

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

*Gorica Pavlovska, Katarina Čundeva, and Trajče Stafilov**

*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
St. Cyril and Methodius University, Skopje, Macedonia*

Received October 15, 1999; revised July 24, 2000; accepted July 26, 2000

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 Fe^{III} and 3 mL 0.1 mol/L 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.

* Author to whom correspondence should be addressed. (E-mail: trajcest@iunona.pmf.ukim.edu.mk)

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.¹⁻⁶ 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 Tl^{I} and Tl^{III} from natural fresh waters where these two ions are present in very low concentrations. Hexamethylenedithiocarbamate anion (HMDTC^-) is a well known reagent for trace metal preconcentration and separation by classical enrichment methods, such as extraction, coprecipitation and sorption,^{4,7-17} 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 Tl^{I} and Tl^{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 ₂ |
| 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.¹⁸⁻²⁵ The equipment for determination of the electrokinetic (ζ) potential of the collector particle surfaces was a device analogous to Chaikovskii's equipment.²⁶⁻²⁸

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^I in the form of TlNO₃ in 1 L water, the stock solution of Tl^I was made as 1 mg/mL. The same commercial standard solution was used for preparation of Tl^{III} stock solution. With the aid of several drops of bromine, the TlNO₃ solution was oxidized and Tl^I was converted to Tl^{III}. 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^I and Tl^{III}, standard solutions were freshly prepared by diluting these stock solutions. Stock solution of Fe^{III} was prepared as 30 mg/mL solution of Fe(NO₃)₃ by dissolving an appropriate mass of high-purity iron metal (Merck) in conc. HNO₃. Diluting this Fe^{III} 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 HNO_3 solution (0.1 mol/L) and solutions of KOH (25% and 10%). A saturated solution of KNO_3 ($c = 2.78$ mol/L) at 20 °C was used to regulate the ionic strength. The solution of 0.1 mol/L NH_4NO_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 KNO_3 solution, an appropriate amount of Fe^{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, τ_1) by means of a magnetic stirrer. Then, a suitable volume of 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, τ_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 NH_4NO_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% HNO_3 , the solid phase in the cell was decomposed and dissolved. When the liquid in the cell become 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 HNO_3 solution. The flask was filled up to the mark with 4 mol/L HNO_3 and the sample was ready for AAS measurements.

RESULTS AND DISCUSSION

Effect of Fe^{III} Mass on Tl^{I} and Tl^{III} Flotation

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

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

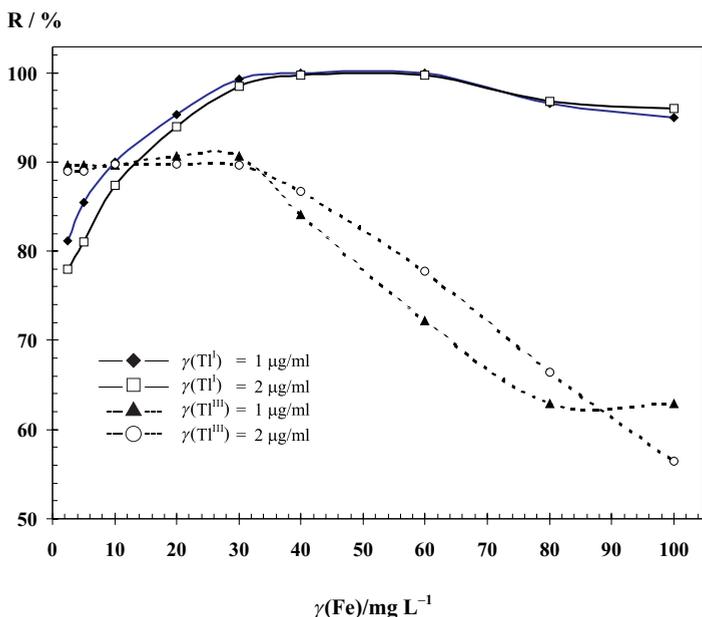


Figure 1. Influence of Fe^{III} mass on thallium recoveries (R) at constant pH = 5.5, $I_c = 0.02$ mol/L and $c(\text{HMDTC}^-) = 2 \times 10^{-4}$ mol/L.

Influence of Medium pH on Tl^{I} and Tl^{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 Fe^{III} mass (30 mg) and amount of HMDTC^- (2×10^{-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/pH curves in Figures 2 and 3.

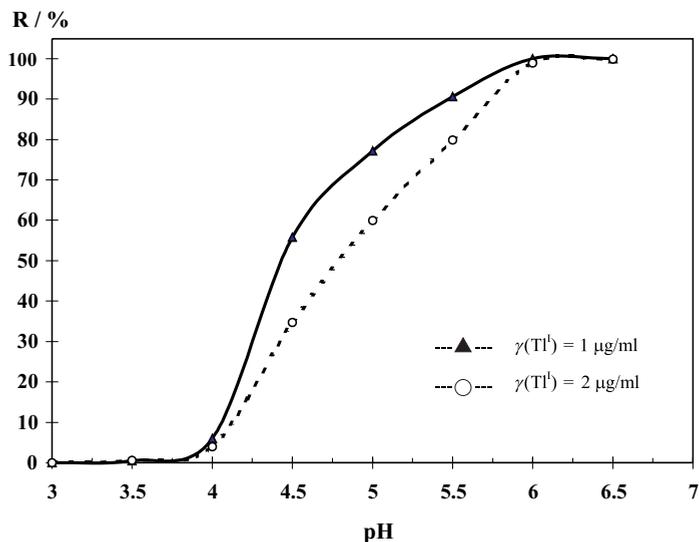


Figure 2. Influence of pH on Tl^{I} recoveries (30 mg Fe, 2×10^{-4} mol HMADTC^- , pH = 5.5, $I_c = 0.02 \text{ mol L}^{-1}$ by KNO_3 , NaDDS as surfactant).

The R/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 Tl^{I} and Tl^{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 Tl^{I} are 99.9–100.0%, while Tl^{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 HMDTC^-

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

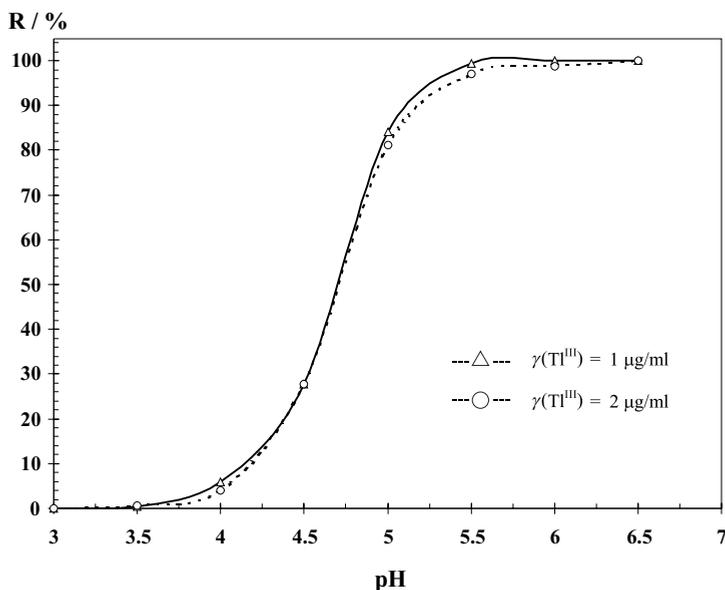


Figure 3. Influence of pH on Tl^{III} recoveries (30 mg Fe, 2×10^{-4} mol HMDTC⁻, pH = 5.5, $I_c = 0.02$ mol L⁻¹ by KNO₃, NaDDS as surfactant).

ions were floated by addition of different amounts of HMDTC⁻ ($(1.3-6) \times 10^{-4}$ 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 µg Tl^I or Tl^{III}. The series of solutions contained 5.0, 10.0, 20.0 and 30.0 mg of Fe^{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 Tl^I were obtained adding 10.0, 20.0 or 30.0 mg of Fe^{III} together with 3×10^{-4} or 6×10^{-4} mol of HMDTC⁻ to 1 L of the test solution. Satisfactory recoveries of Tl^{III} were attained adding all the mass of Fe together with 3×10^{-4} or 6×10^{-4} mol of HMDTC⁻. The lowest Fe^{III} mass (10 mg) and 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 Tl^I and Tl^{III}, respectively, were floated at pH = 6 with 10 mg Fe^{III} and 0.0003 mol HMDTC⁻ without adding any ionic strength adjuster. The standards had varying volumes (250, 500 and 1000 mL). Each standard solution contained 50 µg Tl^I and Tl^{III}, so that the final solutions concentrated by flotation (25 mL) had a concentration of 2 µg/mL. By addition of 1 mL of 0.1791 mol/L solution of Fe(NO₃)₃, each standard so-

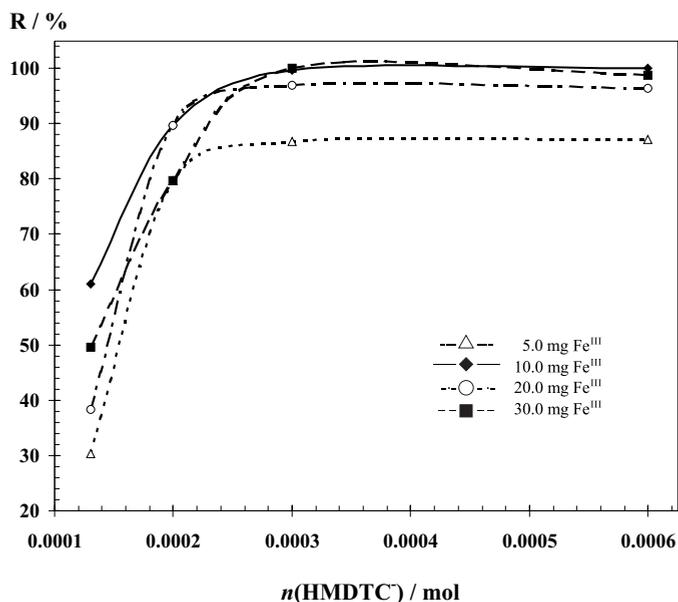


Figure 4. Influence of the amount of HMDTC^- on Tl^{I} flotation recoveries R (%) at constant pH (6.0) and I_c (0.02 mol/L), with 5.0, 10.0, 20.0 and 30.0 mg Fe.

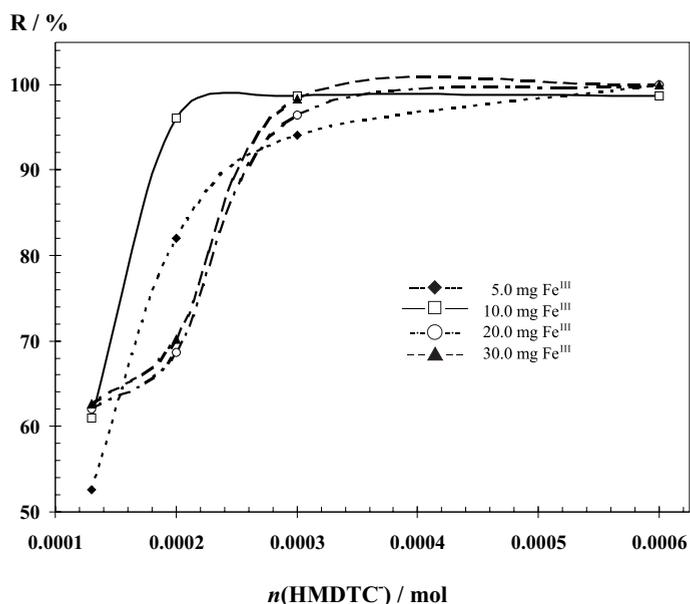


Figure 5. Influence of the amount of HMDTC^- on Tl^{III} flotation recoveries R (%) at constant pH (6.0) and I_c (0.02 mol/L), with 5.0, 10.0, 20.0 and 30.0 mg Fe.

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^I 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^{III} 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^I and Tl^{III} 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 / % | |
|-----------------|-------------------------|-------------------------|---------------------------|------------------------------|--------------------------------|
| | Fe^{3+} | NO_3^- | | Tl ^I ^a | Tl ^{III} ^a |
| 10 mg / 250 mL | 7.162×10^{-4} | 2.1487×10^{-3} | 0.0043 | 100 | 100 |
| 10 mg / 500 mL | 3.581×10^{-4} | 1.0743×10^{-3} | 0.0022 | 100 | 98.7 |
| 10 mg / 1000 mL | 1.791×10^{-4} | 5.372×10^{-4} | 0.0011 | 79.5 | 75.3 |

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

Selection of the Surfactant

By floating a series of solutions (1 L) containing 25 μg Tl^I or Tl^{III} 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^{III} mass (10 mg), the amount of HMDTC⁻ (3.0×10^{-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 Tl^{I} and Tl^{III} flotation preconcentration. Since at 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 pH 's higher than 6.5 were not performed. Within the pH range of 3.0 to 5.0, flotation effectiveness was poor due to protonation of anionic surfactants. Within the 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 Tl^{I} and 98.8–100.0% for Tl^{III}) and was chosen to be the reagent for the method. The recoveries obtained using the pair NaDDS/NaOL for Tl^{I} within pH 's 6.0–6.5 (96.0–96.0%) and for Tl^{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. HNO_3 . When NaDDS was used single, the destroying of the scam proceeded more quickly.

ζ Potential of Collector Particles

The measurements of ζ potential of the collector particles explains why the cationic surfactants tested in the previous section could not be used for flotation of Tl^{I} and Tl^{III} . The values of ζ 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 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. 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 ^a |
|---|--|--------------------------------------|--------------------------------------|----------|--------------------------------------|
| | 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 ^o ^b pH = 7.84) | – | – | 0.125 | – | 0.12 |
| | 0.50 | 0.625 | 0.600 | 96.0 | |
| Sreden Izvor | | | | | |
| (17.65 DH ^o pH = 7.36) | – | – | 0.125 | – | 0.15 |
| | 0.50 | 0.625 | 0.598 | 95.6 | |
| Raduša | | | | | |
| (25.57 DH ^o pH = 8.50) | – | – | 0.030 | – | <0.10 |
| | 0.50 | 0.530 | 0.525 | 99.0 | |
| Rašče | | | | | |
| (16.49 DH ^o pH = 7.18) | – | – | 0.147 | – | 0.16 |
| | 0.50 | 0.647 | 0.625 | 96.5 | |
| Kapištec | | | | | |
| (16.49 DH ^o pH = 7.18) | – | – | 0.250 | – | 0.35 |
| | 0.50 | 0.750 | 0.730 | 97.7 | |

^a Results of comparative ICP-AES determination of Tl (samples were enriched by evaporation).

^b 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.²⁵ 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 HMDTC^- improves separation of both thallium ions from the processed water phase. HMDTC^- anion increases the hydrophobicity of the sublimate, which is the most important criterion of successful flotation. The value of ζ potential of the $\text{Fe}(\text{HMDTC})_3$ flocs is more positive than the ζ 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 Cl^- interferences on the Tl^{I} recoveries, reagents containing Cl^- should not be used.²⁵

REFERENCES

1. B. L. Karger, L. R. Snyder, and C. Horvath, *Adsorptive Bubble Separation Process in an Introduction to Separation Science*, Wiley, New York, 1973.
2. Yu. A. Zolotov and N. M. Kuzmin, *Koncentrirovanie mikroelementov*, Himiya, Moskva, 1982.
3. A. Mizuike, *Flotation*, in: *Enrichment Techniques for Inorganic Trace Analysis*, Chapter 10, Springer-Verlag, Berlin, Heidelberg, New York, 1983.
4. N. M. Kuzmin and Yu. A. Zolotov, *Koncentrirovanie sledov elementov*, Nauka, Moskva, 1988.
5. M. Caballero, R. Cela, and J. A. Pérez-Bustamante, *Talanta* **37** (1990) 275–300.
6. A. Mizuike and M. Hiraide, *Pure Appl. Chem.* **54** (1982) 1556.
7. A. I. Busev, V. M. Byrko, A. P. Tereshenko, N. N. Novikova, V. P. Naidina, and P. B. Terentiev, *Zh. Anal. Khim.* **25** (1970) 665–669.
8. A. I. Busev, V. M. Byrko, A. P. Tereshenko, N. B. Krotova, and V. P. Naidina, *Zh. Anal. Khim.* **28** (1973) 649–662.
9. A. I. Busev, A. P. Tereshenko, N. B. Krotova, T. V. Nolde, V. M. Byrko, and O. G. Puzanova, *Zh. Anal. Khim.* **28** (1973) 858–862.
10. H. Berndt and E. Jackwerth, *Fresenius' Z. Anal. Chem.* **290** (1978) 369–371.
11. A. Dornemann and H. Kleist, *Fresenius' Z. Anal. Chem.* **291** (1978) 349–353.
12. M. Betz, S. Gücer, and F. Fucs, *Fresenius' Z. Anal. Chem.* **303** (1980) 4–9.
13. S. Brüggerhoff and E. Jackwerth, *Fresenius' Z. Anal. Chem.* **326** (1987) 528–535.
14. R. Eidecker and E. Jackwerth, *Fresenius' Z. Anal. Chem.* **328** (1987) 469–475.
15. P. Burba and P. G. Willmer, *Fresenius Z. Anal. Chem.* **329** (1987) 539–545.

16. V. M. Byrko, V. A. Vizhenskii, and T. P. Molchanova, *Zh. Anal. Khim.* **42** (1987) 1576–1581.
17. R. Eidecker and E. Jackwerth, *Fresenius' Z. Anal. Chem.* **331** (1988) 401–406.
18. K. Čundeва, T. Stafilov, and S. Atanasov, *Analisis* **24** (1996) 371–374.
19. K. Čundeва and T. Stafilov, *Fresenius' Z. Anal. Chem.* **352** (1995) 354–356.
20. T. Stafilov and K. Čundeва, *Bull. Chem. Technol. Macedonia* **15** (1996) 93–99.
21. K. Čundeва and T. Stafilov, *Fresenius' Z. Anal. Chem.* **358** (1997) 818–821.
22. K. Čundeва and T. Stafilov, *Anal. Lett.* **30** (1997) 833–845.
23. K. Čundeва and T. Stafilov, *Talanta* **44** (1997) 451–456.
24. G. Pavlovska, K. Čundeва, and T. Stafilov, *Bull. Chem. Technol. Macedonia* **16** (1997) 131–138.
25. T. Stafilov and K. Čundeва, *Talanta* **46** (1998) 1321–1328.
26. O. N. Grigorov, I. F. Karpova, and Z. P. Kozmina *Rukovodstvo k Prakticheskim Rabotam po Kolloidnoi Khimii*, Khimiya, Moskva, 1964.
27. L. D. Skrylev, A. N. Purich, and S. K. Babinetz, *Zh. Prikl. Khim.* **54** (1981) 1832–1835.
28. J. Eggert, L. Hock, and G.-M. Schwab, *Lehrbuch der Physikalischen Chemie*, Hirsel Verlag, Stuttgart, 1960.

SAŽETAK

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

Gorica Pavlovska, Katarina Čundeва i Trajče Stafilov

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 Fe^{III} i 3 mL 0.1 mol/L HMDTC⁻ 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 $\mu\text{g/L}$.