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Dispersive liquid–liquid microextraction and preconcentration of thallium species in water samples by two ionic liquids applied as ion-pairing reagent and extractant phase

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ABSTRACT

In the present work, a simple and highly sensitive analytical methodology for determination of Tl^+ and Tl^{3+} species, based on the use of modern and non-volatile solvents, such as ionic liquids (ILs), was developed. Initially, Tl^+ was complexed by iodide ion at pH 1 in diluted sulfuric acid solution. Then, tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) was used as ion-pairing reagent and a dispersive liquid–liquid microextraction (DLLME) procedure was developed by dispersing 60 mg of 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6mim][PF_6]$ with 500 μL of ethanol in the aqueous solution. After the microextraction procedure was finished, the final IL phase was solubilized in methanol and directly injected into the graphite furnace of an electrothermal atomic absorption spectrometer (ETAAS). An extraction efficiency of 77% and a sensitivity enhancement factor of 100 were obtained with only 5.00 mL of sample. The limit of detection (LOD) was 3.3 ng L^{-1} Tl while the relative standard deviation (RSD) was 5.3% (at 0.4 μg L^{-1} Tl and $n = 10$), calculated from the peak height of absorbance signals. The method was finally applied to determine Tl species in tap and river water samples after separation of Tl^{3+} species. To the best of our knowledge, this work reports the first application of ILs for Tl extraction and separation in the analytical field.

1. Introduction

Thallium (Tl) is widely used in industry for manufacturing of different products including semi conductors, mixed crystals for infrared instruments, low temperature thermometers, jewellery, dyes, pigments and fireworks [1]. However, Tl is a highly toxic element and it is well-known as one of 13 priority metal pollutants listed by the United States Environmental Protection Agency (US EPA) [2]. Thallium can be found in two oxidation states, Tl^+ and Tl^{3+}, each of which manifests different bioavailability and toxicity [3]. In fact, it has been shown that Tl^{3+} is approximately 50,000-fold more toxic than the lower valency and, in comparison with other elements, Tl^{3+} is 43,000-fold more toxic than Cd on a free-ion basis [4]. Therefore, determination of Tl species in environmental samples is of great interest due to its clinical and environmental roles.

Thallium has been determined by laser-excited atomic florescence spectrometry (LEAFS) [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6] and coupled plasma-mass spectrometry (ICP-MS) [7]. Among these, ICP-MS is mainly used for the determination of Tl because of its high sensitivity, selectivity and sample throughput. However, this instrumentation might not be always available in all routine analytical laboratories because of its high cost [8]. On the other hand, electrothermal atomic absorption spectrometry (ETAAS) is still a widely used analytical technique due to its reliability, sensitivity and relatively low cost of instrumentation [9]. Furthermore, ETAAS enables injection of minimal volume of sample and solvents, which is highly convenient when liquid–liquid microextraction (LLME) procedures are developed for elemental preconcentration [10,11].

On the other hand, difficulties are usually experienced because of low abundance levels of trace metals, such as Tl [12]. Therefore, in order to achieve accurate, reliable and sensitive results, it is necessary to perform a preliminary preconcentration step for trace element detection. At present, some methods have been reported for the preconcentration and separation of Tl including

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liquid–liquid extraction (LLE) [13], solid phase extraction (SPE) [14–16] and single-drop microextraction (SDME) [17]. Conventional LLE has been widely used despite the volatility, toxicity and flammability of the employed organic solvents [18]. On the other hand, many of the problems linked to the use of these solvents, such as loss by evaporation can be significantly avoided using ionic liquids (ILs) as alternative solvents. Ionic liquids are very attractive alternatives to substitute regular organic solvents because of their no measurable vapour pressure [19]. Nowadays, ILs are gaining an important recognition as novel solvents in chemistry due to some unique properties, such as thermal stability even at high temperatures, relatively favourable viscosity and miscibility with water and organic solvents, as well as good extractability for several ions [20].

Ionic liquids, such as 1-alkyl-3-methylimidazolium hexafluorophosphates ($[C_n mim][PF_6]$, $n = 4, 6, 8$), have been used for development of single drop microextraction (SDME) procedures [18]. However, the drawbacks of this technique are high instability of the drop hanging from needle tip, limited drop surface and consequently slow kinetics [11]. Dispersive liquid–liquid microextraction based on ILs as extractant phase has been proposed for metal extraction, thus avoiding many of the problems observed with previous methods. Also, it is well documented that 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$) IL has been proposed as a media for extraction of some trace metal [9,21,22]. However, and to the best of our knowledge, ILs have not been applied so far for extraction and preconcentration of Tl species. On the other hand, the use of tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) as ion-pairing reagent has been previously reported [23]. However, the formation of an ion pair between a Tl-complex and an IL was not covered by that study. Thus, the combination of $[C_6mim][PF_6]$ and CYPHOS® IL 101 as ion pair reagent has not been considered so far in none of the analytical extraction/preconcentration technique.

The aim of the current work was the development of a simple analytical methodology based on the combined application of two ILs for determination of Tl species. CYPHOS® IL 101 was assessed for ion-pairing reaction with Tl^+–iodide complex, followed by a dispersive liquid–liquid microextraction (DLLME) technique based on $[C_6mim][PF_6]$ IL as extractant phase. Thallium determination was performed by ETAAS, with a mixture of chemical modifiers involving palladium nitrate and ascorbic acid. The effect of several chemical variables on IL-DLLME efficiency including pH, iodide concentration, CYPHOS® IL 101 concentration, amount of $[C_6mim][PF_6]$ and extraction time were evaluated and optimized. Finally, Tl speciation analysis of tap and river water samples was feasible thanks to the initial separation of Tl^{3+} species with an ion exchange resin followed by DLLME procedure.

2. Experimental

2.1. Instrumentation

Experiments were performed using a Perkin Elmer (Uberlingen, Germany) Model 5100ZL atomic absorption spectrometry equipped with a transversely heated graphite atomizer, a Tl Electrodeless Discharge Lamp (EDL) and a Zeeman-effect background correction system. Instrumental conditions used for Tl determination in IL-enriched phase were as shown in Table 1. A centrifuge (Luguimac, Buenos Aires, Argentina) model LC-15 was used to accelerate the phase separation process. A vortex model Bio Vortex B1 (Boeco, Hamburg, Germany) was utilized for mixing the reagents. A Horiba F-51 pH meter (Kyoto, Japan) was used for pH determinations.

2.2. Reagents

Stock standard solutions ($1000\ mg\ L^{-1}$) of Tl^+ and Tl^{3+} were prepared by dissolving an accurate weight of either $TlNO_3$ (99.9%) (Aldrich, Milwaukee, USA) or $Tl(NO_3)_3{\cdot}3H_2O$ (98%) (Aldrich) in 1% (v/v) HNO_3. Working standard solutions were prepared daily by diluting the stock standard solution with ultrapure water. A $5 \times 10^{-2}\ mol\ L^{-1}$ potassium iodide (KI) solution was prepared by dissolving 415 mg of KI (99.9%) (J.T. Baker, USA) in 50 mL of ultrapure water. Hydrochloric (37%), sulfuric (95–97%), nitric acids (65%) and toluene (99.9%) from Merck (Darmstadt, Germany) were used. For chemical modification, a $1000\ mg\ L^{-1}$ Pd solution was prepared by dissolving 62.7 mg $Pd(NO_3)_2{\cdot}2H_2O$ (Fluka, Buchs, Switzerland) in 25 ml 0.1% (v/v) HNO_3. For ascorbic acid as modifier, 300 mg of solid drug ($\geq$99%) (Merck) were weight and diluted to 10 ml. This modifier was prepared daily. A $10\ g\ L^{-1}$ $AgNO_3$ (Merck) and a $0.15\ g\ L^{-1}$ $Mg(NO_3)_2$ (Merck) solutions were prepared in ultrapure water.

Dowex® 1 × 8 anion exchange resin (100–200 mesh particle size, chloride form) (Sigma–Aldrich, St. Louis, MO, USA) was weighed and placed in 15-ml graduated polyethylene centrifuge tubes.

CYPHOS® IL 101 was kindly donated by Prof. Ullastiina Hakala (University of Helsinki, Finland) and provided by CYTEC Industries Inc. (Canada).

$[C_6mim][PF_6]$ was synthesized according to a method proposed by Huddleston and co-workers [24] and stored in contact with ultrapure water to equilibrate the water content in the IL phase [25]. Qualitative analysis of synthesized IL was performed by comparison of infrared spectra with commercially available $[C_6mim][PF_6]$ (Solvent Innovation GmbH, Köln, Germany).

Ultrapure water (18 MΩ cm) was obtained from a Millipore Continental Water System (Bedford, MA, USA). All glassware used in the experiments were cleaned with pure water, then soaked in $0.1\ mol\ L^{-1}$ HNO_3 solution at least for 24 h and thoroughly rinsed 5 times with ultrapure water before use.

2.3. Sample collection and conditioning

For tap water samples collection, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a beaker. Tap water samples were analyzed immediately after sampling. River water samples were collected in cleaned nitric acid-washed HDPE bottles rinsed three times with water sample prior to collection. A sample volume of 1000 mL was collected at a depth of 5 cm below the surface. The river samples were filtered through 0.45 μm pore size PTFE membrane filters (Millipore Corporation, Bedford, MA, USA) immediately after sampling.

2.4. Thallium species separation and dispersive liquid–liquid microextraction procedure

Before the proposed DLLME procedure was applied, Tl^+ and Tl^{3+} species were separated by using a Dowex 1 × 8 anion exchange resin. Initially, 500 mg of the resin were weighed and placed in 15-ml graduated polyethylene centrifuge tubes. Immediately, the resin was washed several times with 10 mL of ultrapure water and activated with 10 mL of $0.1\ mol\ L^{-1}$ HCl solution. Then, 5 ml of sample solutions containing $0.5\ mol\ L^{-1}$ HCl were added to each tube. Thus, Tl^{3+} species was selectively retained on the resin thanks to its ability to form the tetrachlorothallate (III) anionic complex. On the other hand, Tl^+ was not retained on the resin and it was later on determined following the proposed DLLME procedure. Total Tl was determined by a similar approach, but without initial separation of Tl species with the anion exchange resin. Finally,

Table 1
Instrumental and experimental conditions for Tl species determination.

Instrumental conditions				
Wavelength	276.8 nm			
Spectral band width	0.7 nm			
EDL lamp current	250 mA			
Matrix modifier	2.5 μg Pd 300 μg ascorbic acid			
Graphite furnace temperature program				
Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
Drying 1	110	1	30	250
Drying 2	130	15	30	250
Drying 3	400	20	50	250
Drying 4	550	50	20	250
Pyrolysis	700	10	20	250
	300	1	15	250
Atomization	1800	0	5	–
Cleaning	2400	1	2	250
Extraction conditions				
Sample volume	5 mL			
KI concentration	3×10^{-3} mol L^{-1}			
Working pH	1			
H_2SO_4 concentration	0.9 mol L^{-1}			
CYPHOS® IL 101 concentration (in toluene)	3.08×10^{-5} mol L^{-1}			
C_6mim[PF_6] IL amount	60 mg			
Disperser	500 μL ethanol			

concentration of Tl^{3+} was calculated by difference between total Tl and Tl^{+} concentration.

For the development of DLLME technique, a volume of 5 ml of sample or a 3 μg L^{-1} Tl^{+} standard solution (for optimization), was placed in a 10 ml graduated glass centrifuge tube with 500 μL of 9.2 mol L^{-1} H_2SO_4 and 300 μL of a 5×10^{-2} mol L^{-1} KI solution. The mixture was shaken for 1.5 min and left to stand for 5 min for total formation of complex. Then, 40 μL of a 3.8×10^{-3} mol L^{-1} CYPHOS® IL 101 (in toluene) solution were added, followed by shaking for 1.5 min with a vortex stirrer. Afterwards, a mixture of 60 mg of [C_6mim][PF_6] (extraction solvent) dissolved in 500 μL of ethanol (dispersant solvent) was added to the sample solution. Immediately, the resulting system was shaken for 5 min followed by centrifugation at 1200 rpm (241.5 × g) for 15 min to obtain two well-defined phases. The upper aqueous phase was manually removed with a transfer pipette. The IL sedimented phase was dissolved with 50 μL of methanol and injected into the graphite furnace of ETAAS instrument (conditions as shown in Table 1) with a syringe. Calibration was performed against aqueous standards and blank solutions.

3. Results and discussion

3.1. Study of graphite furnace conditions

In order to obtain high accuracy and precision for ETAAS measurement of Tl in the presence of ILs matrices, optimization of several parameters, including all steps of thermal treatment in the graphite furnace, were carefully studied.

Initially, it was supposed a possible interference effect of CYPHOS® IL 101 on Tl signal due to the presence of chloride in the IL matrix. It has been already reported that the formation of gaseous monohalides is the most frequent case of chemical interferences in ETAAS and the influence of chloride on Tl detection is an example of such interference [26]. For eliminating or diminishing this effect, several alternatives have been proposed, such as the use of different chemical modifiers [26–28]. It is well known that Pd as a modifier is not as effective for Tl as it is for other elements [26]. In this work, a preliminary experiment for atomization was developed by injecting a 100 μg L^{-1} Tl standard solution in presence of 60 mg [C_6mim][PF_6] and CYPHOS® IL 101. It was observed that, without chemical modifier, Tl was lost from very low pyrolysis temperatures. Thus, several chemical modifiers, such as 100 μg Ag, 2.5 μg Pd–3 μg Mg mixture and 2.5 μg Pd–300 μg ascorbic acid mixture were tested. The effect of the modifiers on Tl signal is shown in Fig. 1. In agreement with Shan et al. [29], the most efficient thermal stabilization was observed using a combination between $Pd(NO_3)_2$ and ascorbic acid. Therefore, a mixture of 2.5 μg Pd and 300 μg ascorbic acid was injected as chemical modifier for each measurement (Table 1). Once the above mentioned optimization was developed, the preconcentration procedure using KI, H_2SO_4, CYPHOS® IL 101 and [C_6mim][PF_6] was assayed and significant changes were not observed with respect to previous Tl signals. Thus, accurate Tl determination by ETAAS was feasible even in high organic content of IL-enriched matrix.

The influence of pyrolysis temperatures on Tl absorbance was studied in detail within a range of 400–800 °C. Optimal pyrolysis temperature was observed at 700 °C (Fig. 2), with a hold time of 20 s. Once selected the previous temperature, the effect of atomization temperature on Tl absorbance was studied within the interval of 1300–1900 °C. The highest signal was observed at 1800 °C, with a

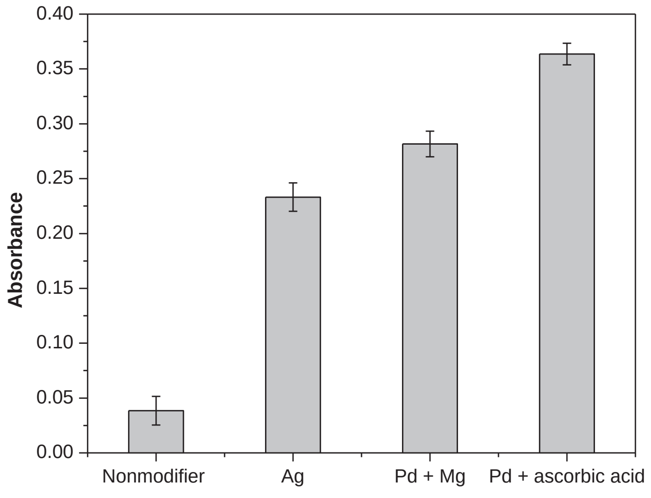

Fig. 1. Effect of different chemical modifiers on Tl signal obtained in the presence of 60 mg of [C_6mim][PF_6] IL. A volume of 20 μL of a 100 μg L^{-1} Tl solution was injected.

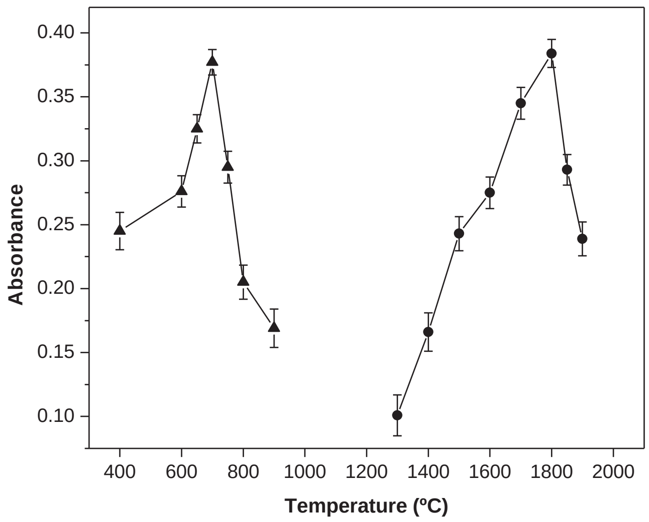

Fig. 2. Pyrolysis (▲) and atomization (●) temperature curves for 100 μg L^{-1} Tl solution mixed with 60 mg [C_6mim][PF_6] IL and using 2.5 μg of Pd and 300 μg of ascorbic acid as chemical modifiers. Other conditions were as mentioned in Table 1.

hold time of 5 s. Moreover, a temperature of 2400 °C and a hold time of 2 s were chosen for the cleaning step.

Furthermore, dissolution of the IL phase in an appropriated solvent was necessary to prevent typical drawbacks associated with direct injection of viscous ILs into the graphite furnace, affecting reproducibility of the injections. For this reason, the use of acetone or methanol was evaluated in this work. Complete dissolution of the IL phase was achieved with 50 μL of methanol as diluent, while no negative effect on analytical sensitivity was observed using this solvent. Thereby, 50 μL of methanol was set up for further experiments.

3.2. Selection of IL and dispersant solvent

Ionic liquids have different properties such as melting point, viscosity, density, and hydrophobicity that can be modified by simple changes to the structure of the ions [30]. In this work, imidazolium-IL containing [PF_6]$^-$ counteranion was chosen. It is well known that [C_4mim][PF_6], [C_6mim][PF_6] and [C_8mim][PF_6] are the most used ILs belonging to this class. In previous contributions, it was observed that solubility in water proportionally decreases with the longitude of alkyl chain, meanwhile viscosity shows an opposite trend [31]. In this work, [C_6mim][PF_6] was chosen because of their relatively high hydrophobicity and suitable viscosity.

The effects of IL amount and type of dispersant solvent on the performance of the proposed DLLME method were evaluated. In order to obtain the highest pre-concentration factor possible, the minimal IL-phase mass required for extraction was determined. Thus, [C_6mim][PF_6] amount was studied between 40 and 80 mg, and using 500 μL of ethanol as dispersant solvent. It was observed that the extraction efficiency of DLLME procedure was remarkably affected by the amount of IL. Thus, the extraction efficiency rapidly increased with the amount of IL and the highest Tl recovery was observed with 60 mg of [C_6mim][PF_6]. However, higher amounts of the extractant solvent did not improve extraction efficiency and only increased the organic content of the solutions injected in ETAAS for Tl determination. Therefore, a 60 mg of [C_6mim][PF_6] was chosen for further experiments.

A variety of disperser solvents including acetone, methanol, ethanol and acetonitrile was assayed in this work. The results revealed that ethanol lead to achieve the highest recovery of the analyte. Subsequently, different volumes of ethanol (100–700 μL) were evaluated. It was observed that the extraction efficiency increased by increasing the ethanol volume up to 500 μL. On the other hand, the extraction efficiency was slightly reduced for volumes exceeding 500 μL, probably due to higher solubilization of the IL phase into the aqueous solution. Therefore, 500 μL of ethanol was chosen as the optimum volume to reach a better and more stable cloudy solution.

3.3. Studies on complexation of Tl and ion-pairing capabilities of CYPHOS® IL 101

In this work, DLLME was developed for Tl extraction because of their simplicity of operation, rapidity, low cost, high recovery, high sensitivity enhancement factor and environmental benignity [32]. Classical IL-DLLME with organic solvents as disperser agents, temperature-assisted IL dispersive liquid-phase microextraction (TILDLME) and ionic liquid-based ultrasound-assisted dispersive liquid–liquid micro-extraction (USA-IL-DLLME) were initially evaluated. However, the highest extraction efficiency was obtained with classical DLLME technique.

Furthermore, the study of some important variables was performed by modifying one variable at the time, while keeping the others constant. The majority of variables were optimized for Tl^+, pH excepted that was optimized for both Tl species. The pH of the sample could affect not only the formation of a complex but also the extraction efficiency of the system. Thereby, the effect of pH on both stages was studied in the interval of 1–10. The suitable pH values were adjusted with H_2SO_4 and NaOH solutions. The optimum pH value for Tl extraction was observed in the interval of 1–2. Thus, samples and standards were adjusted at pH 1. Interestingly, it was observed that both Tl species were equally extracted upon different pH values. This could be explained according to the reaction proposed by Busev and Tiptsova [33] regarding tetraiodide complex formation, in which Tl^{3+} is reduced to Tl^+ by the following reaction pathways:

$$Tl^{3+} + 2I^- \rightarrow Tl^+ + I_2 \tag{1}$$

$$Tl^+ + I^- \rightarrow TlI \tag{2}$$

$$TlI + I_2 \rightarrow TlI_3 \tag{3}$$

$$TlI_3 + I^- \rightarrow TlI_4{}^- \tag{4}$$

Moreover, it is well known that Tl^{3+}/Tl^+ reduction potential is 1.25 V and for iodine (I_2/I^-) is 0.62 V. On the basis of these potentials, the favoured reaction is thus the reduction of Tl^{3+} to Tl^+. Likewise, the effect of iodide concentration on the analytical signal was evaluated. Fig. 3(a) shows a significant improvement of Tl extraction efficiency increasing iodide concentration up to 3×10^{-3} mol L^{-1}. Thus, this iodide concentration was chosen as optimal.

In this work, it was initially supposed the formation of an ion pair between $TlI_4{}^-$anion and the cation of CYPHOS® IL 101 in order to increase the extraction efficiency of analyte, by improving its affinity for the hydrophobic [C_6mim][PF_6] phase. Therefore, it was useful to establish the right concentration of CYPHOS® IL 101 ion-pairing reagent due to its important role in the contribution of counter ions for ion pair formation. On the other hand, it was initially considered the use of a minimal amount of this chloride-containing IL to avoid possible chloride interferences on Tl determination by ETAAS. In this work, the reaction between [TlI_4]$^-$ and CYPHOS® IL 101 was proposed to allow next extraction by [C_6mim][PF_6] IL. CYPHOS® IL 101 concentration was studied within an interval of 7.7×10^{-6}–1.5×10^{-4} mol L^{-1}. As shown in

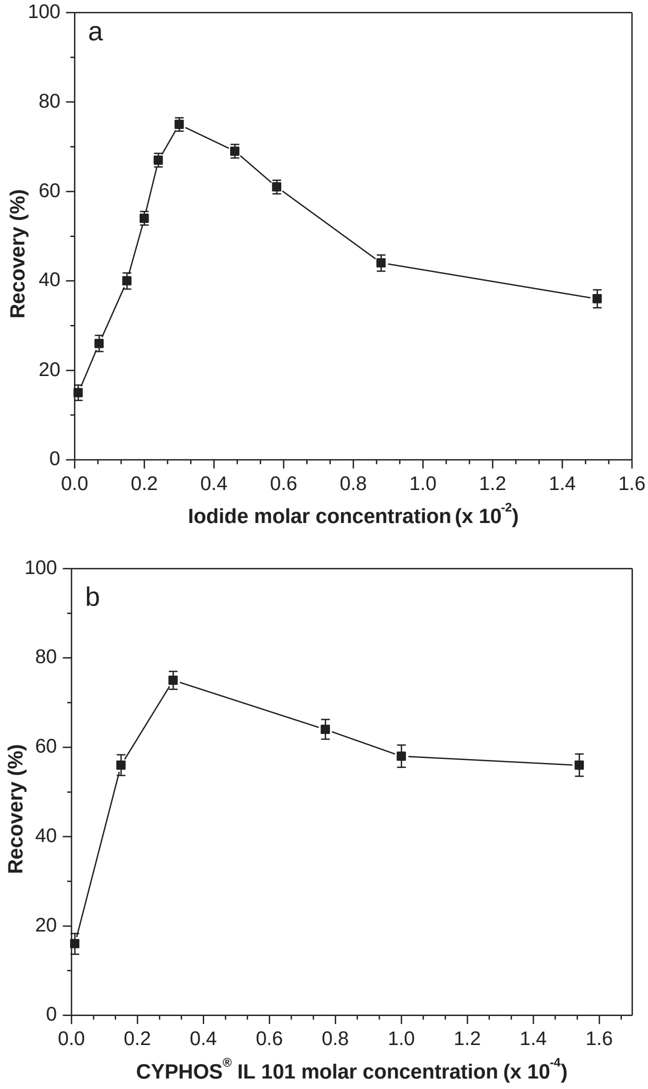

Fig. 3. Effect of (a) Iodide ion concentration and (b) CYPHOS® IL 101 concentration on Tl extraction efficiency. Other conditions were as indicated in Table 1.

Fig. 3(b), optimal results were found when 3.08×10^{-5} mol L^{-1} of the ion-pairing reagent was used.

3.4. Influence of sample volume on extraction efficiency

The effect of the sample volume on Tl recovery was studied. On the one hand, Tl mass was kept constant and sample volume was changed. As can be observed in Fig. 4, sample volume affected directly Tl recovery and remained constant up to 5 mL of sample. This effect could be explained by the fact that higher sample volumes are linked to major IL solubilization into the aqueous phase, thus decreasing Tl extraction efficiency. On a different experiment, Tl concentration was kept constant and the sample volume was varied. Therefore, not only sample volume but also analyte mass were changed. In this case, it can be observed that the sample volume affected analyte recovery. From the comparison of these two cases, it can be concluded that the extraction efficiency of the system is independent of analyte concentration, but certainly affected by sample-to-IL phase volumes ratio. Regarding to the final IL phase sedimented, no differences were observed for different sample volumes. In fact, higher amounts of IL were obtained with lower sample volumes.

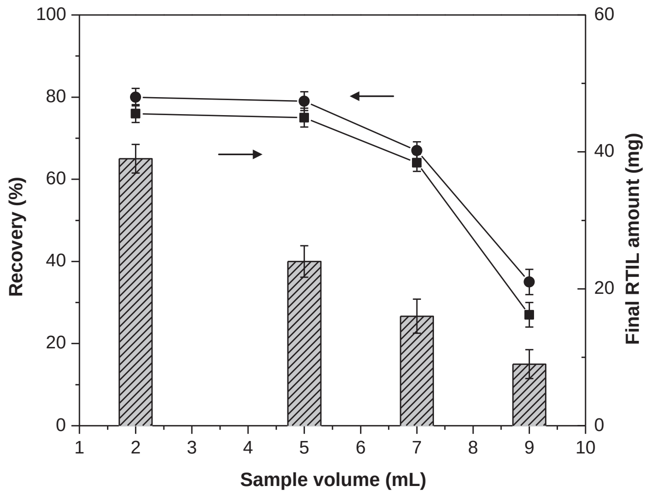

Fig. 4. Influence of sample volume on Tl extraction efficiency at (●) constant Tl mass or (■) constant Tl concentration. Other conditions were as reported in Table 1.

3.5. Evaluation of minimal extraction and centrifugation time

In DLLME method, extraction is defined as interval time between addition of the mixture of disperser solvent (ethanol) and extraction solvent (IL), and before starting the centrifugation step. The effect of extraction time was evaluated in the range of 0–25 min. It was observed that the highest extraction efficiency could be attained since 4 min and longer extraction times did not significantly improve Tl extraction. These results show that IL-DLLME is a very fast extraction process. Therefore, the ion pair diffuses into the extraction solvent quickly due to the large surface area obtained between the IL and the aqueous phase after the formation of a cloudy solution, In order to achieve the highest extraction efficiency in the shortest time, extraction was performed for 5 min only.

Additionally, centrifugation of sample solution in the extraction procedure is the most time-consuming step. For this reason, it is important to establish the right centrifugation time to achieve both phase separation and the highest analysis frequency. Thus, the effect of centrifugation time on Tl recovery was studied in the range of 5–25 min at 1200 rpm ($241.5 \times g$). It was observed that separation of phases improved as time went on, as drops of ILs containing the analyte were fully condensed and separated from the aqueous phase. On the other hand, very long centrifugation times resulted in temperature increasing, leading to a higher dissolution of the IL phase and diminishing of analyte extraction. Thus, 15 min-centrifugation was chosen for complete separation of phases.

3.6. Influence of potential interfering species

Several ions including, Ca^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, $NO_3{}^{-}$, $CO_3{}^{2-}$, $SO_4{}^{2-}$ and $PO_4{}^{3-}$ are common concomitant regularly found in tap and river water samples. For this reason, their influence on Tl determinations was evaluated. The study was performed by analyzing a 1 μg L^{-1} Tl standard solution containing concomitant ions concentration levels at which these ions may occur in these samples, and applying the recommended extraction procedure. A concomitant ion was considered to interfere if it resulted in an analytical signal variation of ±5%. Among the foreign ions tested, positively charged ions could be tolerated up to at least 2000 μg L^{-1} and it was not observed interference within the range under study. On the other hand, the amounts of anions usually present in the samples under study did not produce any interference.

Table 2
Analytical methods reported in the literature for Tl preconcentration and determination.

	Speciation analysis	LOD (ng L^{-1})	RSD (%)	EF	Sample volume (mL)	Calibration range (μg L^{-1})	Analysis frequency (h^{-1})	CI (μL)	Ref.
SDME – ETAAS	Yes	700	5.1	50	10	3–22	[a]	0.20	[17]
SPE – FAAS	Yes	2500	2.6	77	25	30–300	7[b]	0.33	[38]
CPE – ICP-MS	Yes	0.02	2.3	125	50	0.002–0.5	[a]	0.40	[7]
SPE – ETAAS	No	50	5.7	45	5	0.1–20	[a]	0.11	[39]
IL-DLLME-ETAAS	Yes	3.3	5.3	100	5	0.033–4	30	0.05	This work

SDME: single drop microextraction; FAAS: flame atomic absorption spectrometry; CPE: cloud point extraction.

[a] Non reported.

[b] On-line preconcentration.

3.7. Analytical performance

The calibration graph for ETAAS determination of Tl was linear from levels near the limit of detection (LOD) and up to at least 4000 ng L^{-1}, with a correlation coefficient of 0.9971. The LOD, calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve [34], was 3.3 ng L^{-1} Tl. The relative standard deviation (RSD) for ten replicate measurements of 0.4 μg L^{-1} Tl was 5.3%. The sensitivity enhancement factor (EF) was obtained from the slope ratio of calibration graph after and before application of the DLLME procedure [21]. Thus, the EF obtained with a sample volume of 5 mL was 100.

Extraction recovery (ER) was defined as the percentage of total analyte extracted into the IL phase:

$$ER = \frac{m_{ILphase}}{m_{aq}} = \frac{C_{ILphase} \times V_{ILphase}}{C_{aq} \times V_{aq}} \times 100 \qquad (1)$$

where $m_{ILphase}$ and m_{aq} are the mass of analyte in the final IL phase and the initial concentration in the sample solution, respectively. $C_{ILphase}$ and C_{aq} are the concentration of the analyte in the IL phase and in the sample phase, respectively. $V_{ILphase}$ and V_{aq} are the volumes of the phases involved [35]. In this work, an extraction recovery of 77% was obtained when the procedure was developed under optimal experimental conditions (Table 1).

Furthermore, the consumptive index (CI) can be defined for practical purposes as:

$$CI = \frac{V_s}{EF} \qquad (2)$$

where V_s is the volume of sample (in mL) consumed to achieve the EF value [36]. The CI obtained for the proposed method was 0.05 mL. Regarding the frequency of analysis, although the whole preconcentration procedure (metal complexation, ion-pair formation, extraction into the dispersed IL phase, and centrifugation) could take about 30 min, it is possible to simultaneously treat as many samples as can be placed in the centrifugation equipment. For our work, the frequency of analysis was at least 30 samples per hour based on the time required for performing analyte determination in ETAAS.

Finally, a comparative study on analytical performance allows us to show the strengths of the proposed method with respect to others already reported in the literature. Our method shows a LOD that is comparable to, or better than others developed for Tl determination in water samples (Table 2). A high EF was obtained with a reduced sample volume, yielding a low CI. Thus, CI is a useful tool for selecting a preconcentration method.

3.8. Validation study and determination of Tl in water samples

The proposed IL-DLLME method was applied to the determination of Tl species in several tap and river water samples. For validation, the proposed method was applied to the analysis of a certified reference material (CRM), natural water NIST SRM 1643e "Trace Elements in Water", with a declared Tl concentration of 7.445 ± 0.096 μg L^{-1}. Since the certified concentration value in the CRM was higher than the upper limit of the lineal range achieved by this method, a 3-fold dilution had to be implemented prior to the analysis. Using the IL-DLLME developed in this work, Tl concentration found in the CRM was 7.404 ± 0.980 μg L^{-1}, thus indicating an acceptable accuracy of the method. Moreover, a recovery study can be considered as a validation alternative in elemental speciation studies. Thus, the recovery of an amount of Tl^{+} and Tl^{3+} ions added to water samples was evaluated by this procedure. The recovery values were found in the interval of 96.8–104% for Tl^{+} and

Table 3
Concentrations of Tl^{+} and Tl^{3+} in river and tap water samples (95% confidence interval; $n = 6$).

Water sample	Tl^{+} species			Tl^{3+} species		
	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)[a]	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)[a]
Tap 1	0	0.98 ± 0.04	–	0	0.33 ± 0.02	–
	1.5	2.54 ± 0.12	104	1.5	1.87 ± 0.16	103
Tap 2	0	1.26 ± 0.07	–	0	0.36 ± 0.02	–
	1.5	2.77 ± 0.15	101	1.5	1.89 ± 0.17	102
Tap 3	0	1.34 ± 0.08	–	0	0.42 ± 0.02	–
	1.5	2.82 ± 0.17	98.7	1.5	1.88 ± 0.16	97.3
Tap 4	0	1.40 ± 0.08	–	0	0.48 ± 0.04	–
	1.5	2.90 ± 0.16	100	1.5	1.97 ± 0.18	99.2
River 1	0	n.d.[b]	–	0	0.07 ± 0.01	–
	1.5	1.47 ± 0.07	98.4	1.5	1.58 ± 0.13	101
River 2	0	n.d.[b]	–	0	0.06 ± 0.01	–
	1.5	1.45 ± 0.08	96.8	1.5	1.54 ± 0.11	98.7
River 3	0	n.d.[b]	–	0	0.08 ± 0.01	–
	1.5	1.49 ± 0.09	99.6	1.5	1.57 ± 0.12	99.3
River 4	0	0.05 ± 0.01	–	0	0.09 ± 0.01	–
	1.5	1.58 ± 0.10	102	1.5	1.56 ± 0.13	98.1

[a] [(Found-base)/added] × 100.

[b] Not detected.

97.3–103% for Tl^{3+} (Table 3). The results indicate that the procedure is reliable for speciation analysis of Tl in tap and river water samples. Finally, the concentrations found in river water samples were in the range of 0.06–0.09 $\mu g\,L^{-1}$ for Tl^{3+}, while Tl^{+} was generally not detected. On the other hand, concentrations of Tl species in tap water were in the range of 0.98–1.40 $\mu g\,L^{-1}$ for Tl^{+} and 0.33–0.48 $\mu g\,L^{-1}$ for Tl^{3+}. These results keep similarities to those obtained by Gil et al. [37].

4. Conclusions

This work has reported the first application of ILs for Tl extraction and preconcentration in the analytical field. Moreover, it has been demonstrated the several and potential applications of ILs for development of novel LLME techniques. Our experiments indicate that this "greener extraction methodology" resulting from the use of two ILs, CYPHOS® IL 101 as ion-pairing reagent and $[C_6mim][PF_6]$ as extractant, can be a successful alternative method for Tl^{+} and Tl^{3+} extraction and preconcentration. An extraction efficiency of 77% and an analytical sensitivity enhancement factor of 100 were obtained with only 5.00 mL of sample. Direct analysis and accurate determination of Tl by ETAAS are demonstrated even in the presence of complex organic matrix, such as that occurring in ILs. In summary, a simple method with high sensitivity and selectivity has been developed, while its successful application was demonstrated for Tl species determination at trace levels with good accuracy and reproducibility.

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