen from the data presented in Figures 4 and 5,  $n(\text{HMDTC}^-)$  influences the collection of both thallium ions. Quantitative recoveries of  $\text{Tl}^{\text{I}}$  were obtained adding 10.0, 20.0 or 30.0 mg of  $\text{Fe}^{\text{III}}$  together with  $3 \times 10^{-4}$  or  $6 \times 10^{-4}$  mol of  $\text{HMDTC}^-$  to 1 L of the test solution. Satisfactory recoveries of  $\text{Tl}^{\text{III}}$  were attained adding all the mass of Fe together with  $3 \times 10^{-4}$  or  $6 \times 10^{-4}$  mol of  $\text{HMDTC}^-$ . The lowest  $\text{Fe}^{\text{III}}$  mass (10 mg) and  $\text{HMDTC}^-$  amount (0.0003 mol) were chosen as most appropriate for the procedure.

#### *Ionic Strength*

The effect of ionic strength ( $I_c$ ) was very important for the coagulation of the system. Three standards of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$ , respectively, were floated at pH = 6 with 10 mg  $\text{Fe}^{\text{III}}$  and 0.0003 mol  $\text{HMDTC}^-$  without adding any ionic strength adjuster. The standards had varying volumes (250, 500 and 1000 mL). Each standard solution contained  $50 \mu\text{g Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$ , so that the final solutions concentrated by flotation (25 mL) had a concentration of  $2 \mu\text{g/mL}$ . By addition of 1 mL of 0.1791 mol/L solution of  $\text{Fe}(\text{NO}_3)_3$ , each standard so-

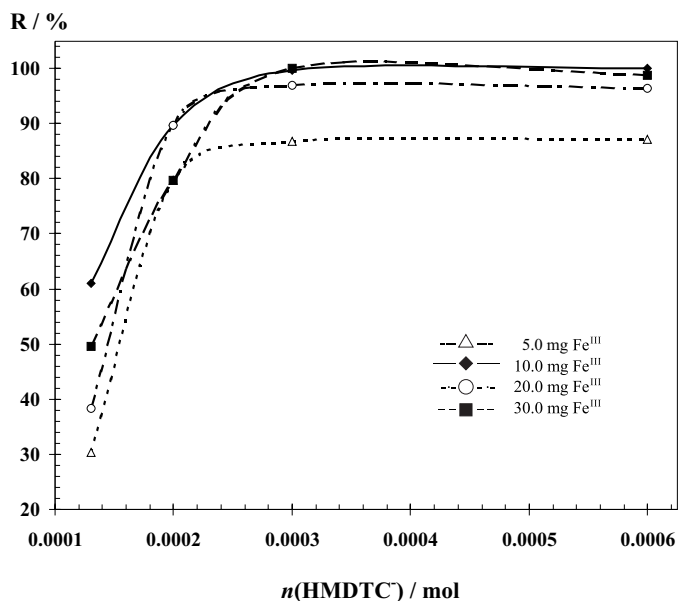


Figure 4. Influence of the amount of  $\text{HMDTC}^-$  on  $\text{Tl}^{\text{I}}$  flotation recoveries  $R$  (%) at constant pH (6.0) and  $I_c$  (0.02 mol/L), with 5.0, 10.0, 20.0 and 30.0 mg Fe.

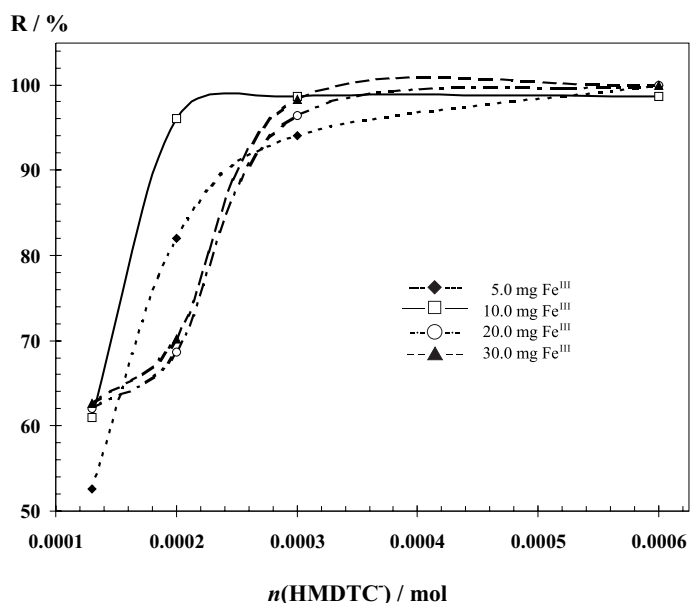


Figure 5. Influence of the amount of  $\text{HMDTC}^-$  on  $\text{Tl}^{\text{III}}$  flotation recoveries  $R$  (%) at constant pH (6.0) and  $I_c$  (0.02 mol/L), with 5.0, 10.0, 20.0 and 30.0 mg Fe.



lution contained 10 mg Fe. The ionic strength of the first, second and third solution, respectively, were 0.0043 mol/L, 0.0022 mol/L and 0.0011 mol/L. After flotations, the thallium was determined by AAS. The results of these investigations are given in Table II. The values of Tl<sup>I</sup> flotation recoveries of the first and the second solution were 100%, while of the third they were 79.5%. The recoveries of the first, second and third flotation of Tl<sup>III</sup> were 100.0, 98.7 and 75.3%, respectively. These data have proved that to obtain proper coagulation, it is necessary to adjust the ionic strength of the system to some higher value than 0.0011 mol/L. Therefore, an ionic strength of 0.02 mol/L is regarded appropriate for the procedure.

TABLE II  
Dependence of the Tl<sup>I</sup> and Tl<sup>III</sup> flotation recoveries on the ionic strength ( $I_c$ ) of the solutions

$m(\text{Fe})$	$c / \text{mol L}^{-1}$		$I_c / \text{mol L}^{-1}$	R / %	
	$\text{Fe}^{3+}$	$\text{NO}_3^-$		Tl <sup>I</sup> <sup>a</sup>	Tl <sup>III</sup> <sup>a</sup>
10 mg / 250 mL	$7.162 \times 10^{-4}$	$2.1487 \times 10^{-3}$	0.0043	100	100
10 mg / 500 mL	$3.581 \times 10^{-4}$	$1.0743 \times 10^{-3}$	0.0022	100	98.7
10 mg / 1000 mL	$1.791 \times 10^{-4}$	$5.372 \times 10^{-4}$	0.0011	79.5	75.3

<sup>a</sup>  $\gamma(\text{Tl})$ , mass concentration of Tl<sup>I</sup> i.e. Tl<sup>III</sup> = 2  $\mu\text{g mL}^{-1}$ .

### *Selection of the Surfactant*

By floating a series of solutions (1 L) containing 25  $\mu\text{g}$  Tl<sup>I</sup> or Tl<sup>III</sup> the selection of the most effective foaming reagent was carried out. Several anionic (NaDDS, NaOL, NaPL and NaST), cationic surfactants (BTC and CTAB), as well as one non-ionic tenside (TX100), were investigated within the pH range of 3.5 to 6.5. To each test solution, 1 mL of 0.5% solution of the surfactant was added. Fe<sup>III</sup> mass (10 mg), the amount of HMDTC<sup>-</sup> ( $3.0 \times 10^{-4}$  mol) and ionic strength (0.02 mol/L) were those established in previous sections.

The attempt of flotation with BTC and CTAB, as well as TX100, was unsuccessful. BTC and CTAB, as well as non-ionic TX100, frothed very well over a wide pH interval of investigation, but there was no flotation (Table III). These tensides could not help separate the solid phase from the liquid water phase. A copious white scum was formed at the top of the water in the

flotation cell, but the black precipitate of coagulated  $\text{Fe}(\text{HMDTC})_3$  remained in the liquid. These investigations suggest that the surface of  $\text{Fe}(\text{HMDTC})_3$  particles might be of the same charge as the cationic surfactants.

Anionic surfactants were tested singly (NaDDS, NaOL, NaPL and NaST) and in pair (NaDDS/NaOL, NaPL/NaOL and NaST/NaOL). These investigations (Table III) confirm that  $\text{pH} = 6$  is the optimal value for  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$  flotation preconcentration. Since at  $\text{pH}$  higher than 6.5 the collector  $\text{Fe}(\text{HMDTC})_3$  begins to hydrolyze (which can be seen by the change of the black colour of the solid phase in the system to red-brown – the colour of hydrated iron(III) oxide,  $\text{Fe}_2\text{O}_3 \times x\text{H}_2\text{O}$ ), investigations at  $\text{pH}$ 's higher than 6.5 were not performed. Within the  $\text{pH}$  range of 3.0 to 5.0, flotation effectiveness was poor due to protonation of anionic surfactants. Within the  $\text{pH}$  range of 5.5 to 6.5, flotations were more successful. Among anionic surfactant testing at  $\text{pH} = 6.0\text{--}6.5$ , the single NaDDS was shown to be the most appropriate for flotation of both thallium ions (97.3–96.9% for  $\text{Tl}^{\text{I}}$  and 98.8–100.0% for  $\text{Tl}^{\text{III}}$ ) and was chosen to be the reagent for the method. The recoveries obtained using the pair NaDDS/NaOL for  $\text{Tl}^{\text{I}}$  within  $\text{pH}$ 's 6.0–6.5 (96.0–96.0%) and for  $\text{Tl}^{\text{III}}$  at  $\text{pH} = 6.5$  (95.2%) were also satisfactory, but this combination of surfactants gave unnecessarily a too copious scam, which it was very difficult to destroy with conc.  $\text{HNO}_3$ . When NaDDS was used single, the destroying of the scam proceeded more quickly.

### *$\zeta$ Potential of Collector Particles*

The measurements of  $\zeta$  potential of the collector particles explains why the cationic surfactants tested in the previous section could not be used for flotation of  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$ . The values of  $\zeta$  potentials of  $\text{Fe}(\text{HMDTC})_3$  collector floc surface are 68.4–69.0 mV. The same sign of the cationic surfactant charge and that of the collector particle surface explains their ineffectiveness for flotations.

### *Detection Limit*

The detection limit of the method was estimated as three values of the standard deviation ( $s = 0.008 \mu\text{g/L}$ ). For this purpose, ten successive blank measurements were made. The ETAAS detection limit of thallium is  $0.024 \mu\text{g/L}$ . The relative standard deviation of the method was 4.28%.

### *Application of the Method*

The basic procedure was applied for uncontaminated natural water samples (spring and tap waters from the neighborhood of the city of Skopje,

TABLE III  
 Applicability of diverse foaming reagents for flotation of thallium (pH = 6.0,  $I_c = 0.02$  mol/L,  $\gamma(\text{Fe}) = 10$  mg/L,  $c(\text{HMDTC}^-) = 3 \times 10^{-4}$  mol/L)

pH	3.5	4.0	4.5	5.0	5.5	6.0	6.5
BTC				$R(\text{TI}^I) / \%$			
CTAB				foam, no flotation			
NaDDS	no foam	no foam	30.1	71.5	83.6	97.3	96.9
NaOL	no foam	no foam	27.4	68.9	87.7	96.5	95.6
NaPL	no foam	no foam	no foam	32.7	83.3	83.3	78.1
NaST	no foam	no foam	no foam	77.3	89.6	89.6	59.1
TX-100				foam, no flotation			
NaDDS/NaOL	no foam	no foam	41.3	70.5	83.9	96.2	96.0
NaST/NaOL	no foam	no foam	62.1	65.0	65.0	69.8	71.3
NaPL/NaOL	no foam	no foam	26.8	29.3	83.5	89.5	89.5
				$R(\text{TI}^{III}) / \%$			
BTC				foam, no flotation			
CTAB				foam, no flotation			
NaDDS	no foam	no foam	59.3	84.6	98.8	98.8	100.0
NaOL	no foam	no foam	19.8	44.2	81.8	79.9	93.9
NaPL	no foam	no foam	no foam	35.3	49.6	53.3	81.8
NaST	no foam	no foam	no foam	35.3	47.8	64.5	79.9
TX-100				foam, no flotation			
NaDDS/NaOL	no foam	no foam	4.8	51.4	70.2	81.8	95.2
NaST/NaOL	no foam	no foam	3.2	37.1	44.2	58.2	64.5
NaPL/NaOL	no foam	no foam	14.7	51.4	58.8	72.1	79.8

Macedonia). Samples were collected in polyethylene containers (pretreated by concentrated  $\text{HNO}_3$ , washed with deionized redistilled water and then with a portion of the water sample) without filtration. To prevent the possible hydrolytic precipitation of some mineral salts, a few milliliters of conc.  $\text{HNO}_3$  had to be added to 1 L of natural water. The pH had to be about 3.

Water samples were analyzed using a calibration curve and by the method of standard additions. For this purpose, known amounts of thallium were added to 1000 mL aliquots of each water sample. Then, the samples were floated by the established method and 40-fold concentrated. The results obtained by ETAAS were compared with the results obtained by ICP-AES determinations (Table IV).

TABLE IV

ETAAS determination of thallium in natural water samples by the method of standard additions and a comparison with ICP-AES results

Water sample	ETAAS				ICP-AES <sup>a</sup>
	Added	Estimated	Found	Recovery	Found
	$\gamma(\text{Tl})/\mu\text{g L}^{-1}$	$\gamma(\text{Tl})/\text{mg L}^{-1}$	$\gamma(\text{Tl})/\text{mg L}^{-1}$	%	$\gamma(\text{Tl})/\text{mg L}^{-1}$
Pantelejmon					
(15.05 DH <sup>o</sup> <sup>b</sup> pH = 7.84)	– 0.50	– 0.625	0.125 0.600	– 96.0	0.12
Sreden Izvor					
(17.65 DH <sup>o</sup> pH = 7.36)	– 0.50	– 0.625	0.125 0.598	– 95.6	0.15
Raduša					
(25.57 DH <sup>o</sup> pH = 8.50)	– 0.50	– 0.530	0.030 0.525	– 99.0	<0.10
Rašče					
(16.49 DH <sup>o</sup> pH = 7.18)	– 0.50	– 0.647	0.147 0.625	– 96.5	0.16
Kapištec					
(16.49 DH <sup>o</sup> pH = 7.18)	– 0.50	– 0.750	0.250 0.730	– 97.7	0.35

<sup>a</sup> Results of comparative ICP-AES determination of Tl (samples were enriched by evaporation).

<sup>b</sup> DH (Deutsche Härte), German degree of water hardness.

## CONCLUSION

The investigations have proved that  $\text{Fe}(\text{HMDTC})_3$  is a better collector than iron (III) tetramethylenedithiocarbamate,  $\text{Fe}(\text{TMDTC})_3$ , for flotation separation of thallium from diluted fresh water samples.<sup>25</sup> When  $\text{Fe}(\text{TMDTC})_3$  is used, the flotation of thallium requires two surfactants, NaDDS and NaOL, while  $\text{Fe}(\text{HMDTC})_3$  needs only one. The recommended method extends the concentration range of the conventional AAS determination of thallium. A relative standard deviation was found to be 4.28% using  $\text{Fe}(\text{HMDTC})_3$  as collector, while by applying  $\text{Fe}(\text{TMDTC})_3$  it was 5.02%. The detection limit of the method was found to be 0.024  $\mu\text{g/L}$  for thallium with  $\text{Fe}(\text{HMDTC})_3$ , while with  $\text{Fe}(\text{TMDTC})_3$  it was 0.08  $\mu\text{g/L}$ . All these facts show that the presence of  $\text{HMDTC}^-$  improves separation of both thallium ions from the processed water phase.  $\text{HMDTC}^-$  anion increases the hydrophobicity of the sublute, which is the most important criterion of successful flotation. The value of  $\zeta$  potential of the  $\text{Fe}(\text{HMDTC})_3$  flocs is more positive than the  $\zeta$  potential of  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  and  $\text{Fe}(\text{TMDTC})_3$  flocs, resulting in a better separation efficiency. To avoid  $\text{Cl}^-$  interferences on the  $\text{Tl}^{\text{I}}$  recoveries, reagents containing  $\text{Cl}^-$  should not be used.<sup>25</sup>

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## SAŽETAK

### **Određivanje tragova talija u vodenim otopinama elektrotermičkom atomskom apsorpcijskom spektrometrijom uz predhodnu uporabu željezova(III) heksametilenditiokarbamata kao flotacijskog kolektora**

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Heksametilenamonijev heksametilenditiokarbamat (HMA-HMDTC) upotrijebljen je kao novi flotacijski reagens za obogaćivanje i odjeljivanje tragova talija iz vodenih otopina. Dodan prvomu taložnom kolektoru – hidratiziranom željezovu(III) oksidu ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) – HMA-HMDTC daje drugi taložni kolektor – željezov(III) heksametilenditiokarbamat,  $\text{Fe}(\text{HMDTC})_3$ . Za vrijeme koprecipitacije talijevi se ioni ugrađuju u strukturu čestica kolektora, koje se zatim odvajaju flotacijom. Nakon postupka ugušćivanja i odjeljivanja provodi se kvantitativno određivanje elektrotermičkom atomskom apsorpcijskom spektrometrijom (ETAAS). Ispitani su razni eksperimentalni parametri koji utječu na djelotvornost flotacije te su određeni oni koji daju najbolje rezultate. Predloženim postupkom talij se može kvantitativno odijeliti dodatkom 10 mg  $\text{Fe}^{\text{III}}$  i 3 mL 0.1 mol/L HMDTC<sup>-</sup> kod pH = 6.0. Primjenljivost predloženog postupka provjerena je analizom uzoraka prirodnih voda metodom dodatka standarda, a kao usporedbena metoda upotrijebljena je atomska emisijska spektrometrija s induktivno spregnutom plazmom (ICP-AES). Detekcijski prag za talij određen opisanom metodom jest 0.024  $\mu\text{g/L}$ .