Sensitive determination of thallium species in drinking and natural water by ionic liquid-assisted ion-pairing liquid–liquid microextraction and inductively coupled plasma mass spectrometry

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HIGHLIGHTS

► Speciation studies of Tl at ultratrace levels in water samples.
► Straightforward speciation analysis of Tl.
► Investigation of ionic liquid as ion pairing reagent.
► Microextraction approach with minimal waste production and sample consumption.
► Fast separation and determination of Tl species with high frequency of analysis.

ARTICLE INFO

ABSTRACT

A fast and simple method involving separation and determination of thallium (Tl) species, based on novel ionic liquid-assisted ion pairing dispersive liquid–liquid microextraction (DLLME) method, was developed. Initially, Tl(III) was selectively complexed with chloride ion to form $[TlCl_4]^-$ chlorocomplex. Subsequently, tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) was used to form the ion-pair with $[TlCl_4]^-$ anion followed by extraction. The DLLME procedure was developed by dispersing 80 μL of carbon tetrachloride with 100 μL of ethanol added to the aqueous solution. After DLLME, the upper aqueous phase containing Tl(I) only was removed and analysed by inductively coupled plasma-mass spectrometry (ICP-MS). In contrast to Tl(III), Tl(I) species does not form neither stable nor anionic complexes with chloride ions and it was not extracted into the organic phase. Total Tl concentration was obtained by direct introduction of sample into ICP-MS instrument. The calibration graph for the analyte was linear with a correlation coefficient of 0.9989. Under optimal conditions, detection limit of Tl species was 0.4 ng L^{-1}. The relative standard deviation ($n = 10$) at 1 ng mL^{-1} Tl concentration level was 1.3% for Tl(I) and 1.5% for Tl(III). The method was successfully applied for fast speciation analysis of Tl at ultratrace levels in real water samples.

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1. Introduction

Thallium (Tl) is an emerging pollutant that is introduced into the environment mainly as waste from the production of lead and cadmium and by coal combustion [1]. Thallium is an element with greater toxicity to mammals than Hg, Cd, Pb, or Cu [2]. Thus,

the United States Environmental Protection Agency (US EPA) has included Tl in the list of priority pollutants in drinking water, defining 0.5 μg L^{-1} Tl as maximum permissible concentration. Thallium is mainly present as monovalent [Tl(I)] and trivalent [Tl(III)], and each oxidation state is different from a toxicological point of view [3]. In fact, it has been stated that Tl(III) is more toxic than Tl(I) [4]. Therefore, considerable interest on Tl species separation and determination has come up in the research field.

The determination of Tl is not an easy task as natural content of this analyte in environmental samples is at ng L^{-1} level or less. For this reason, the application of analytical methods with high

sensitivity and low detection limit is required. Furthermore, the number of analytical methods reporting Tl species separation is limited. Thus, electrothermal atomic absorption spectrometry (ETAAS) has been successfully employed for determination of Tl species in water samples [4–6] due to satisfactory analytical performance, such as reliability, sensitivity and relatively low cost of instrumentation [7]. Nevertheless, it is well known that chloride interferences are one of the most frequent cases of chemical interferences in ETAAS [8]. Unquestionably, inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most powerful techniques for trace elements analysis due to its numerous advantages, such as extremely high sensitivity, low limits of detection, ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of ICP source. Moreover, high sample throughput and the capability to obtain isotopic information are among the main strengths of ICP-MS [9–11]. Despite these notorious advantages, separation of Tl species is required before these can be individually detected by ICP-MS. Thus, it has been reported the separation of Tl species by reversed phase HPLC prior to ICP-MS [12]. Also, ion chromatography (IC) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) or ICP-MS has been proposed for Tl speciation analysis [13]. However, it must be pointed out the need of additional instrumentation and the significant time required for analysis when HPLC separation is used with ICP-MS detection.

On the other hand, common preconcentration and separation techniques for Tl species determination at trace levels include solid phase extraction (SPE) [14,15] and liquid–liquid extraction (LLE) [16] with organic solvents. However, some drawbacks arise from the application of this class of techniques, such as the use of significant volumes of toxic and expensive solvents, generation of a large volume of wastes and reduced frequency of analysis [17]. On the other hand, liquid–liquid microextraction technique (LLME) effectively overcomes these difficulties by reducing organic solvent consumption as well as allowing sample extraction and preconcentration to be performed in a simple and single step [18]. Furthermore, the use of modern solvents known as ionic liquids (ILs) has become an attractive tool to replace environmentally unfriendly solvents that generate volatile organic compounds. Ionic liquids exhibit unique properties, including negligible vapour pressure, high thermal stability, high ionic conductivity and wide electrochemical window [19]. Usually, ILs have a high concentration of ions (more than $5\,mol\,L^{-1}$) [20] and hence, ion-pairing reactions are expected to occur in these media [21,22]. Particularly, tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) has been used as ion-pairing reagent for determination of Tl species in water samples [23]. Nevertheless, separation of Tl(I) and Tl(III) species was not feasible by direct application of the IL during preconcentration step. Thus, an additional separation step involving the use of ion exchange resins was required.

In this work, a simple analytical methodology based on the application of ILs for rapid and effective separation of Tl(I) and Tl(III) species is presented. Tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) was assessed for ion-pairing reaction with $[TlCl_4]^{-}$ chlorocomplex followed by its selective separation from Tl(I) species using dispersive liquid–liquid microextraction (DLLME) technique. Furthermore, the effect of several ion-pairing reagents such as tetrabutylammonium bisulfate, cetyltrimethylammonium bromide (CTAB) and trimethyltetradecylammonium bromide (TTAB) was investigated. Determination of Tl(I) in the upper phase was performed by ICP-MS. Evaluation of total Tl concentration was performed by direct analysis of the samples with ICP-MS, while Tl(III) species concentration was obtained as the difference between total Tl and Tl(I) concentration.

Table 1
Instrumental and experimental conditions for Tl species determination.

|	
ICP-MS parameters	
RF power (W)	1550
Sampler and skimmer cones	Nickel
Plasma gas flow rate ($L\,min^{-1}$)	15.0
Auxiliary gas flow rate ($L\,min^{-1}$)	0.9
Carrier gas flow rate ($L\,min^{-1}$)	0.99
Sample introduction flow ($mL\,min^{-1}$)	1.5
Spray chamber temperature (°C)	2
Gas flow ($mL\,min^{-1}$) in the collision cell	0.03 [He]
Nebulizer	MicroMist
Isotopes monitored	^{203}Tl, ^{205}Tl, and ^{115}In (as internal standard)
DLLME conditions	
Sample volume	5 mL
HCl concentration	$1\,mol\,L^{-1}$
CYPHOS® IL 101 concentration	$2 \times 10^{-5}\,mol\,L^{-1}$
Extractant solvent	Carbon tetrachloride
Volume of extractant solvent	80 μL
Disperser solvent	Ethanol
Volume of dispenser solvent	100 μL

2. Experimental

2.1. Instrumentation

An Agilent 7700x ICP-MS (Agilent Technologies, Tokyo, Japan) fitted with standard glass concentric nebulizer, quartz double-pass spray chamber and nickel sampler and skimmer cones was used for Tl determination. The ICP-MS instrument can operate the collision cell in either no gas mode or helium collision mode. In this work, individual application of both modes was studied. The optimal ICP-MS operating conditions are summarized in Table 1.

A centrifuge (Luguimac, Buenos Aires, Argentina) and a vortex model Bio Vortex B1 (Boeco, Hamburg, Germany) were used for speeding up the phase separation step and mixing the reagents, respectively.

2.2. Chemicals and standards

Stock standard solutions of $1000\,mg\,L^{-1}$ of Tl(I) and Tl(III) were prepared from an accurate weight of $TlNO_3$ (99.9%) (Aldrich, Milwaukee, USA) or $Tl(NO_3)_3\cdot 3H_2O$ (98%) (Aldrich) dissolved in 1% (v/v) ultrapure HNO_3 (Merck, Darmstadt, Germany). A $1000\,mg\,L^{-1}$ In-standard solution obtained from Inorganic Ventures (Lakewood, NJ, USA) was used as internal standard to correct for any instrumental drift during analysis. Working standard solutions were prepared by appropriate dilution with ultrapure water. Toluene and methanol from Merck were used. HCl (Ultra pure grade, Figmay, Córdoba, Argentina) was used to form the anionic complexes. Chloroform and carbon tetrachloride from Merck were assessed as extractant phases. Lithium chloride (>99%) (Merck) and sodium chloride (>99%) (Merck) were also selected as sources of chloride ion for complexing of Tl(III) species. Tetrabutylammonium bisulfate (99%) (Fluka, Suiza), cetyltrimethylammonium bromide (CTAB) (99%) (Merck) and trimethyltetradecylammonium bromide (TTAB) (99%) (Aldrich) were used for evaluation of ion pairing reaction. Fig. 1 exhibits the molecular structure of these reagents. CYPHOS® IL 101 was obtained by a donation from Prof. Ullastiina Hakala (University of Helsinki, Finland) and provided by CYTEC Industries Inc. (Canada). A Milli-Q Academic A-10 Millipore Water Purification System (Billerica, MA, USA) was used for obtaining ultrapure water ($18\,M\Omega\,cm$). All glasswares were washed with pure water, soaked in $0.5\,mol\,L^{-1}$ HNO_3 solution for 24 h and finally rinsed 5 times with ultrapure water.

I

II

III

IV
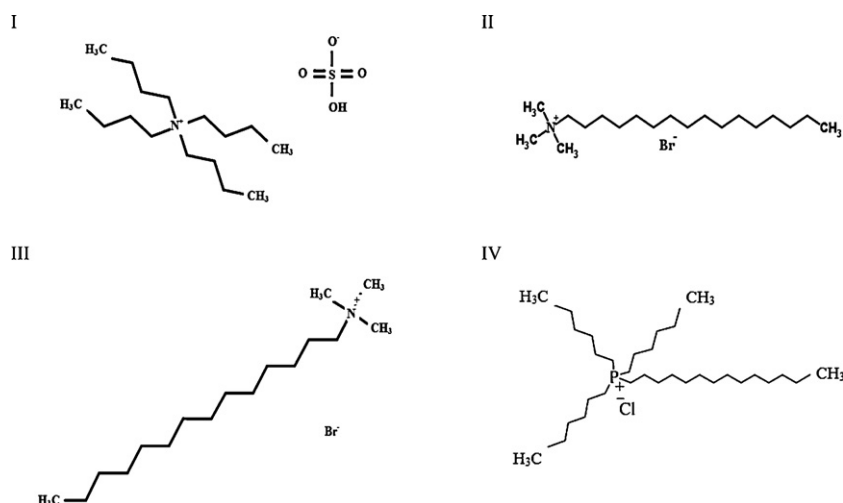
Fig. 1. Molecular structures of the ion pairing agents studied in this work. (I) Tetrabutylammonium bisulfate; (II) cetyltrimethylammonium bromide (CTAB); (III) trimethyl-tetradecylammonium bromide (TTAB); (IV) tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101).

2.3. Sample collection and preparation

For the collection of tap water samples, domestic water was allowed to run for 20 min, then collected in a 1000 mL HDPE bottles and analysed immediately after sampling. River water samples were collected in 1000 mL bottles (previously rinsed three times with the sample) and filtered through 0.45 μm pore size PTFE membrane filters (Millipore Corporation, Bedford, MA, USA). Sampling was performed at a depth of 5 cm below the surface. All materials were previously washed overnight with a 10% (v/v) HNO_3 water solution and rinsed with ultrapure water.

2.4. Separation and determination of Tl species

An aliquot of 5 mL of sample (or Tl(III) standard solution for optimization) was placed in a 10 mL graduated glass centrifuge tube and added with 418 μL of concentrated HCl. The mixture was shaken for 10 s with a vortex and remain for 2 min to ensure the complete formation of the anionic complex $[TlCl_4]^-$. Afterward, a volume of 266 μL of a 3.8×10^{-6} mol L^{-1} CYPHOS® IL 101 (prepared in toluene) solution was added to the tube and the resulting system was shaken for 60 s with vortex stirrer. Then, a volume of 80 μL of carbon tetrachloride (extraction solvent) dissolved in 100 μL of ethanol (dispersant solvent) was added to the sample solution. Immediately, the mixture was shaken for 100 s. Finally, a centrifugation step at 1500 rpm (125.8 × g) during 5 min was applied to obtain two well-defined phases. Centrifugation tubes were hence placed in the autosampler of the ICP-MS instrument from where the upper aqueous phase was directly sampled for Tl(I) determination. ^{203}Tl, ^{205}Tl isotopes were monitored. Likewise, ^{115}In was monitored as internal standard by constant mixing with the sample flow using a Y-shape connexion before introduction of the mixture into nebulizer. Calibration was performed against aqueous standards and blank solutions.

For determination of total Tl, direct introduction of sample into ICP-MS instrument was performed. Finally, Tl(III) concentration was calculated by difference between total Tl and Tl(I) concentration.

3. Results and discussion

3.1. Studies on complexation of Tl and ion-pairing reaction

Separation of Tl species was feasible thanks to initial formation of the complex between ion chloride and Tl(III). Considering that the trivalent species can be hydrolysed in alkaline or neutral solutions, stabilization of the cation by a complexing agent is a convenient approach [24]. Furthermore, the high reduction potential shown by Tl(III) could favour its fast reduction to Tl(I) species. In fact, a reduction potential of 1.25 V for Tl(III)/Tl(I) redox couple is usually stated in the literature. Therefore, potential reagents for complex formation should be carefully selected to avoid possible conversion of Tl(III) species. Based on these considerations, Tl(III) species was complexed with chloride ion. Thus, the formation of $[TlCl_4]^-$ complex avoided both undesirable hydrolysis and reduction of Tl(III). Moreover, original speciation of Tl was preserved under these conditions.

Initially, the influence of chloride source for complex formation was studied in detail. The trivalent species were complexed with chloride ions originated from HCl acid and different salts. In this work, the extraction of Tl(III) from HCl, NaCl and LiCl solution was evaluated. Chloride ions from salts were conditioned in an HClO₄ medium. It was observed that Tl(III) could be completely extracted into the organic phase using chloride anions from both acid and salts. It has to be pointed out that an increase of experimental errors could be factible when salts are used as they have to be weighed, solubilized and transferred to a volumetric flask. Moreover, the choice of anions from salts comes with the incorporation of another reagent, such as HClO₄ (for adjusting the pH of medium). For this reason, HCl acid was selected as source of chlorides due to higher simplicity. Fig. 2 shows the dependence of extraction efficiency on the initial HCl concentration in aqueous solution. Furthermore, as the complex formation with the trivalent valency state is selective, Tl(III) was the only species able to form the ion pair with CYPHOS® IL 101, and hence the only one that could be extracted into the organic phase. On the other hand, considering that Tl(I) do not form complexes with chloride anions, it remains completely in the aqueous phase. Therefore, the selective complex formation allowed complete separation of both species. Finally, a concentration of 1 mol L^{-1} was selected to ensure complete extraction of Tl(III).

It is well known that Tl(III) forms a very stable chlorocomplex in HCl solutions, showing a high stability constant ($\log K = 18.3$) [25]. On the other hand, it is expected that $[TlCl_4]^-$ shows good extractability into the organic phase because of this anionic complex is tetrahedral, and hence the coordination sites of Tl(III) are fully occupied by chloride [26]. Therefore, water molecules do not bind to $[TlCl_4]^-$. Nevertheless, it was supposed that the formation of an ion pair between $[TlCl_4]^-$ anionic complex and a
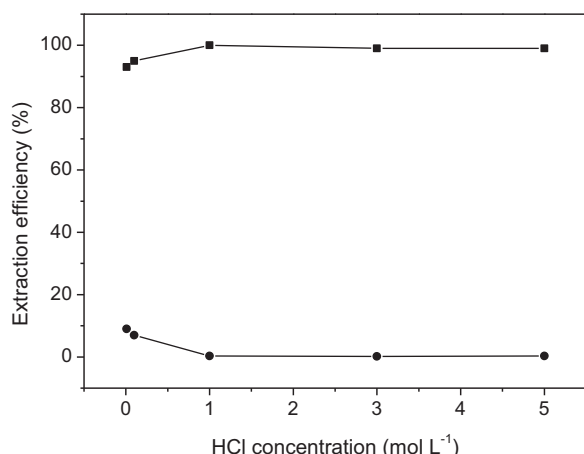
Fig. 2. Effect of HCl concentration on extraction efficiency of (●) Tl(I) and (■) Tl(III) species. Other experimental conditions are as mentioned in Table 1.

specific cation would allows to obtain total extraction of analyte. In this case, tetrabutylammonium bisulfate, cetyltrimethylammonium bromide (CTAB), trimethyltetradecylammonium bromide (TTAB) and CYPHOS® IL 101 were evaluated as ion-pairing agents. Furthermore, it was useful to establish the right concentration of the ion-pairing reagent due to its important role in the contribution of counter ions for ion pair formation with $[TlCl_4]^-$ anion. For this reason, concentration was studied within an interval of 2.0×10^{-6} to 2.0×10^{-2} mol L^{-1}. As shown in Fig. 3, the best results were obtained when CYPHOS® IL 101 was used as ion-pairing reagent. An extraction of 100% was reached using CYPHOS® IL 101 as ion-pairing agent. It could probably be explained because the ion pair containing CYPHOS® IL 101 would exhibit a lower polarity in comparison with the others ion-pairing agents studied in this work. On the other hand, no significant differences were observed when tetrabutylammonium, cetyltrimethylammonium or trimethyltetradecylammonium were used as ion-pairing reagents, which could be due to their similar cationic structures.

Furthermore, a concentration of 2.0×10^{-5} mol L^{-1} CYPHOS® IL 101 was essential to achieve the highest extraction efficiency, meaning that a molar ratio of 1:100 Tl to CYPHOS® IL 101 was enough to assure full ion pair formation between $[TlCl_4]^-$ and CYPHOS® IL 101. Although this relation is higher compared to the minimal theoretical molar ratio needed to form the ion pair, it could
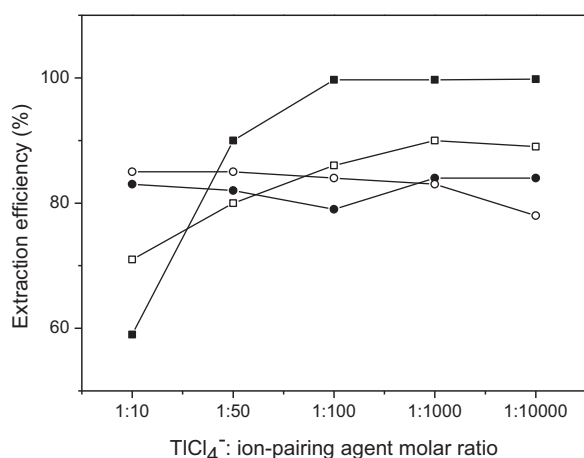
Fig. 3. Influence of $TlCl_4{}^-$/ion-pairing agent molar ratio on extraction efficiency of Tl(III). (■) CYPHOS® IL 101, (●) tetrabutylammonium bisulfate, (□) CTAB and (○) TTAB. Other conditions are shown in Table 1.

be possible that equilibrium displacement towards total ion pair formation occurs upon an excess of IL in solution.

3.2. Selection of the extraction solvent

The selection of extraction solvent is a critical matter to be considered in DLLME. The extraction solvent must show higher density than water for efficient phases separation, good extraction capability towards different compounds and relatively low solubility in aqueous medium. In this work, chloroform and carbon tetrachloride were evaluated as extractant solvents. No marked differences were observed in the extraction efficiency of Tl(III) species using both chloroform or carbon tetrachloride (99.2 and 99.9%, respectively). As carbon tetrachloride has lower solubility in water than chloroform (1 g L^{-1} vs. 8.22 g L^{-1} (both at 20 °C)), the former solvent was preferred to chloroform. Thus, any organic solvent effects on ICP measuring conditions were prevented. Considering the previous information, carbon tetrachloride was selected as the extraction solvent for subsequent experiments. Furthermore, aliquots of sample were examined by using 500 μL of ethanol (as dispersant solvent) containing different volumes of the selected extraction solvent (40–150 μL). The highest recovery was observed since 80 μL of carbon tetrachloride.

3.3. Influence of the disperser solvent on extraction efficiency

In order to perform DLLME, the disperser solvent must be miscible in both water and the extraction solvent. Therefore, different disperser solvents such as acetone, methanol and ethanol were evaluated. The highest extraction efficiency of Tl(III) (∼99%) was reached with all the assayed solvents (at different volumes). Due to its lower toxicity as compared to methanol and acetone, ethanol was chosen as the disperser solvent for following experiments. Moreover, it was observed that a stable and cloudy solution was obtained since 100 μL of the disperser solvent led to the highest extraction efficiency for Tl(III). Higher volumes of the disperser caused, even though not markedly, a deterioration of the extraction efficiency. Finally, 100 μL of ethanol were chosen for further experiments.

3.4. Speed of the overall extraction procedure

The extraction time, considered as the time between addition of the mixture of ethanol and carbon tetrachloride up to the moment the centrifugation process started, was studied between 0 and 6 min. The highest extraction efficiency was obtained within 2 min only, and no significant improvement was shown at longer extraction times.

The infinitely large interfacial area obtained between the extraction solvent and aqueous phase after the formation of cloudy solution determines the short time required for extraction of analyte. Thus, the ion pair diffuses into the extraction solvent so fast that the extraction equilibrium can be achieved in a very short time. A time of 2 min was enough for achieving an extraction efficiency of 100%.

Centrifugation of sample solution during the extraction procedure is an important parameter to be considered because of their contribution to the time of analysis. In this work, the effect of centrifugation time on Tl(III) extraction was evaluated in the interval between 2 and 15 min at 1500 rpm. The centrifugation speed was chosen as it was the maximum keeping the integrity of the glass centrifuge tubes used in this study. It was observed that a minimal centrifugation time of 4 min was required to fully separate the organic phase containing Tl(III) species from the aqueous phase. Then, this last phase was ready for determination of Tl(I) species

Table 2
Characteristic performance data reported in the literature for separation and determination of Tl species by ICP-MS.

Method	Sample	Speciation	LOD (ng L^{-1})	RSD (%)	Analysis frequency (h^{-1})	Ref.
SF–ICP-MS	Sea water	No	0.1	<4	1.6	[35]
RP-HPLC–ICP-MS	Sea water	Yes	2	<3.4	a	[12]
ECS–ICP-MS	River water	Yes	100	a	a	[36]
VG–ICP-MS	Sea water	No	10	2.4	a	[37]
CPE–ICP-MS	Tap and sea water	Yes	0.02	1–3	a	[38]
IL-DLLME–ICP-MS	Tap and river water	Yes	0.4	1.5	50	This work

SF: high resolution sector field; IC: ion chromatography; RP-HPLC: reversed-phase high performance liquid chromatography; ECS: exchange column system; VG: vapour generation; CPE: cloud point extraction.

a Non reported.

by direct injection into ICP-MS instrument. A 5 min-centrifugation resulted to be optimum for complete IL phase separation.

3.5. Interferences study

It has been reported that the measurement of ^{205}Tl isotope in ICP-MS is practically free of interferences since no other stable isotopes occur at this mass number [13]. However, interference from adjacent peaks could be possible only if large concentrations of ^{206}Pb and ^{204}Hg occur in the samples. In this work, it was not included a spectral interference study involving these elements because it was assumed that concentrations of Pb and Hg in water samples are generally low to cause some interference during measurement of ^{205}Tl isotope. However, it was necessary to evaluate the individual effect of possible interfering ions on [TlCl$_4$]$^-$ complex formation. Thus, a procedure was performed with 5 mL of 1 μg L^{-1} Tl solutions containing concomitant ions at concentration levels at which these ions may occur in the samples under study or even higher. The foreign ions tested were Cu(II), Fe(III), Zn(II), Cd(II), Co(II) and Hg(II). It was observed that these cations, forming complexes with chloride ion, could be tolerated up to at least 3500 μg L^{-1}. Moreover, Fe(III) could be tolerated up to 3000 μg L^{-1}. Therefore, the determination of Tl was successful even when foreign ions were at higher concentrations than those normally found in water samples.

3.6. Analytical performance

The analytical characteristics of the development method, including limit of detection, correlation coefficient, linear range, calibration graph and precision were determined to evaluate method performance.

Extraction recovery (ER) is an important parameter to analyse due to it reflects if separation of Tl species is complete. It was defined as the percentage of total analyte extracted into the organic phase:

$$ER = \frac{m_{\text{org-phase}}}{m_{\text{aq}}} = \frac{C_{\text{org-phase}} \times V_{\text{org-phase}}}{C_{\text{aq}} \times V_{\text{aq}}} \times 100$$

where $m_{\text{org-phase}}$ and m_{aq} are the mass of analyte in the final organic phase and the initial concentration in the sample solution, respectively. $C_{\text{org-phase}}$ and C_{aq} are the concentration of the analyte in the organic phase and in the sample phase, respectively. $V_{\text{org-phase}}$ and V_{aq} are the volumes of the phases involved [27]. Therefore, the maximum extraction efficiency for Tl(III) species was achieved under optimum experimental conditions (Table 1). Therefore, it ensures that separation of Tl(I) and Tl(III) species was complete.

The limit of detection (LOD) was calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve [28]. Since Tl detection by ICP-MS is not species-dependant, detection limits for Tl(I), Tl(III) and total Tl were 0.4 ng L^{-1}. The relative standard deviation (RSD) for ten replicate measurements of 1 μg L^{-1} Tl was 1.3% for Tl(I) and total Tl, and

1.5% for Tl(III). Therefore, the proposed method not only offers a low limit of detection derived from the application of a highly sensitive technique such as ICP-MS, but also consumes very small volumes of sample and reagents.

Finally, a comparison on analytical performance between the proposed method and others reported in the literature is presented. As shown in Table 2, our method shows a detection limit that is comparable or better than others previously reported using IC–ICP-MS. Furthermore, considering that this method does not involve the need of additional instrumentation besides ICP-MS, as it is with chromatography-based methods, it is quite economic in comparison with previous publications. In fact, the consumption of reagents is lower and the use of large volumes of toxic solvents is avoided. Unfortunately, the frequency of analysis is not reported by the majority of the authors. It is certain that separation of Tl species by chromatography methods takes longer time compared to the proposed methodology. On the other hand, the use of ion exchange resins for Tl species separation is not a fast step and significant contact time between sample solution and resins is necessary to achieve equilibrium in the adsorption. In contrast to these aforementioned works, the proposed method is amazingly rapid and hence it leads to a high frequency of analysis. Although the whole extraction procedure (metal complex and ion pairing formation, extraction into the organic phase and centrifugation) could take about 10 min, it is possible to simultaneously treat as many samples as can be placed in the centrifugation equipment. Thanks to this advantage and the help of a continuous elemental detector such as ICP-MS, a frequency of analysis of 50 samples per hour was obtained.

3.7. Validation study and speciation analysis of Tl in water samples

In order to validate the proposed analytical method, it was applied to the determination of total Tl in a certified reference material (CRM), natural water NIST SRM 1643e "Trace Elements in Water". The concentration of total Tl was found to be 7.428 ± 0.109 μg L^{-1}, which was not significantly different ($p < 0.01$) from the certified value of 7.435 ± 0.096 μg L^{-1}. On the other hand, since there are not available CRMs certifying concentration of individual elemental species of Tl, a recovery study could be a validation alternative in speciation studies [29]. Thus, the recovery of a known amount of Tl(I) and Tl(III) ions in the presence of the matrix sample was studied. The proposed IL-DLLME method was applied for the rapid separation and determination of Tl species in several tap and river water samples. Tap and river water samples spiked at 0.5 μg L^{-1} Tl(I) and 0.5 μg L^{-1} Tl(III) concentration levels were analysed by IL-DLLME–ICP-MS method. As can be observed in Table 3, satisfactory recoveries ranging 98.2–104% for Tl(I) and 96.3–103% for Tl(III) were obtained. These results obtained with the proposed method indicate that it is a reliable alternative for fast speciation analysis of Tl in the samples under study.

Table 3
Determination of Tl(I) and Tl(III) species in river and tap water samples (95% confidence interval; $n = 6$).

Water sample	Tl(I) species			Tl(III) species		
	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)[a]	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)[a]
Tap 1	0	0.11 ± 0.03	–	0	0.06 ± 0.04	–
	0.5	0.60 ± 0.05	98.2	0.5	0.57 ± 0.07	102
Tap 2	0	0.17 ± 0.03	–	0	0.08 ± 0.04	–
	0.5	0.67 ± 0.05	100	0.5	0.56 ± 0.08	96.4
Tap 3	0	0.24 ± 0.04	–	0	0.14 ± 0.05	–
	0.5	0.75 ± 0.06	102	0.5	0.65 ± 0.07	102
Tap 4	0	0.32 ± 0.04	–	0	0.17 ± 0.06	–
	0.5	0.84 ± 0.06	104	0.5	0.67 ± 0.08	100
River 1	0	0.02 ± 0.02	–	0	0.04 ± 0.04	–
	0.5	0.51 ± 0.04	98.6	0.5	0.55 ± 0.12	102
River 2	0	0.03 ± 0.02	–	0	0.05 ± 0.04	–
	0.5	0.54 ± 0.08	101	0.5	0.53 ± 0.11	96.3
River 3	0	0.04 ± 0.03	–	0	0.06 ± 0.05	–
	0.5	0.55 ± 0.09	102	0.5	0.57 ± 0.12	103
River 4	0	0.06 ± 0.04	–	0	0.08 ± 0.06	–
	0.5	0.55 ± 0.08	98.2	0.5	0.57 ± 0.13	98.1

[a] [(found − base)/added] × 100.

Finally, concentrations of Tl species were evaluated. It has been previously studied that from a thermodynamic point of view, Tl(I) species seems to be favoured in natural water in most cases due to high reduction potential of Tl(III)/Tl(I) redox couple. Nevertheless, the formation of complexes with Tl(III) species may cause the persistence of this species in the samples [30–32]. Moreover, it has been shown that dissolved Tl fraction in natural waters represents about 95% of total Tl, meanwhile Tl in particulate can barely reach an insignificant fraction of the total concentration of this element [33]. Therefore, determination of Tl(I) and Tl(III) species turns into a useful tool for the full knowledge of the majority of analyte concentration occurring in the samples under study. Thus, concentrations of Tl species in river water samples were in the range of 0.04–0.08 $\mu g\,L^{-1}$ for Tl(III), and 0.02–0.06 $\mu g\,L^{-1}$ for Tl(I). The concentrations found in tap water samples were in the interval of 0.11–0.32 $\mu g\,L^{-1}$ for Tl(I) and 0.06–0.17 $\mu g\,L^{-1}$ for Tl(III). These results expressed for both tap and river water samples are in good agreement with those previously obtained by other authors [6,34].

4. Conclusions

The novel use of ILs on the development of a methodology for Tl species separation coupled with ICP-MS detection is for the first time reported in this work. In our study, it has been demonstrated that the ionic liquid CYPHOS® IL 101 can be an excellent ion-pairing reagent to obtain highly efficient extraction and separation of Tl species in water samples. A fast, accurate and interference-free IL-DLLME–ICP-MS methodology was developed in this work. Furthermore, the proposed method required no additional instrumentation for separation of Tl species and hence, it can be considered as a cost-effective approach for elemental speciation analysis. Moreover, potential recycling of wastes is feasible as organic solvents are not introduced into the ICP source.

Compared to previous contributions, the proposed method offers rapidity and simplicity as main advantages. The proposed method showed high selectivity, while its successful application was demonstrated for Tl species separation and determination at ultratrace levels with good accuracy and reproducibility. Furthermore, isotope dilution analysis could be perfectly combined with the proposed method as chlorocomplex formation is feasible with Tl isotopes.

Finally, the method opens the possibility of developing preconcentration of Tl as extractant IL phase resulting from DLLME could be subjected to back extraction and applied for detection by ICP-MS.

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