Eurasian Journal of Analytical Chemistry
Volume 3, Number 1, 2008

Preconcentration Methods for Determination of Thallium in Natural Waters

Sonja Arpadjan[a], Pavleta Petrova[b], Jesper Knutsson[b]

[a]Faculty of Chemistry, bld. J. Bourchier 1, 1164 Sofia
[2]Fysikgränd 3, 41296 Gothenburg, Sweden,

Abstract

Two preconcentration procedures for electrothermal atomic absorption (ETAAS) determination of thallium in mineral, spring, tap, river, underground and sea water were developed and compared: (i) Column solid phase extraction with new sandwich type disposable sorbent columns (*CSPE*) and (ii) Filtration of thallium dithiocarbamates through a Millipore filter of 0.45 μm pore size followed by dissolution of the filter + precipitate in IBMK (*PP*) and introduction of the obtained organic slurry into the graphite furnace. With addition of indium as sorption and precipitation collector enrichment factors of 100 (*CSPE*) and 200 (*PP*) were achieved.

Keywords: thallium, water, preconcentration, solid-phase extraction, precipitation

1. Introduction

Thallium is an emerging pollutant with increasing importance due to its high toxicity [1, 2]. The US Environment Protection Agency included Tl in the list of priority pollutants in drinking water defining 0.5 μg L^{-1} Tl as maximum permissible concentration. The major part of the thallium in the environment studies has been carried out in waters [3]. The extremely low concentration of Tl in natural waters (below ng L^{-1} level) requires application of analytical methods with high sensitivity and low detection limit as inductively coupled plasma-mass spectrometry (ICP-MS) [4] and laser-excited atomic fluorescence spectrometry (LEAFS) [5]. However, ICP-MS needs expensive instrumentation with high running cost, and LEAFS is less frequently used. That is why the development of new reliable methods for preconcentration of this metal prior to its determination using more available analytical technique as electrothermal atomic absorption spectrometry (ETAAS), common reagents and materials continues to be a challenging problem. Solid phase extraction procedures ensure high preconcentration factors, possibilities for sample preconcentration on field, ability to handle large volume samples. An effective preconcentration technique was developed using a water-insoluble ligand, such as

ISSN: 1306-3057

hexamethyleneammonium hexamethylenedithiocarbamate (HMDTC), physically immobilized on polyurethane foam, and disposable syringes as micro columns [6-8]. This procedure allows multielement preconcentration with reagents and materials available in each laboratory without the need for additional chemical syntheses, but the sorbent preparation requires soaking of polyurethane foam pieces in a solution of HMDTC in chloroform, followed by solvent evaporation at room temperature thus prolonging the time for analysis and polluting the laboratory environment.

Precipitation of heavy metals with ammonium pyrrolidinedithiocarbamate (APDC) allowed their fast determination in waters using X-ray fluorescence spectrometric method [9, 10]. The main advantage of this precipitation procedure is the possibility to handle with large sample volume achieving high concentration factor, but investigations for Tl are not yet published.

The aim of the present work is to develop i) a new sandwich-type preconcentration column for thallium preconcentration; ii) a preconcentration procedure based on thallium precipitation with APDC in presence of indium as collector, filtration through a Millipore filter of 0.45 µm pore size and slurry injection into ETAAS.

2. Experimental

2.1. Apparatus

The ETAAS measurements were performed on a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 atomic absorption spectrometer with an HGA-600 atomizer. The light source used was a hollow-cathode lamp for Tl. The spectral band pass and the wavelength used were as recommended by Perkin-Elmer. Uncoated graphite tubes with pyrolytic platforms were used as atomizers. Solutions (10 µL) were introduced into the graphite atomizer manually after heating the furnace to 50 °C (Step I), thus improving the reproducibility of injection. The optimized graphite furnace operating parameters are presented in Table 1. In all instances only peak areas were used for quantification.

Table 1. Electrothermal atomization programme for determination of Tl by ETAAS with Zeeman background correction

	Step				
Parameter	I	II	III	IV	V
Temperature/°C	50	120	450	1400	2600
Ramp time/s	2	10	5	0	2
Hold time/s	8	15	20	3	3
Read	-	-	-	On	-
Gas flow (mL min^{-1})	0	300	300	0	300

2.2. Reagents

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout. The ligand studied, hexamethyleneammonium hexamethylene dithiocarbamate (HMDTC) (p.a Merck, Darmstadt) as well as the organic solvent isobutyl methyl ketone (IBMK) (p.a Merck, Darmstadt) were used without additional purification. Working aqueous standard solutions were prepared by serial dilution of a commercial aqueous stock solution containing 1g L^{-1} Tl(I) (Merck, Darmstadt) with 0.2 M nitric acid. Multi-element organometallic oil standard containing 0.1 µg g^{-1} Tl (SpexCertiPrep, France) was used as stock standard solution for daily preparation of working organic standard solutions by appropriate dilution with IBMK. Indium standard solution for AAS with concentration 1g L^{-1} In(III) (Merck, Darmstadt) was used as collector.

2.3. Sorbent Column Preparation

As preconcentration column a commercially available disposable syringe (2 ml, 8 mm i.d. and 60 mm long) was used. The end of the column was filled with a small wad of cotton wool and covered with two discs of filter paper in order to retain the sorbent in the column. The syringe was filled with four pieces of polyurethane foam (commercially available polyurethane foam was cut into pieces with edges 8 mm long, then soaked consecutively in hydrochloric acid(1+1) for 12 h, in redistilled water and ethyl alcohol and dried prior to use). Three layers of the ligand HMDTC (3 x 100 mg HMDTC) were placed between each foam piece forming in this way a sandwich-type sorbent column.

2.4. General procedures

2.4.1. Column solid-phase extraction preconcentration (CSPE)

The pH of the water samples (100 mL) acidified with nitric acid was adjusted by means of dilute (1:1) ammonia solution to pH 3÷7. Then 1000 µg In (III), 5 mL acetate buffer solution (pH 5) was added and the sample solution was passed through the sorbent column using a peristaltic pump at a flow rate of 2 mL min^{-1}. For the ETAAS measurements the loaded organic ligand HMDTC together with the formed Tl-dithiocarbamate complex were completely dissolved in 1.0 mL of IBMK. For this purpose the solvent was placed in a small dry quartz beaker and was passed six consecutive times through the sorbent with the aid of the syringe plunger.

2.4.2. Precipitation preconcentration (PP)

One liter of the water sample was placed in a 1.5 L PE flask, the pH value was adjusted with dilute ammonia to pH 3÷7, 2 ml 1000 µg L^{-1} In (III), 5 mL acetate buffer solution (pH 5) and

10 mL 2% (m v^{-1}) aqueous solution of APDC were added. The mixture was shaken several times and the precipitate formed was immediately filtered under vacuum through a Millipore filter of 0.45 µm pore size. The filter with the precipitate was placed in a clean and dry small quartz beaker and 5.0 mL of IBMK were added. After vigorous manual shaking, an aliquot (10 µL) of the obtained sample slurry was injected into the graphite furnace. The sample blank was prepared by dissolving a new clean filter in the same amount of IBMK. For calibration slurry preparation new filters were placed in quartz beakers and 5.0 mL of the working organic standard solution containing 2 – 100 ng g^{-1} Tl were added. After vigorous shaking, the calibration slurries were introduced into the graphite furnace in the same way as the sample slurry.

3. Results and Discussion

All investigations were performed after spiking the water samples with Tl(I) in the concentration range 0.02 – 1 µg L^{-1} Tl. Previous studies showed that there is no difference in the behaviour of Tl(I) and Tl(III) concerning formation of dithiocarbamate complexes [11].

The solid-phase extraction of Tl (*CSPE*) with sandwich type sorbent columns depends on the volume of water sample due to the physical nature of ligand immobilization on the polyurethane foam and the connected herewith possibility for mechanical washing out of the sorbed complexes. As can be seen from Fig.1 the sorpion of thallium is quantitative up to 50 mL sample. Hence the enrichment factor achieved for the proposed sorbent preconcentration ETAAS method is 50 (elution of the sorbed Tl-dithiocarbamate complex with 1.0 mL of IBMK). It was registered that for more contaminated water samples with heavy metals concentration at the mg L^{-1} level the sorption of thallium is quantitative for water sample solution volumes up to 100 mL. Hence, for all water types the enrichment factor could be enhanced twice with addition of appropriate element which forms dithiocarbamate complexes and is not determined in waters as indium. The obtained results for thallium sorption recovery in dependence on the sample volume in presence of 1000 µg In are presented in Fig. 2. In this case the enrichment factor is 100. Indium forms dithiocarbamate complexes and being in higher concentration promotes the cosorption of thallium which is present in water samples in very low concentration. Using the *CSPE* preconcentration procedure recoveries higher than 94% were found for thallium in mineral, spring, tap, river, underground and sea water (Fig. 3).

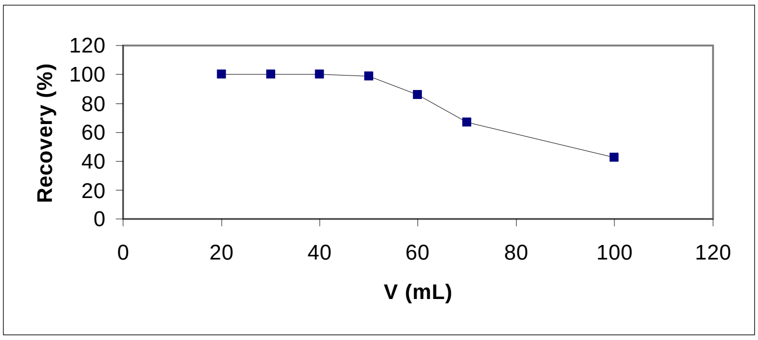

Fig. 1. Effect of the water sample volume on the solid-phase extraction recovery of thallium

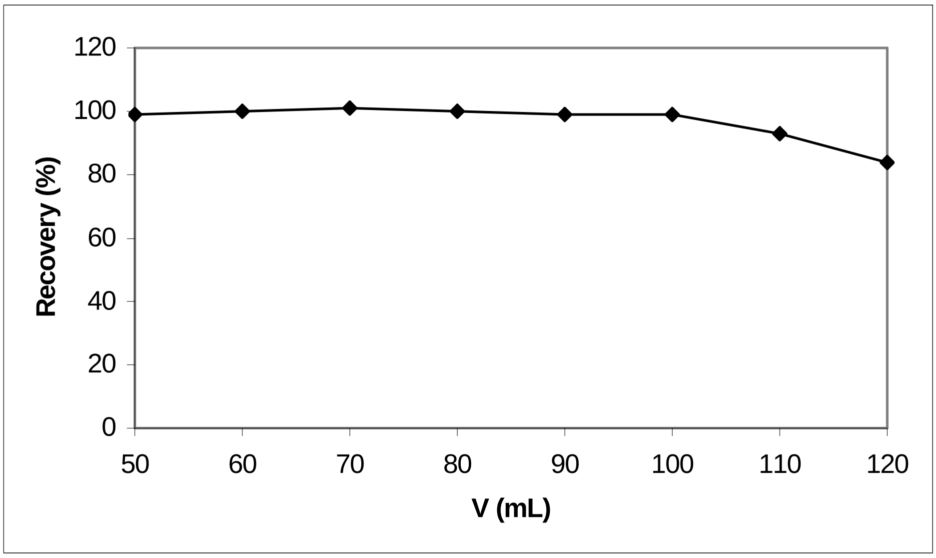

Fig. 2. Effect of the water sample volume on the solid-phase extraction recovery of thallium in presence of indium (1000 μg In)

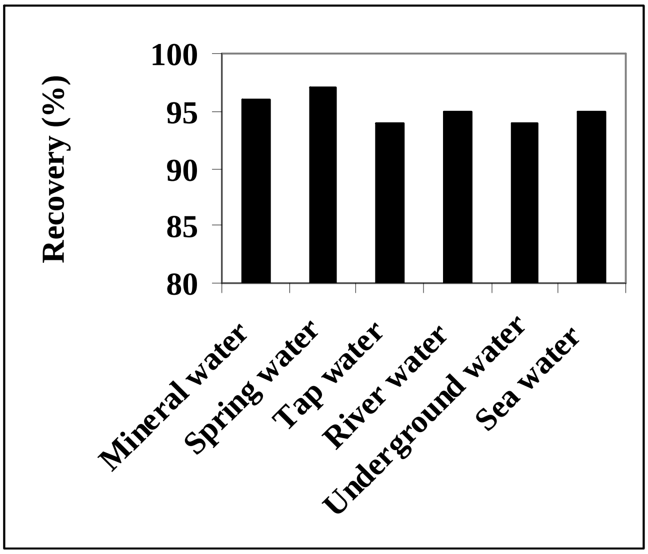

Fig. 3. Column solid phase extraction recovery of thallium added to water samples (0.3 μg L^{-1} Tl)

The results obtained from recovery studies when Tl is precipitated with APDC (*PP*) are presented in Fig. 4. Obviously the addition of indium is a useful tool as in the case of *CSPE,* particularly when the concentration of thallium in water sample is less than 0.2 µg L^{-1} Tl. The higher indium content ensures quantitative coprecipitation of the Tl-DTC complex with the formed In-DTC precipitate. In presence of collector the described procedure allows high recoveries achieving enrichment factor 200.

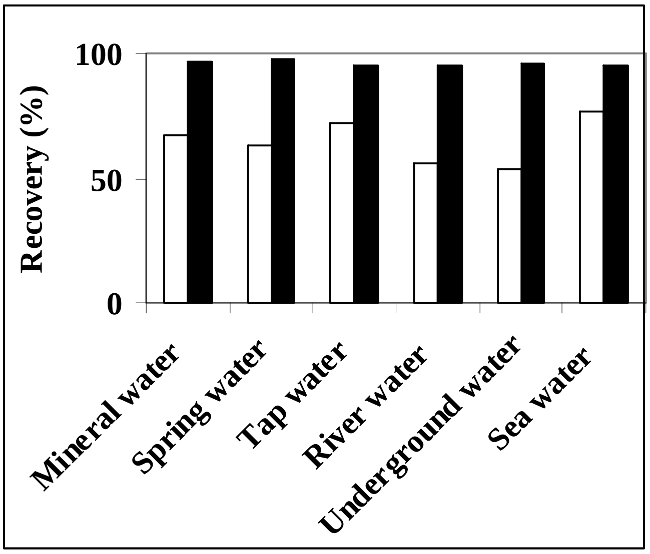

Fig. 4. Recovery of thallium (spike concentration 0.2 µg L^{-1} Tl) after precipitation with APDC with(■) and without (□) addition of indium to water samples

The important analytical performance characteristics of the proposed preconcentration procedures are presented in Table 2.

Table 2. Analytical performance characteristics of the preconcentration methods

Characteristic	***CSPE***	***PP***
Preconcentration factor	100	200
Recovery, %	93 - 105	94 - 102
Detection limit, µg L^{-1} (3σ)	0.02	0.01
RSD, % (concentration range 0.2 – 1.0 µg L^{-1} Tl)	4 – 12	4 - 14
RSD, % (concentration range 0.02 – 0.05 µg L^{-1} Tl)	8 - 24	7 - 20
Speciation possibilities	no	no
Matrix influences	not found	not found
Duration	2h	1h
Cost effectiveness	+++ (lowest cost)	++

3.1. Determination of thallium in natural waters

Mineral (9 samples), spring (3 samples) and tap water (3 samples) were analyzed as sampled and stabilized with HNO_3. River (Struma, Dupnitsa, Bulgaria) underground (sampled near a coil energy plant) and sea (Black sea, port Burgas, Bulgaria) water samples were filtered through Millipore filter of 0.45 µm pore size and then the filtrate was acidified with HNO_3. Approximately two milliliters of concentrated nitric acid were added for one liter water sample. The determination of thallium was performed as described in the general procedures. In all analyzed mineral, spring and tap water samples the concentration of thallium was less than the detection limit given in Table 2. The results for river, underground and sea water samples are presented in Table 3.

Table 3. Determination of thallium in natural waters

Procedure		River water (n = 4)	Underground water (n = 5)	Sea water (n = 3
CSPE	Tl measured/ ng L^{-1}	43 ± 5	57 ± 6	28 ± 4
	Tl added/ ng L^{-1}	50	50	30
	Tl found/ ng L^{-1}	87 ± 9	101 ± 8	54 ± 7
	Mean recovery/ %	93.5	94.4	93.1
PP	Tl measured/ ng L^{-1}	39 ± 6	60 ± 8	25 ± 5
	Tl added/ ng L^{-1}	50	50	30
	Tl found/ ng L^{-1}	84 ± 8	106 ± 8	52 ± 7
	Mean recovery/%	94.4	96.4	94.5

4. Conclusion

The developed preconcentration procedures *CSPE* and *PP* allow the determination of low levels of thallium in natural waters with recoveries between 93 and 105% and relative standard deviation 4 – 24%. The *CSPE* procedure is of lower cost, but of twice higher detection limit (0.02 µg L^{-1} Tl) and duration in comparison to the *PP* procedure. Both procedures do not allow thallium speciation.

Acknowledgement

The authors gratefully acknowledge the financial support provided by the Bulgarian Ministry of Education (N ВУ-Х-207/06)

References

1. Nriagu J O (1998) Thallium in the environment, Wiley-VCH, New York.
2. Fergusson J E (1990) The Heavy Elements: Chemistry, Environmental Impact and Health Effects, Pergamon Press, Oxford
3. Das A K, Dutta M, Cervera M L and Guardia M (2007) Determination of thallium in water samples. Microchem J 86: 2.
4. Saleh M A, Ewane E, Jones J and Wilson B L (2001). Chemical evaluation of commercial bottled drinking water from Egypt. J Food Compos Anal 14: 127.
5. Cheam V, Lawson G, Lechner J, Desrosiers R and Nriagu J (1996) Fresenius J Anal Chem 355: 332.
6. Alexandrova A, Arpadjan S (1993) Determination of trace elements in analytical-reagent grade sodium salts by atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry after preconcentration by column solid phase extraction. Analyst 118 : 1309.
7. Alexandrova A, Arpadjan S (1995). Column solid phase extraction as preconcentration method for trace element determination in oxalic acid by atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry. Anal Chim Acta 307: 71.
8. Arpadjan S, Vuchkova L and Kostadinova E (1997) Sorption of arsenic, bismuth, mercury, antimony, selenium and tin on dithiocarbamate loaded polyurethane foam as a preconcentration method for their determination in water samples by simultaneous inductively coupled plasma atomic emission spectrometry and electrothermal atomic absorption spectrometry. Analyst 122: 243
9. Gentscheva G, Jordanov J, Ivanova E, Petrova V and Vladeva L (2005) X-ray fluorescence spectrometric determination of trace amounts of Bi, Sb, Co, Ni, Pb, Cu, Fe and Zn in mineral waters after precipitation with ammonium pyrrolidinedithiocarbamate. Bulg Chem Comm 37: 69.
10. Ellis A T, Leyden D, Wegscheider W, Jablonsky B B and Bodnar W B (1982) Anal Chim Acta 142: 73.
11. Cvetkovich J, Arpadjan S, Karadjova I and Stafilov T (2002) Determination of thallium in wine by electrothermal atomic absorption spectrometry after extraction preconcentration. Spectr Acta Part B 57: 1101.

Corresponding author: Sonja Arpadjan

Address: 1164 Sofia, bld. J. Bourchier 1, Faculty of Chemistry

Phone: (+359) 2 8161 277

Fax: (+359) 2 962 54 38

Email: sganeva@chem.uni-sofia.bg