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Speciation analysis of thallium in water samples after separation/ preconcentration with the Empore™ chelating disk

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Speciation analysis of thallium in water samples after separation/ preconcentration with the Empore^{TM} chelating disk

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A simple, reliable and novel solid phase extraction procedure using the Empore^{TM} chelating disk has been developed for determination of Tl(I) and Tl(III) in environmental water samples by electrothermal atomic absorption spectrometry (ETAAS). The influence of humic acids on separation/preconcentration of thallium species with the Empore^{TM} chelating disk is investigated. The preconcentration factor and detection limit are 500 and $5 \, ng \, L^{-1}$, respectively. The recoveries are in the range 93–103% for mineral, pond, sea, snowmelt, waste waters at $28–500 \, ng \, L^{-1}$ Tl and in the range 82–112% for river waters at $18–28 \, ng \, L^{-1}$ Tl.

Keywords: thallium speciation; Empore chelating disk; ETAAS; humic acids; interferences, water analysis

1. Introduction

Thallium in its both oxidation states is an emerging pollutant with increasing importance due to the level of toxicity of Tl, which is comparable to that of mercury, lead and cadmium [1–6]. The major sources of thallium releases to the environment include coal combustion, nonferrous metals, cement, iron and steel manufacturers, and various mining, refining, ore-processing, semiconductor and optical industries [1,7]. Thallium is lethal to aquatic insects and invertabrates at $2–4 \, mg \, L^{-1}$ and kills fish slowly at concentrations of $1–60 \, mg \, L^{-1}$ [8]. An oral intake of 20 to $60 \, mg \, Tl \, kg^{-1}$ body weight is lethal for humans within one week [9]. In concentrations lower than the lethal dose, thallium causes mainly neuropathy, brain tumour, alopecia, nerve disorders, cardiac, hepatic, renal effects and congenital abnormalities in humans [10,11]. The main reason for thallium toxicity is based on its rapid distribution to all body tissues, the ability to bind to sulphhydryl groups and to substitute potassium in cells, thus interfering with the proper functioning of important bioprocesses [12,13]. That is why the need for highly sensitive and reliable methods for the determination of ultratrace level Tl has been recognised in analytical and environmental chemistry. The most studied environmental sample for Tl is water [14]. The concentration of Tl in non-contaminated natural waters is below $\mu g \, L^{-1}$ level. Organic forms as $(CH_3)_2Tl^+$ were detected in some surface water samples from the Atlantic Ocean in concentration range of <0.4 to $3.2 \, ng \, L^{-1}$ [15]. A large number of enrichment and separation techniques including solid phase extraction [16–25], flotation [26] and cloud

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

Stage no.	Stage	Temp. (°C)	Time (s) ramp	Time (s) hold	Gas flow (mL min^{-1})
1	Dry	120	10	10	300
2	Ash	400	5	10	300
3	Atomisation	1400	0	3	0
4	Clean	2300	2	3	300

Note: [a]Wavelength 276.7 nm; samples in 0.3 mol L^{-1} HNO$_3$; sample volume: 20 μL; without matrix modifier.

point extraction [27] have been used for Tl determination in water. The chemical form of thallium in environmental waters affects its toxicity, distribution, mobility and bioavailability which explains the importance of speciation analysis. Separation of Tl(III) and Tl(I) is achieved using solid phase [16,18,22–25] and cloud point extraction [27] techniques. Most of the reported chemical speciation methods are unsatisfactory for thallium because of (i) high method detection limits; (ii) the necessity of preliminary oxidation of Tl(I) or reduction of Tl(III) for quantitation of both species; and (iii) missing investigations concerning the complexation of thallium species with naturally occurring humic substances which might influence separation/preconcentration behaviour of the species. The development of new methods for selective separation, preconcentration and determination of thallium continues to be a challenging problem. To our knowledge, the Empore[TM] chelating disk has not been applied for thallium speciation. The objective of this study was to investigate (i) the possibilities for determination of Tl(I) and Tl(III) in natural and waste water samples by electrothermal atomic absorbance spectrometry after preconcentration with the Empore[TM] chelating disk and (ii) the influence of humic acids on separation/preconcentration behaviour of thallium species. The proposed new approach for thallium speciation has subsequently been used to determine the thallium species in mineral, pond, river, sea, snowmelt and waste water samples.

2. Experimental

2.1 *Instrumentation*

The ETAAS measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light source was a hollow cathode lamp for Tl. The spectral bandpass was 0.7 nm. Standard uncoated graphite tubes were used as atomiser. Autosampler AS-60 was used for injections of 20 μL sample solutions into the graphite tube. Only peak areas were used for quantification. The graphite furnace operating parameters for modifier-free ETAAS measurements of Tl are presented in Table 1.

2.2 *Reagents and materials*

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout. The stock standard solution of 1g L^{-1} Tl(III) was prepared by dissolving

thallic nitrate (99.999%, Kodak) in $0.5 \, mol \, L^{-1}$ nitric acid (p.a. Merck). For Tl(I) a ready for use standard solution for AAS (Merck, Darmstadt, Germany) with concentration $1 g \, L^{-1}$ Tl(I) in $0.5 \, mol \, L^{-1}$ HNO_3 was used. Intermediate standard solutions with concentration $10 \, \mu g \, mL^{-1}$ Tl(I) and Tl(III) were prepared weekly by appropriate dilution with $0.3 \, mol \, L^{-1}$ HNO_3. The standard solutions at $ng \, mL^{-1}$ level were prepared daily. Humic acid was supplied by Fluka, Switzerland.

The 3M Company's Empore[TM] disk (diameter 47 mm, thickness 0.5 mm) made of 90% adsorbent particles and 10% inert carrier (polytetrafluoroethylene) was used for solid phase extraction and speciation of thallium. The adsorbent particles consist of resin R (polystyrene polymer cross-linked with divinylbenzene) with iminodiacetic acid sodium salt $–N–(CH_2COONa)_2$ functional groups. The disk is situated in a device for filtration (3M Company) connected by a peristaltic pump. Vacuum was applied to the dried disk, then the disk was wetted with about 20 mL of water. The disk was washed with 20 mL of $3 \, mol \, L^{-1}$ nitric acid, followed by three-four 50 mL water washes (till neutral reaction). Between each wash the disk was vacuum dried for about one minute. After this procedure, the disk is in H^+ form ($R–N–(CH_2COOH)_2$). In order to put the disk in the ammonium form ($R–N–(CH_2COONH_4)_2$, 50 mL $0.5 \, mol \, L^{-1}$ ammonium acetate/ammonia buffer solution at pH 10 was passed through the disk and then washed with water till neutral reaction.

2.3 *Sample collection and preparation*

River, sea, pond and waste water samples were collected in high density polyethylene (PE) bottles and filtered through $0.45 \, \mu m$ membrane filters. The filtrates were then immediately transferred to the laboratory and the separation/preconcentration procedure was finished within 8 hours of sample collection. Pond water samples were collected from places near to a coal burning power plant. Waste water samples were from a copper production factory. Snow samples (3 days old snow) were obtained from a $\sim 10 \, m^2$ area (around a coal burning plant) and $\sim 5 \, cm$ deep using PE vials. The snow samples were transported frozen to a clean box, left to thaw and filtered through $0.45 \, \mu m$ membrane filters. Speciation studies for mineral water samples were performed without preliminary filtration. Mineral water samples were collected in PE bottles in and around Sofia city (Central Bad (pH 9.5, $47^{\circ}C$), Gorna Bania (pH 9.7, $41.5^{\circ}C$), Knyajevo (pH 9.6, $31^{\circ}C$), Bankia (pH 9.6, $36.5^{\circ}C$)). They contained mainly HCO_3^- ($42–109 \, mg \, L^{-1}$), Na^+ ($34–89 \, mg \, L^{-1}$) and SO_4^{2-} ($17–63 \, mg \, L^{-1}$).

2.4 *Procedure for preconcentration and determination of total dissolved thallium*

To one litre water sample 10 mL acetic buffer solution with pH 5.6 were added and mixed. The sample was transferred to the glass funnel of the filtration device and was passed through the Empore[TM] chelating disk in NH_4^+ form at flow rate $20 \, mL \, min^{-1}$. The disk was washed with 20 mL redistilled water and dried by vacuum. The elution of the retained on the disk thallium was performed with two 10 mL aliquots of $3 \, mol \, L^{-1}$ nitric acid at flow rate $2 \, mL \, min^{-1}$. The eluates were collected and carefully evaporated on sandbad to a moist residue. This residue was then dissolved in 2.0 mL $0.3 \, mol \, L^{-1}$ HNO_3 and analysed by graphite furnace atomic absorption spectroscopy (Table 1).

2.5 *Analytical procedure for thallium speciation*

One litre water sample was acidified with nitric acid to adjust the pH value to pH 2–3. The sample was transferred to the glass funnel of the filtration device and was passed through the Empore[TM] chelating disk in H^+ form at flow rate $20\,mL\,min^{-1}$. During this process, thallium(III) was removed from the water sample onto a chelating disk, Tl(I) was in the effluate. The disk was washed with $20\,mL$ redistilled water and dried by vacuum. The elution of the retained on the disk thallium(III) was performed with two $10\,mL$ aliquots of $3\,mol\,L^{-1}$ nitric acid at flow rate $2\,mL\,min^{-1}$. The eluates were collected and carefully evaporated on sandbad to a moist residue (the eluates were with low saline content; the chelating disks do not retain Na, K, Ca, Mg). This residue was then dissolved in $2.0\,mL$ $0.3\,mol\,L^{-1}$ HNO_3 and analysed by graphite furnace atomic absorption spectroscopy (Table 1). The enrichment factor attained was 500. After elution of Tl(III) the chelating disk was water washed and converted to ammonium form as described in section 2.2 in order to achieve higher capacity of the disk. The effluate containing Tl(I) was alkalised with NH_4OH (1 : 1) to obtain pH values between pH 5 and pH 8 and then it was treated again via the same process to concentrate and analyse Tl(I).

3. Results and discussion

3.1 *Effect of pH on adsorption of Tl(I) and Tl(III)*

The adsorption of thallium(I) and thallium(III) on the Empore[TM] chelating disk is based on the mechanism of ion exchange ($–R–N–(CH_2COOTl)_2$) and of formation of metal chelate complexes (chemosorption).
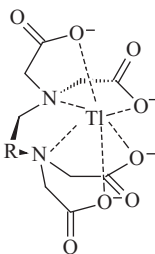
The sorption degree depends on the sample pH value and on the ionic form of the disk.

The effect of pH on the retention of Tl(I) and Tl(III) on the chelating disk was investigated separately. The pH values of water samples were adjusted, ranging from 1.5 to 8.2 with diluted ammonia and nitric acid. The results of the effect of pH on the recoveries of Tl(I) and Tl(III) on disks in H^+ form are shown in Figure 1. It can be seen that the sorption of Tl(III) on the Empore[TM] chelating disk in H^+ form is quantitative for the entire studied range from pH 1.5 to pH 8.2. At pH range from pH 1.5 to pH 3, Tl(I) was not retained on the disk at all. It means that at pH 1.5–3 the Empore[TM] chelating disk in H^+ is selective towards Tl(III) and that it is possible to separate quantitatively Tl(I) and Tl(III) by selecting the suitable pH and ionic form of the sorbent. The reason for different adsorption behaviour of the Empore[TM] chelating disk in H^+ form for Tl(I) and Tl(III) may be explained as follows: as known, the selectivity of Empore[TM] chelating membrane roughly follows the EDTA complex formation constants (β) [28]. The separation of Tl(III)
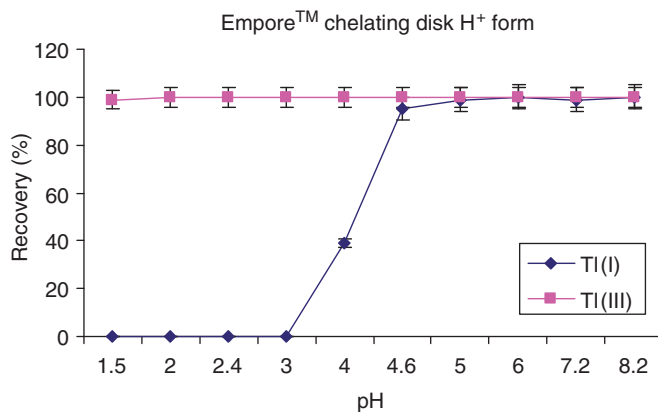
Figure 1. Effect of pH on the sorption recovery of thallium species using chelating disk H^+ form. Spikes $(100 \, ng \, L^{-1} \, Tl)$ to redistilled water.

from Tl(I) is possible due to the big difference in the stability of their complexes with EDTA $\{\log \beta(Tl(I)\text{-EDTA}) = 5.3; \log \beta \, Tl(III)\text{-EDTA} = 21.5\}$. The high recovery values for Tl(III) even at low pH values using disks in their less active H^+ form can be explained with the high conditional formation constant (β') of Tl(III)-EDTA complex at pH 2 $(\log \beta' = 8)$. At low pH values Tl(I) actually does not form complexes with EDTA (at pH 2 the conditional formation constant $\lg \beta' = -8.3$), hence chemosorption for thalloic ions is not possible. In acidic media the equilibrium

$$-R–N–(CH_2COOH)_2 + 2Tl(I) \leftrightarrow -R–N–(CH_2COOTl)_2 + 2H^+$$
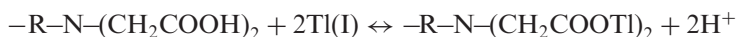
is shifted to the left and the protons on the sorbent functional groups cannot be exchanged with Tl(I). These are the reasons for non-absorptivity of thalloic ions at pH 1.5–3 and the consequent possibility for quantitative separation of Tl(III) and Tl(I). The results obtained in our work are in agreement with the results reported for thallium speciation analysis with Chelex-100 resin [16]. The most probable explanation is that both Chelex-100 resin and the Empore^{TM} chelating disk contain the same polymeric part (polystyrene + divinylbenzene) and active ion exchange and complex forming functional groups (iminodiacetic acid).

The effect of pH on the sorption of Tl(I) and Tl(III) on Empore^{TM} helating disk in the NH_4^+ form was also investigated. The results are presented in Figure 2. As can be seen, when the chelating disk is in its more active ammonium form, both thallium species were quantitatively sorbed on the Empore^{TM} chelating disk ranging from pH 4 to pH 8. At pH 2 around 40% and at pH 3 around 75% sorption of Tl(I) was registered. The mechanism of sorption of Tl(I) at pH 2 and 3 is ion exchange.

$$-R–N–(CH_2COONH_4)_2 + 2Tl(I) \leftrightarrow -R–N–(CH_2COOTl)_2 + 2NH_4^+$$
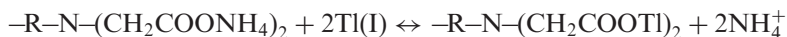
It means that the chelating disks in NH_4^+ form are appropriate for preconcentration and determination of the total dissolved thallium (pH range 4–8) and cannot be applied for speciation purposes.

In comparison to thallium speciation with Chelex-100 (sample flow rate $8 \, mL \, min^{-1}$) [16], the developed in this work speciation procedure with the Empore^{TM} chelating disk is faster (sample flow rate $20 \, mL \, min^{-1}$), allows higher enrichment factor and excludes the necessity of oxidation of Tl(I) to Tl(III) with bromine.
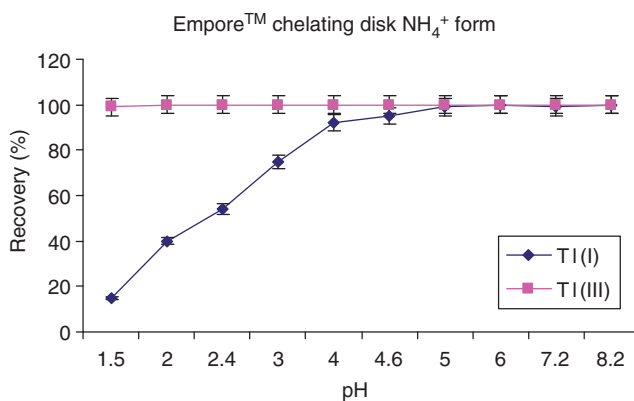
Empore^{TM} chelating disk NH$_4^+$ form

Figure 2. Effect of pH on the sorption recovery of thallium species using chelating disk NH$_4^+$ form. Spikes (100 ng L^{-1} Tl) to redistilled water.
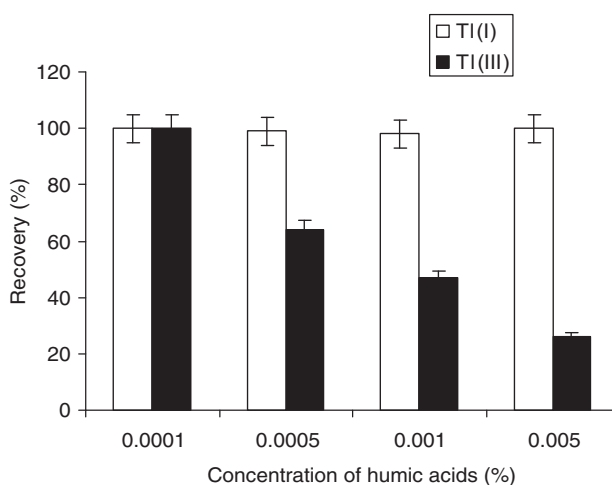

Figure 3. Recovery of thallium species applying the separation/preconcentration procedure in the presence of humic acids. Empore^{TM} chelating disk: in H$^+$ form Tl(III) (pH 2–3) and in NH$_4^+$ form for Tl(I) (pH 5.6). Spikes (100 ng L^{-1} Tl(I) or 200 ng L^{-1} Tl(III)) to redistilled water.

3.2 *Interferences*

From the naturally occurring in water samples ligands (chlorides, carbonates, hydroxides, sulphates, phosphates and organic substances) it could be expected that only complex formation with humic acids may influence thallium speciation with the Empore^{TM} chelating disk, because only the stability of Tl(III)–humic acid complexes could be comparable to the stability of Tl(III)–EDTA complexes [29]. The effect of humic substances on thallium speciation was studied by adding humic acid to the test solutions containing 100 ng L^{-1} Tl(I) or Tl(III) and then treated according to the recommended procedure. The results for the sorption recovery of thallium species in presence of humic acids are presented in Figure 3. It can be seen that the sorption of Tl(III) is quantitative only for waters with humic acids content lower than 0.0001%. The organic substances do

Table 2. Effect of humic acids on the sorption of Tl(I) and Tl(III) on Empore[TM] chelating disk in NH_4^+ form on the concentration of humic acids. Spikes (100 ng L^{-1} Tl) to mineral water ($n = 3$)*.

pH	Concentration of humic acids (%)	Recovery (%)	
		Tl(I)	Tl(III)
2	0.0001	43 ± 4	98 ± 3
	0.0005	42 ± 8	97 ± 2
	0.001	40 ± 9	46 ± 5
	0.005	43 ± 6	32 ± 7
5	0.0005	99 ± 3	99 ± 2
	0.001	98 ± 4	76 ± 5
7	0.0005	97 ± 4	76 ± 7
	0.001	95 ± 3	69 ± 6
8	0.0005	97 ± 3	64 ± 6
	0.001	96 ± 3	60 ± 8

Note: *Mineral water Gorna Bania.

not influence the sorption behaviour of Tl(I) and the recovery remains sufficiently high. It means that Tl(I) does not form stable Tl(I)–humic complexes.

In the presence of humins the sorption of Tl(III) on disks in the ammonium form depends strongly on the pH value of water samples, as can be seen from the results presented in Table 2. Sorption recovery is lower for samples with higher pH values. It could be explained with the higher stability of Tl(III)-humic complexes at higher pH values. Obviously organic substances stabilise Tl(III) and regardless of the ionic form of the Empore[TM] chelating disk, quantitative retention of Tl(III) cannot be achieved. As expected, the results for Tl(I) (Figure 3 and Table 2) indicate that the humic substances do not change the sorption behaviour of Tl(I) because Tl(I) does not form stable Tl(I)-humic complexes. The end conclusion from these results is that the sum of total Tl(I) content and the labile forms of Tl(III) can be determined using the described procedure for preconcentration of thallium with Empore[TM] chelating disks. Considering that only the free and labile thallium ions are bioavailable, the toxicologically relevant total thallium concentration can be evaluated.

3.3 *Analytical performance*

Quantification has been performed based on calibration using aqueous standards prepared in 0.3 mol L^{-1} HNO_3. The calibration curve was linear in the investigated range of 2.5–100 ng mL^{-1} Tl. The correlation coefficient R^2 was 0.9990 (number of points 7). The detection limit (evaluated as the concentration corresponding to three times the standard deviation of seven replicate measurements of a blank sample) of this method with an enrichment factor of 500 was 5 ng L^{-1} Tl (2.5 ng mL^{-1} Tl in the 500-fold preconcentrated sample). The relative standard deviations (RSDs) for spiked samples were lower than 8%. But for samples and species fractions with thallium content around the detection limit, RSDs up to 20% were registered. The analysis time was around one and half hour. The EmporeTM chelating disks can be used 5–10 times. Recovery studies of Tl(I) and Tl(III) were performed sequentially after spiking water samples with these species. As shown in

Table 3, the mean recoveries for mineral, pond, sea and waste waters were between 93 and 103%, i.e. in the accepted range for recovery (90–110%) [30, 31]. The accuracy of the proposed procedure was validated by comparing the sum of the concentrations of individual thallium species with the total thallium concentration. The differences between the sum of the values for Tl(I) and Tl(III) determined individually (Section 2.5 above) and total thallium concentration (Section 2.4) were in the range 3–7%. In addition, the waste water sample (100 mL sample taken) was analysed for Tl(I) and Tl(III) using Chelex-100 resin as described by Lin and Nriagu [16] (the eluates for the both thallium forms were evaporated to 2.0 mL). The difference between the obtained mean results for Tl(I) and Tl(III) using the EmporeTM disk and Chelex-100 resin were not statistically significant (*t*-test).

For river waters, the recoveries varied between 83 and 112% (Table 4). It means that some river waters contain organic substances like humic acids in concentrations higher than 0.0001%. In these cases, a part of Tl(III) was not retained on the disk in H^+ form at

Table 3. Determination of thallium species in waters (mean $\pm$ standard deviation, $n = 3$).

Samples	Added (ng L^{-1})		Found (ng L^{-1})		Recovery (%)	
	Tl(I)	Tl(III)	Tl(I)	Tl(III)	Tl(I)	Tl(III)
Mineral water*	0	0	<5	<5		
	100	0	95 ± 5	<5	95 ± 5	
	0	100	<5	94 ± 4		94 ± 4
	100	100	94 ± 4	103 ± 5	94 ± 4	103 ± 5
	100	150	102 ± 3	148 ± 3	102 ± 3	99 ± 2
	150	100	154 ± 4	95 ± 3	103 ± 3	95 ± 3
Pond water	0	0	13.7 ± 1.4	26 ± 2		
	20	20	32 ± 1	45 ± 1	96 ± 4	97 ± 3
Sea water	0	0	12 ± 2	16 ± 3		
	50	50	58 ± 3	67 ± 3	93.5 ± 6.5	101.5 ± 6.5
Snowmelt	0	0	63 ± 4	37 ± 3		
	100	100	156 ± 5	130 ± 6	96 ± 2	95 ± 3
Waste water**	0	0	242 ± 11	251 ± 13		
	250	250	475 ± 22	516 ± 24	96.5 ± 4.5	103 ± 5

Notes: *Mineral water Gorna Bania.
**100 mL sample taken.

Table 4. Determination of thallium species in river waters (mean $\pm$ standard deviation, $n = 3$).

River	Added (ng L^{-1})		Found (ng L^{-1})		Recovery (%)	
	Tl(I)	Tl(III)	Tl(I)	Tl(III)	Tl(I)	Tl(III)
Struma	0	0	10.5 ± 1.4	17.2 ± 1.8		
	10	10	22.8 ± 1.7	23.2 ± 1.7	111 ± 8	85 ± 7
Mariza	0	0	8.2 ± 1.4	14.3 ± 1.3	112 ± 7	82 ± 6
	10	10	20.4 ± 1.4	19.9 ± 1.5		
Belasiza	0	0	6.8 ± 1.3	11.6 ± 1.5	96 ± 6	93 ± 6
	10	10	16.2 ± 1.4	20.1 ± 1.3		

pH 2–3 (recovery lower than 90%) and then it was sorbed together with Tl(I) on disk in NH_4^+ form at pH 5–8 (recovery higher than 110%).

3.4 *Sample analysis*

The optimised procedure for thallium speciation is described in Section 2.5 and schematically presented in Figure 4. After elution of Tl(III) the disk is in H^+ form and
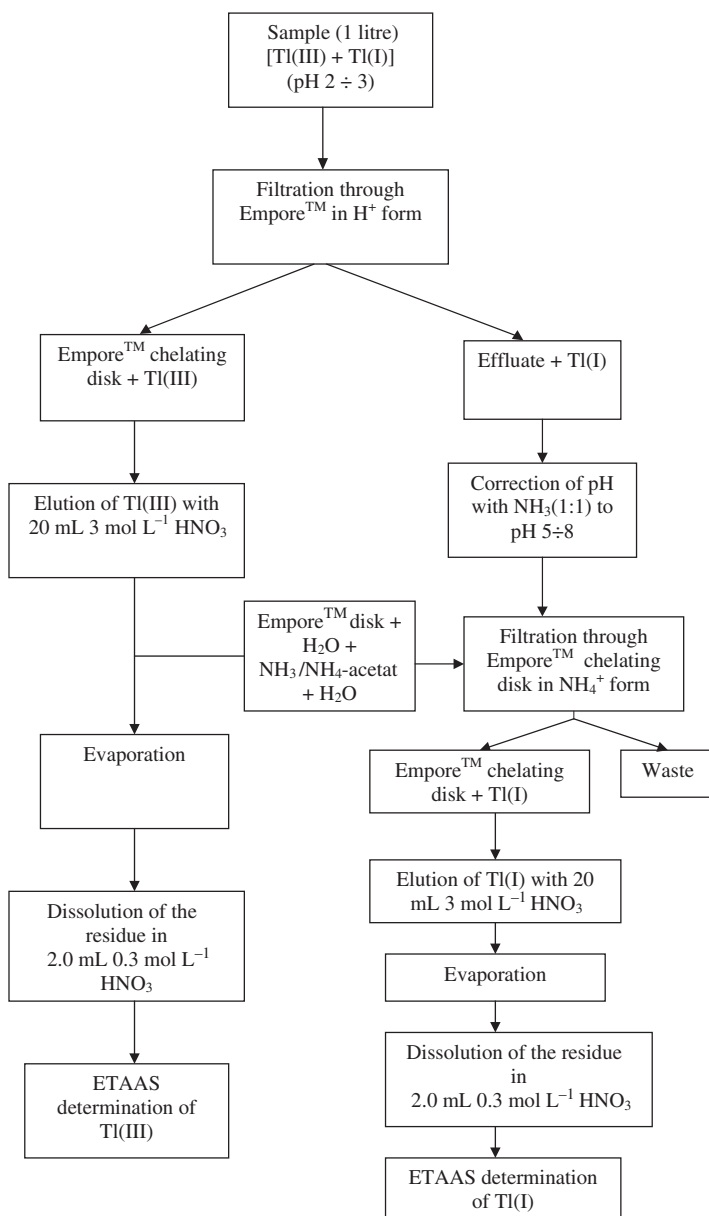
Figure 4. Schematic presentation for separation and preconcentration procedure for determination of Tl(I) and TL(III) in waters.

Table 5. Distribution of thallium species in environmental waters.

Sample	Separation/measurement procedure	Ratio [Tl(III)]/ [Tl(I) + Tl(III)] (%)	References
Hiron river, USA	Chelex-100 resin/ETAAS	68 ± 3	[16]
Raisin river, USA		64 ± 13	
Lakes Michigan, Huron, Erie, USA	Chelex-100 resin/ETAAS	68 ± 6	[24]
Third Sister Lake, USA	Chelex-100 resin/ETAAS	41.7 ± 23.3	[25]
Sample from			
• Surface		70.4	
• 5 m depth		49.3	
• 8 m depth		16.8	
• 13 m depth		30.3	
Surface water	Cloud point extraction of Tl(III)-DTPA* complex/ ICP-MS	70 ± 3	[27]
Tap water		76 ± 4	
Sea water		62 ± 3	
River water	Empore™/ETAAS	63 ± 5	Present work
Pond water		66 ± 4	
Sea water		57 ± 7	
Snowmelt		37 ± 3	
Waste water		50 ± 4	

Note: *DTPA: diethylenetriaminepentaacetic acid.

could be used in this form (Figure 1) for preconcentration of Tl(I) after pH correction of the effluate to pH 5–8. But in order to achieve a higher sorption capacity (important for analysis of real samples), the chelating disk was converted into ammonium form prior to preconcentration of Tl(I). The results for thallium species in environmental water samples are given in Tables 3 and 4. In mineral water samples, the total dissolved Tl was lower than the detection limit of the method. As expected, the highest was the total thallium concentration in waste water ($500 \, ng \, L^{-1}$) and the lowest – in sea ($28 \, ng \, L^{-1}$) and in river ($18–28 \, ng \, L^{-1}$) waters. The concentration of Tl in pond water was $40 \, ng \, L^{-1}$, in snowmelt – $100 \, ng \, L^{-1}$. The results for thallium species distribution expressed as a ratio between the concentration of Tl(III) to the sum of Tl(I) + Tl(III) are summarised in Table 5. The results for surface and sea waters agree with the results of Lin and Nriagu [16,24,25] and of Meeravali and Jiang [27] that Tl(III) is the predominant form (Table 5). As known, coal combustion is the primary source of Tl contamination [1] and that is the reason for the detection of Tl in snow around a coal burning plant. In this snow sample, 73% of the total dissolved Tl was found to be Tl(I). It could be explained with the formation of Tl_2O as combustion product [1]. Thalloic oxide decomposes readily in water and the resulting Tl(I) cation is stable, particularly in the presence of reductive acting coal ash constituents. In the case of pond water, Tl(III) comprised 66% of total dissolved Tl despite the closeness to a coal burning plant. Thallic ions were found as the predominant form in pond water also by Twining *et al.* [32], demonstrating that planctonic bacteria are responsible for oxidising the thermodynamically stable Tl(I)

to Tl(III). In waste water from the copper production industry, the ratio between Tl(I) and Tl(III) was approximately 1 : 1.

4. Conclusion

Solid phase extraction with Empore^{TM} chelating disks in H$^+$ ionic form allows simple and reliable separation/preconcentration of Tl(I) and Tl(III). The method was used for the speciation of thallium in mineral, pond, snowmelt, sea, river (humic acids content <0.0001%) and waste waters with satisfactory precision and accuracy. For river waters with higher humic acids content, some cross-contamination of these two thallium forms was observed. It was found that in environmental waters, the predominant form is Tl(III) with the exception of the snow sample, collected around a coal burning power plant.

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