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Selective preconcentration of thallium species as chloro and iodo complexes on Chromosorb 105 resin prior to electrothermal atomic absorption spectrometry

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ABSTRACT

A selective preconcentration method was described for the determination of inorganic thallium species by electrothermal atomic absorption spectrometry (ETAAS). Thallium(III) and thallium(I) as chloro and iodo complexes were selectively retained by a column containing 0.5 g of Chromosorb 105 resin and quantitatively eluted by 10 mL of pure acetone. The calibration graph was linear with a correlation coefficient of 0.997 at levels near the detection limit and up to at least 0.8 $\mu g\,L^{-1}$. The detection limits for the determination of total thallium and thallium(III) employing the proposed method by ETAAS were estimated as three values of the standard deviations, 0.050 $\mu g\,L^{-1}$ and 0.034 $\mu g\,L^{-1}$, respectively. Verification of the accuracy was carried out by the analysis of standard reference materials (GBW 07402 soil, NIST 2710 Montana soil, GBW 07309 and GBW 07310 stream sediments). The relative errors were found to be in the range of −7.7% to +4.8%. The relative standard deviations were generally found to be below 10%. The effect of potential interfering ions on the determination was studied. The proposed method was successfully applied to the determination of total thallium in five different brand cements, soils around two cement plants and metallic zinc samples. The speciation of thallium(I) and thallium(III) was applied to synthetic solutions.

1. Introduction

Thallium has been identified to be an environmentally significant element because of its toxic effects. The toxicity of thallium is higher than that of Hg, Cd, Pb and Cu [1,2]. Moreover, thallium is known to have mutagenic, carcinogenic, and teratogenic activity [3]. Whereas the elemental form of thallium has essentially no toxicity, its monovalent and trivalent salts are highly toxic. Thallium is found in nature as Tl(I) and Tl(III) ions but its univalent state has higher stability, whereas its trivalent state forms complexes of greater stability.

Thallium enters the environment primarily from coal-burning and smelting, in which it is a trace contaminant of the raw materials. Larger quantities of thallium may also be found in stack gases and airborne dust, particularly from cement works [4,5], which will end up in soils, sediments and waters following atmospheric deposition. The main source of elevated thallium concentrations in water is the leaching of thallium from ore processing operations. Thallium stays in the air, water, and soil for a long time and is not broken down; however, the total concentration of thallium in environmental samples is generally quite low. Therefore, development of new methods for selective and sensitive determination of thallium at submicro levels especially in environmental samples is of continuing interest which needs separation and preconcentration steps prior to analysis.

Atomic absorption spectrometry (AAS) [6–8], inductively coupled plasma-mass spectrometry (ICP-MS) [9–11] and electroanalytical methods [12,13] in conjunction with preconcentration techniques have been used for determination of thallium at trace level. AAS is very useful; however, when the analyte concentration is extremely low, even for ETAAS, thallium determination needs a preconcentration procedure. Among the preconcentration procedures, such as solvent extraction, ion-exchange, coprecipitation, and flotation, solid-phase extraction (SPE) proves to be very simple. The conventional solvent extraction and co-precipitation are laborious and apt to carry a risk of contamination. Solid-phase extraction techniques allow handling of large volumes of sample and considerable saving in organic solvent, because of replacement of organic phase solvent with a solid phase material reused many times. A survey of the literature revealed that various adsorbents such as Amberlite XAD resins [14,15], silica C-18 [16], activated carbon [17], polyethylene [18], microcrystalline naphthalene [19] and carbon nanotubes [20] have been investigated for preconcentration of thallium by SPE based on adsorption. To the best of the authors'

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knowledge, no report is found in the literature for preconcentration of thallium as chloro and iodo complexes using a column filled with Chromosorb 105 resin.

Thallium(III) strongly binds to unidentate ligands such as Cl^- and I^- to form charged anionic species $TlCl_4{}^-$ or $TlI_4{}^-$ [21,22]. The ionic species have been extracted using a solvent extraction method based on salting-out upon addition of electrolytes to mixed solvents of water and water-miscible organic solvents [23,24]. The organic phase separated by salting-out from an aqueous–organic solvent mixture always contains a lot of salt, resulting in a highly polar solvents compared to the corresponding pure organic solvents [25]. Because of spectral and non-spectral interferences from the presence of chloride salt in aqueous solution, the determination of thallium using graphite furnace AAS involves many difficulties [26]. These problems can be prevented using a solid phase extraction method where excess salt is eliminated. For this, few attempts have been made to examine the retention of Tl(III) and Tl(I) as chloro-complexes, on Amberlite XAD-4, -7 and -8 resins and Chelex-100 chelating resin [14]. The studies do not include analytical applications, however, give us most important clues.

Thus, the goals of the present paper are focused on the use of a Chromosorb 105 resin column for the preconcentration of total thallium and speciation of chemical forms of mono- and tri-valence thallium species as halogeno complexes in aqueous media. The determination of total thallium in cement, soil and water samples have been also included.

2. Experimental

2.1. Instruments

The absorbance measurements were performed using a Perkin–Elmer AAnalyst 700 atomic absorption spectrometer (Norwalk, USA) equipped with graphite furnace atomizer HGA-800, an autosampler AS-70 and a deuterium-arc background correction system. A thallium hollow-cathode lamp operated at 25 mA was used as a radiation source. All measurements were performed using integrated absorbance signals in the form of peak area and/or peak height at 276.8 nm with a spectral bandwidth of 0.2 nm. The sample solutions were injected as 10 μL. Uncoated graphite furnace tubes (Perkin–Elmer, Germany, part no.: B0070699) were used as an atomizer. The recommended operating conditions for thallium determination are given in Table 1. The argon flow-stop was used during the atomization step. The pH adjustment was controlled using WTW pH 340-A/SET 2 pH meter.

2.2. Reagents and solution

All solutions were prepared from high purity analytical-reagent grade compounds using ultra-pure (UP) quality water (resistivity18.2 $M\Omega\,cm^{-1}$) obtained with a reverse osmosis system (Human Corporation, Seoul, Korea). The water did not contain any detectable concentration of thallium under optimum working conditions with ETAAS. All the plastic and glass wares were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with ultrapure water prior to use.

Table 1
Graphite furnace program for the determination of thallium by ETAAS.

Steps	Temperature (°C)	Ramp time (s)	Hold time (s)
Drying 1	100	5	20
Drying 2	140	15	15
Pyrolysis	700	10	20
Atomization[a]	1600	0	5
Cleaning	2600	1	3

[a] Gas flow (argon) was set to 0 $L\,min^{-1}$ for atomization step and 250 $mL\,min^{-1}$ for the other steps.

Thallium(I) and thallium(III) stock standard solutions, 1000 $mg\,L^{-1}$, were prepared from $TlNO_3$ (Merck) and $Tl(NO_3)_3{\cdot}3H_2O$ (Merck), respectively, in 0.5 $mol\,L^{-1}$ HNO_3. The Pd chemical modifier added in solution was prepared by dilution of 1000 $mg\,L^{-1}$ Pd atomic absorption standard solutions (Fluka, Buchs, Switzerland) in 0.05% (v/v) Triton X-100 (Union Carbide). The calibration solutions and synthetic test solutions were daily prepared by serial dilution of the stock standard solution. The calibration standards were not submitted to the preconcentration/separation procedure.

Chromosorb 105 resin (Sigma Chem. Co., St. Louis) was used as a solid-phase extractant. To remove organic and inorganic contaminants Chromosorb 105 was washed successively with methanol, water, 1 $mol\,L^{-1}$ HNO_3 in acetone, water, 1 $mol\,L^{-1}$ NaOH and water, respectively. A bead size of resin 20–50 mesh was selected for the preconcentration procedure. Smaller resin particles could have improved retention capacity, but the flow rates of sample solution and eluent solution ought to have been reduced, with subsequent increase in separation/preconcentration time.

The following CRMs were used in this work: GBW 07402 soil, NIST 2710 Montana soil, GBW 07309 stream sediment and GBW 07310 stream sediment. Cement, soil and metallic zinc samples were analysed. Cement samples were taken from different cement plants in Kayseri-city of Turkey, and soil samples in the vicinity of the cement plants were collected. Metallic zinc samples were taken from a military plant in Kayseri.

2.3. Method developed

A glass column (10 cm length and 1.0 cm diameter) with a fritted glass and a stopcock has been used for preconcentration of thallium. The column was packed with 500 mg of Chromosorb 105 resin and the resin was fixed in the column with small pieces of glass wool. To remove organic and inorganic contaminants, the packed Chromosorb 105 resin was washed successively with methanol, water, 1 $mol\,L^{-1}$ HNO_3 in acetone, water, 1 $mol\,L^{-1}$ NaOH, water, acetone and water. After each use, the resin in the column was washed thoroughly with water and related buffer solution, and then stored in water for further applications. The height of the column section containing the resin bed (bed height) was almost 2.0 cm.

The performance of column method was tested with synthetic solutions before its application to real samples. For the preconcentration of Tl(I) and Tl(III) as total thallium, the defined amount of NaI as a complexing agent was added to 50 mL of synthetic thallium solutions, including Tl(I) and Tl(III) as 10 $\mu g\,L^{-1}$. Both NaI and HCl concentrations in these synthetic solutions were 0.5 $mol\,L^{-1}$, in changing the concentration from 0 to 1.0 $mol\,L^{-1}$ for both HCl and NaI. The solutions were loaded to the top of the preconditioned column and gravitationally passed at a flow rate of 6.0 $mL\,min^{-1}$. The column was washed with 5–10 mL of a blank solution prepared with the corresponding agent and acid solution. The retained thallium species were eluted with acetone. The effluent was evaporated to near dryness on a hot plate adjusted ca. 30–40 °C and then cooled. 0.5 μg of palladium as a matrix modifier was added to the residue. Finally, the residues were diluted to 1.0 mL of 1 $mol\,L^{-1}$ HNO_3. The content of thallium in the final solutions was determined by ETAAS. The matrix-matched calibration standards were prepared in ranging of 10–100 $\mu g\,L^{-1}$ by using reagent blank solutions including sample preparing and column procedures.

For selective preconcentration of thallium(III) in presence of thallium(I), 50 mL of synthetic thallium solutions including Tl(I) and Tl(III) as 10 $\mu g\,L^{-1}$ was prepared with 0.5 $mol\,L^{-1}$ HCl and then the column procedure was applied to the synthetic solution. The con-

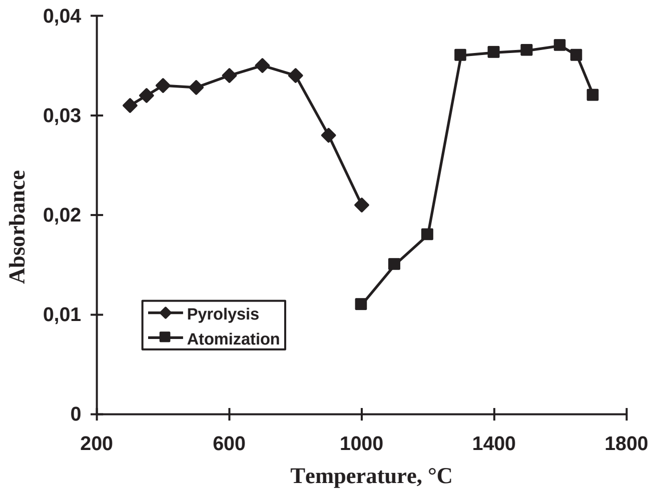

Fig. 1. Pyrolysis and atomization temperature curves of thallium in obtaining effluent with SPE.

centration of thallium(I) was calculated by the difference between the value of total thallium and thallium(III).

2.4. Real sample analysis

The solid samples were weighed (approximately 0.500 g) into pre-cleaned glass beakers, and then 10 mL of conc. HNO_3 added. The beakers were then covered with clean watch glasses and placed on a hotplate and boiled for at least 1.5 h. If the sample neared dryness, 1 mL of conc. HCl was added into the residue and again the beaker content was heated to the neared dryness. Then, 25–30 mL of 0.5 mol L^{-1} HCl was added into the beaker. To determine thallium(III), the solution was then filtered to remove undigested material and diluted to 50 mL with 0.5 mol L^{-1} HCl, prior to being analysed using the proposed column method given above. To determine the total thallium, after the filtration above, sufficient NaI (0.5 mol L^{-1} in the final volume of 50 mL) was added to the beaker. The total thallium content in the beaker was determined using the proposed column method given above.

Metallic zinc samples were weighed as approximately 0.500 g into pre-cleaned glass beakers and then aqua regia (10 mL) added. The content of the beaker was boiled for at least one hour. If the sample neared dryness (a few milliliters), a further volume (5 mL) of aqua regia was added. Again the beaker content was heated to the neared dryness. 25–30 mL of 0.5 mol L^{-1} HCl was added into the beaker. The solution was filtered, then sufficient NaI (0.5 mol L^{-1} in the final volume of 50 mL) and diluted to 50 mL with 0.5 mol L^{-1} HCl. The total thallium was determined according to the proposed column method given above.

3. Results and discussion

3.1. Effect of pyrolysis and atomization temperatures on the absorbance of thallium

Obtaining sensitive and reproducible analytical results in the determination of elements by ETAAS depends on optimizing the temperatures of pyrolysis and atomization of the analyte. The optimization of the furnace heating program was therefore focused on the temperature of the pyrolysis and atomization steps. The pyrolysis and atomization curves were drawn, based on the composition of final solution obtained after the SPE procedure given above (Fig. 1). For this, the blank solutions obtained by applying SPE procedure recommended above were spiked with thallium as 10 μg L^{-1}. The optimal pyrolysis and atomization temperatures throughout this study were kept at 700 °C and 1600 °C, respectively, to obtain high sensitivity and prevent the loss of analyte, and also to prolong the tube life.

Until now, palladium for thallium determination with ETAAS has been used as a matrix modifier [27–29]. Therefore the effect of palladium was evaluated on absorbance of thallium prepared using the obtaining blank solution with the SPE procedure. Fig. 2 shows that the absorbance of thallium increased with increasing amount of palladium up to 400 ng, but not almost changed from 400 ng up, declining quickly after 700 ng, in examined amount range of palladium. Under these established conditions, 500 ng of palladium as a modifier was added into the effluent solution, through this study.

3.2. Effect of hydrochloric acid and sodium iodide concentrations on retention of thallium

Thallium(III) forms charged anionic species such as $TlCl_4^-$ or TlI_4^- [21,22]. The ionic species as ion association complexes have been extracted into the organic phase. On the other hand it is well known that the iodo complexes of Tl(I) and Tl(III) are formed in acidic solutions [30]. The solvent extraction of Tl(I) and Tl(III) as iodide compounds, and Tl(III) as a chloride compound is well documented in the literature. Thallium(III) as a chloro complex from hydrochloric acid solution is extracted while both thallium(I) and thallium(III) as iodo complexes are extracted [31,32]. On the other hand, thallium(III) is efficiently adsorbed on Amberlite XAD-8 and Chelex 100 from 0.1 to 8 M hydrochloric acid solutions [14].

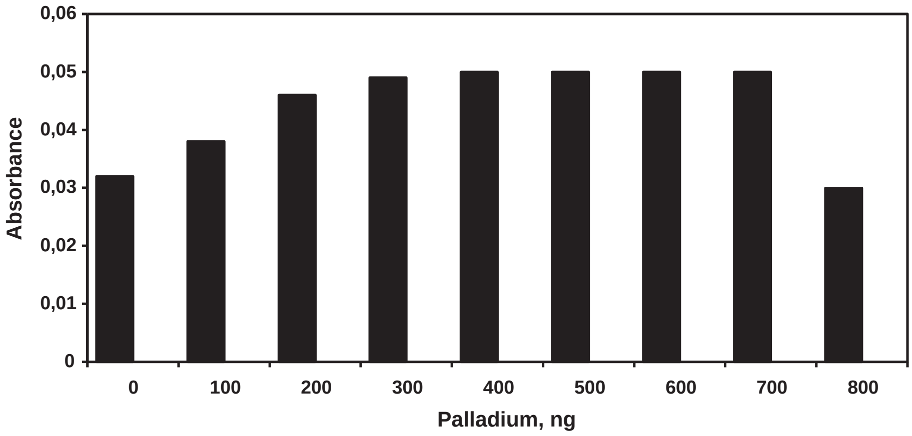

Fig. 2. Effect of palladium amount on absorbance of thallium in obtaining effluent with SPE.

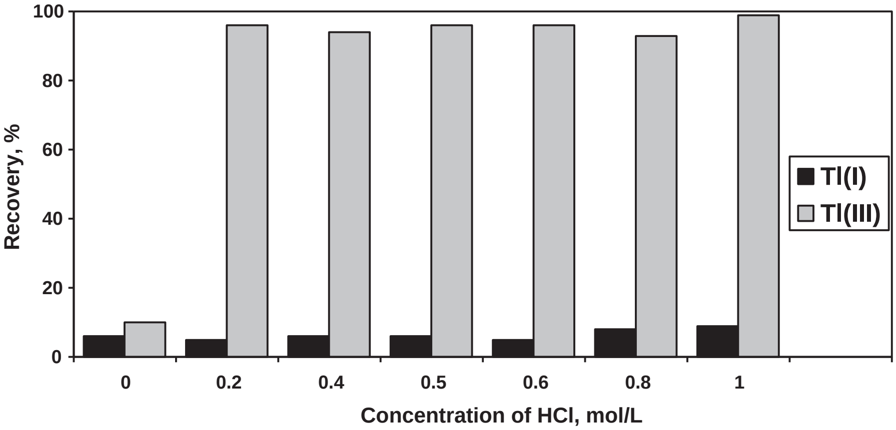

Fig. 3. Effect of HCl concentration on recoveries of Tl(I) and Tl(III) (*n*: 3).

Based on the knowledges given above, the influences of acidity, chloride and iodide concentrations as critical key parameters in achieving quantitative retentions of Tl(I) and Tl(III) on Chromosorb 105 resin were investigated with the proposed column technique. Fig. 3 shows that Tl(III) is retained quantitatively from a model solution having concentration range of 0.2–1.0 mol L^{-1} HCl, but not Tl(I). The lower recovery values of Tl(I) are probably because of unstable chloro complexes of Tl(I). Because of acidic solution, $TlCl_4^-$ as H^+ $TlCl_4^-$ is neutralized by H^+, resulting in the retention of thallium(III) on Chromosorb 105 resin having hydrophobic properties.

The effect of NaI concentrations in 0.5 mol L^{-1} hydrochloric acid solution was also investigated on the retentions of Tl(I) and Tl(III). The retention behaviors of Tl(I) and Tl(III) are almost same (Fig. 4). In light of the information given above, Tl(I) is retained as an iodo complex (TlI_2^-), while Tl(III) is retained as TlI_4^- or $TlCl_4^-$ from 0.5 mol L^{-1} HCl solutions including NaI. Thus, it may be concluded that the adsorption might be due to the formation ø-$H^+TlI_4^-$ or ø-$H^+TlCl_4^-$ and ø-$H^+TlI_2^-$ from a styrene–divinylbenzene network of Chromosorb 105 resin and iodo and/or chloro complexes, using of general comments given by Koshima [14].

3.3. Effect of the sample volume on retention of thallium

In order to explore the possibility of enriching low concentrations of analyte from large volume, the effect of sample volume on the recovery of thallium ions was investigated. For this purpose, sample solutions prepared in different volumes, containing 1.0 μg of Tl(I) and Tl(III) were passed through the column of Chromosorb 105 resin at optimum flow rate. The quantitative recovery (≥95%) was obtained for thallium ions up to a sample volume of 150 mL (Table 2). Thus, 150 mL of sample solution can be adopted for the preconcentration of thallium ions from aqueous solutions, the adsorbed thallium ions can be eluted with 10 mL of pure acetone, because of evaporating effluent up to 1.0 mL with 1.0 mol L^{-1} nitric acid, a enrichment factor of 150 is achieved by this procedure.

Table 2
Effect of sample volume on recoveries of Tl(III) and total Tl (*n*: 3).

Sample volume (mL)	Recovery (%)	
	Tl(III)	Total Tl
25	99 ± 2	98 ± 2
50	98 ± 2	100 ± 2
100	98 ± 3	98 ± 1
150	96 ± 1	97 ± 2
200	92 ± 2	92 ± 2
300	90 ± 3	88 ± 3
400	90 ± 4	61 ± 3
500	87 ± 3	13 ± 3

3.4. Eluent types

To achieve a quantitative recovery, the influence of eluent types on the recoveries of Tl(III) and total thallium was investigated using various eluting solutions, such as pure acetone, 1 mol L^{-1} HNO_3 in acetone, ethanol, 1.0 mol L^{-1} HNO_3, 1.0 and 2.0 mol L^{-1} HCl, 1.0 mol L^{-1} NH_3 and 1.0 mol L^{-1} NaOH. The quantitative recoveries (≥95%) for Tl(III) and total thallium were obtained with 10 mL of pure acetone, 1 mol L^{-1} HNO_3 in acetone and ethanol (except for

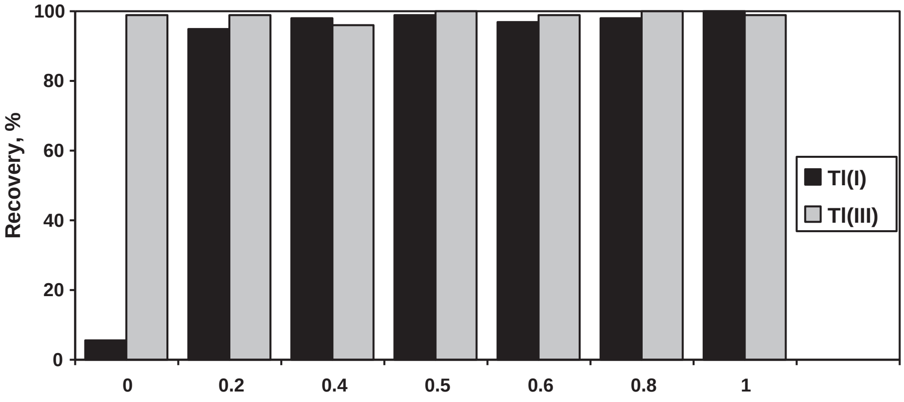

Fig. 4. Effect of concentration of NaI in 0.5 mol L^{-1} HCl on recoveries of Tl(I) and Tl(III) (*n*: 3).

Table 3
Effect of coexisting ions for recoveries of Tl(III) and total Tl (*n*: 3).

Ions	Added (mg L^{-1})	Recovery (%)	
		Tl(III)	Total Tl
Na^+	25,000	95 ± 2	100 ± 3
K^+	25,000	97 ± 3	96 ± 2
Ca^{2+}	5000	97 ± 3	96 ± 2
Mg^{2+}	20,000	98 ± 1	97 ± 2
Fe^{3+}	50,000	97 ± 2	96 ± 3
Fe^{2+}	50,000	95 ± 2	93 ± 3
Al^{3+}	50,000	95 ± 2	102 ± 2
Zn^{2+}	5000	96 ± 3	94 ± 2
Co^{2+}	250	93 ± 1	94 ± 2
Ni^{2+}	250	96 ± 2	98 ± 3
Cu^{2+}	250	100 ± 2	97 ± 2
Mn^{2+}	250	75 ± 2	99 ± 2
Cr^{3+}	250	88 ± 3	97 ± 2
$SO_4{}^{2-}$	10,000	95 ± 3	102 ± 3
Cl^-	50,000	95 ± 2	99 ± 3
$NO_3{}^-$	5000	93 ± 3	95 ± 3
$CO_3{}^{2-}$	2500	98 ± 1	94 ± 2
$PO_4{}^{3-}$	2500	99 ± 1	97 ± 2

Table 4
Thallium content of certificated soil and sediment samples (*n*: 5).

Sample	Certificated values (μg g^{-1})	Found[a] total Tl (μg g^{-1})	Relative error (%)
GBW 07402 soil	0.62	0.58 ± 0.03	6.4
NIST 2710 Montana soil	1.3[b]	1.20 ± 0.34	−7.7
GBW 07309 stream sediment	0.49	0.46 ± 0.03	−6.1
GBW 07310 stream sediment	0.21	0.22 ± 0.02	4.8

[a] $\pm ts/\sqrt{n}$, *n*: 5, *P*: 0.95.
[b] Noncertified value.

Tl(III)). Pure acetone as a best eluent was preferred because of low blank value for thallium and low evaporation temperature. After the elution, the effluent was evaporated to dryness and filled up 1.0 mL using 1.0 mol L^{-1} HNO_3.

3.5. *Effect of flow rates on the extraction efficiency of thallium*

Flow rate of sample solution through the column is a very important parameter to obtain the quantitative retention and to control the time of pre-concentration. Thus the effect of sample flow rates on the retention was investigated in the range of 1–8 mL min^{-1} at constant elution flow rate as 2 mL min^{-1}. A flow rate ranging between 1 and 6 mL min^{-1} was found to be suitable for quantitative retention of Tl(III) and total Tl. Higher flow rates of sample solution did not lead to quantitative retention of thallium species. Another study showed that varying the eluent flow rates in the range of 1–8 mL min^{-1} did not significantly influence the elution efficiency of the thallium species. The results reflect the same adsorption–desorption rates of thallium species. Based on these results, we used the same flow rates as 5 mL min^{-1} for both retention and elution steps in subsequent experiments.

3.6. *Column reuse*

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL of 2.0 mol L^{-1} HCl and 20 mL distilled water, respectively, and stable up to at least 500 adsorption–elution cycles without obvious decrease in the recoveries for the studied ions.

3.7. *Effects of coexisting ions*

The effects of common coexisting ions on the retention of thallium on Chromosorb 105 resin were investigated. In these experiments, solutions of 10 μg L^{-1} of thallium containing the added interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of thallium less than 95%, were given in Table 3. It can be seen that the presence of major cations and anions has no obvious influence on the adsorption of thallium ions under the selected conditions.

3.8. *Analytical performance of the proposed procedures*

The solid phase extraction/preconcentration method developed using Chromosorb 105/HCl/NaI system allowed the determination of total thallium in the concentration range of 0.0–0.8 μg L^{-1} by ETAAS. The calibration equation was $A = 0.34 \times C$[Tl, μg L^{-1}] − 2.74×10^{-3} ($r^2 = 0.999$). Without preconcentration, in the concentration range of 0.0–100.0 μg L^{-1} Tl, the calibration equation was $A = 2.43 \times 10^{-3} \times C$[Tl, μg L^{-1}] + 5.13×10^{-3}($r^2 = 0.997$). The experimental enhancement factor, calculated from the ratio of the slopes of the calibration equations, was 139.9. The theoretical preconcentration factor, calculated as the ratio of the sample volume (150.0 mL) to the final effluent volume (1.0 mL) was 150.0. The relative error was calculated to be −6.7%.

The validation method for the total thallium determination was checked with the analysis of two standard reference soils and two standard reference sediments. The samples were dissolved according to a procedure given in Section 2. The solid-phase extraction procedure was applied to the sample solutions. Good agreement was obtained between the estimated content by the proposed procedure and certified values for total thallium (Table 4). The relative errors were found to be in the range −7.7% to +4.8%. The relative standard deviations were found to be below 10%.

In order to further check the accuracy of zinc and cement analysis, the recovery tests were also performed using the sample spiking thallium ions. Thallium ions were spiked before the filtration in the procedure given in Section 2. The results in Tables 5 and 6 show, those favorable recoveries from the real samples are achieved. Recoveries from 92% to 101% were estimated indicating that the procedure is free from matrix effects.

To evaluate the detection limit of the method, twenty successive blank measurements were carried out in the effluent obtained after 150 mL of the blank samples was passed through the column. The detection limits of thallium species preconcentrated from 0.5 mol L^{-1} HCl solution and a mixture of 0.5 mol L^{-1} HCl and

Table 5
Recoveries of thallium(III) and total thallium from the cement sample (*n*: 3).

Thallium(III)			Total Thallium			
Added Tl(III) (μg)	Found Tl(III) (μg)	Recovery (%)	Added Tl(I) (μg)	Added Tl(III) (μg)	Found total Tl (μg)	Recovery (%)
0	2.88 ± 0.80	–	0	0	5.5 ± 0.5	–
0.5	3.37 ± 0.03	98 ± 5	0.5	0.5	6.49 ± 0.12	100 ± 10
1.0	3.81 ± 0.03	93 ± 3	1.0	1.0	7.47 ± 0.05	99 ± 1
2.0	4.67 ± 0.03	92 ± 3	2.0	2.0	9.27 ± 0.12	94 ± 3

Table 6
Recoveries of Tl(III) and total thallium from zinc sample (*C*) (*n*: 3).

Thallium(III)			Total Thallium			
Added Tl(III) (μg)	Found Tl(III) (μg)	Recovery (%)	Added Tl(I) (μg)	Added Tl(III) (μg)	Found total Tl (μg)	Recovery (%)
0	0	–	0	0	–	–
0.5	0.49 ± 0.02	99 ± 2	0.25	0.25	0.49 ± 0.03	97 ± 3
1.0	1.07 ± 0.10	101 ± 10	0.5	0.5	0.97 ± 0.02	96 ± 2
2.0	1.95 ± 0.10	97 ± 10	1.0	1.0	1.85 ± 0.03	92 ± 3

Table 7
Total thallium concentrations in cement, soil and metallic zinc samples.

Sample	Total Tl (μg g^{-1})[a]
Cement A	0.035 ± 0.004
Cement B	0.062 ± 0.013
Cement C	0.070 ± 0.008
Cement D	0.098 ± 0.011
Cement E	0.090 ± 0.007
Soil A	0.714 ± 0.051
Soil B	0.251 ± 0.022
Zinc A	0.013 ± 0.002
Zinc B	0.011 ± 0.003
Zinc C	Not detected

[a] $\pm ts/\sqrt{n}$, *n*: 5, *P*: 0.95.

0.5 mol L^{-1} NaI, were estimated as three values of the standard deviations, 0.050 μg L^{-1} and 0.034 μg L^{-1}, respectively.

3.9. Applications

To evaluate the capability of the proposed procedure accomplishing the analysis of several cement samples taken from different cement plants in Kayseri-city and two soil samples collected in the vicinity of the cement plants were carried out (Table 7). The content of thallium of metallic zinc samples taken from a military plant were also determined using the proposed procedure (Table 7).

4. Conclusion

The procedure studied takes advantage of the combination of a very simple, reliable way of preconcentrating aqueous solutions for thallium determination with the sensitive, widely available ETAAS technique. With 50.0 mL preconcentration volume, six samples can be almost analysed in an hour. It can be used in practically all laboratories. In this study, possibility of speciation of the monovalent and trivalent inorganic forms of thallium has been shown by the analysis of synthetic aqueous solutions. It is concluded that the proposed procedure will be successfully applied to determination of total thallium in a wide range of real samples.

References

[1] J.O. Nriagu, Advances in environmental science and technology , in: J.O. Nriagu (Ed.), Thallium in the Environment, vol. 29, Wiley, Chichester, 1998, p. 1.
[2] G. Repetto, A. Del Peso, M. Repetto, Advances in environmental science and technology , in: J.O. Nriagu (Ed.), Thallium in the Environment, vol. 29, Wiley, Chichester, 1998, p. 167.
[3] A. Leonard, G.B. Gerner, Mutat. Res. -Rev. Mutat. 387 (1997) 47–53.
[4] J. Falbe, M. Reglitz (Eds.), Römpp Chemie Lexikon, vol. 6, 9th ed., Georg Thieme, Stuttgart, 1992, pp. 4549–4550.
[5] Y. Yang, P.J. Faustino, J.J. Progar, C.R. Brownell, N. Sadrieh, J.C. May, E. Leutzinger, D.A. Place, E.P. Duffy, L.X. Yu, M.A. Khan, R.C. Lyon, Int. J. Pharm. 353 (2008) 187.
[6] A.E. Hubert, T.T. Chao, Talanta 32 (1985) 568.
[7] V. Otruba, J. Stepankova, L. Sommer, Talanta 41 (1994) 1185.
[8] Y. Li, Y. Peng, Y. Ma, Q. Hu, G. Yang, Asian J. Chem. 21 (2009) 4593.
[9] H.H. Lu, S.J. Jiang, Anal. Chim. Acta 429 (2001) 247.
[10] H. Altundag, M.S. Dundar, Fresen. Environ. Bull. 18 (2009) 98.
[11] K.O. Beata, M. Asztemborska, J. Golimowski, K. Strusinska, J. Anal. Atom. Spectrom. 23 (2008) 1632.
[12] M.A. Allus, R.G. Brereton, Analyst 117 (1992) 1075.
[13] N. Spano, A. Panzanelli, P.C. Piu, M.I. Pilo, G. Sanna, R. Seeber, A. Tapparo, Anal. Chim. Acta 553 (2005) 201.
[14] H. Koshima, Anal. Sci. 2 (1986) 255.
[15] X. Yang, Untersuchungen zur Adsorptiven Anreicherung von Spuren Verbindungen, PhD Thesis, Ruhr Universität, Bochum, 1989.
[16] K. Urbankova, L. Sommer, Microchim. Acta 162 (2008) 127.
[17] H. Koshima, H. Onishi, Anal. Sci. 1 (1985) 237.
[18] D. Bohrer, P.G. do Nascimento, Microchim. Acta 126 (1997) 159.
[19] B. Rezaei, S. Meghdadi, N. Majidi, Spectrochim. Acta 67A (2007) 92.
[20] P.H. Pacheco, R.A. Gil, P. Smichowski, G. Polla, L.D. Martinez, Anal. Chim. Acta 656 (2009) 36.
[21] A.E. Martell, R.M. Smith, Critical Stability Constants, vol. 4 , Plenum Press, New York, 1976.
[22] R.G. Vibhute, S.M. Khopkar, Anal. Chim. Acta 222 (1989) 215.
[23] M. Tabata, M. Kumamoto, J. Nishimoto, Anal. Sci. 10 (1994) 383.
[24] H.C. Nguyen, J. Nishimoto, O. Kato, M. Tabata, Anal. Chim. Acta 477 (2003) 243.
[25] S. Haiping, J. Nishimoto, M. Tabata, Anal. Sci. 13 (1997) 119.
[26] I. Nukatsuka, R. Horiguchi, H. Seitoh, K. Ohzeki, F. Miyashita, J. AOAC Int. 87 (2004) 986.
[27] A.F. Silva, D.L.G. Borges, B. Welz, M.G.R. Vale, M.M. Silva, A. Klassen, U. Heitmann, Spectrochim. Acta 59B (2004) 841.
[28] B. Welz, G. Schlemmer, J.R. Mudakavi, Anal. Chem. 60 (1988) 2567.
[29] L. Husakova, T. Cernohorsky, J. Sramkova, K. Hubackova, I. Dolezalova, Anal. Chim. Acta 614 (2008) 38.
[30] M. Hosseini, Y. Naseri, Anal. Sci. 19 (2003) 1505.
[31] T.R. Dulski, A manual for the chemical analysis of metals , in: ASTM Manual Series, 1996 (Chapter 9).
[32] R. Pribil, Analytical Application of EDTA , Pergamon Press, Oxford, 1977.