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# Capabilities of several phosphonium ionic liquids for arsenic species determination in water by liquid–liquid microextraction and electrothermal atomic absorption spectrometry

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The capabilities of several phosphonium-ionic liquids (PILs) to form ion-pairs with a complex obtained by reaction of arsenate species with molybdate were evaluated. Phosphonium-ILs containing the tetradecyl(trihexyl)phosphonium cation but different anions (dicyanamide and decanoate) and tributyl(methyl)phosphonium methylsulphate IL were studied. The size, polarity and localization of charges in PIL cations were shown to influence their capability to form ion-pairs with the arsenomolybdate ( $\text{AsMo}_{12}\text{O}_{40}^{3-}$ ) complex and to extract As(v). The performance of PILs was compared with that of a widely used ion-pairing reagent, cetyltrimethylammonium bromide (CTAB). Finally, the IL tetradecyl(trihexyl)phosphonium dicyanamide was chosen to develop a liquid–liquid microextraction (LLME) procedure using only 80  $\mu\text{L}$  of tetrachloroethylene as the extractant. The organic phase was directly injected into the graphite furnace of an electrothermal atomic absorption spectrometer (ETAAS) for As determination. An extraction efficiency of 100% and a sensitivity enhancement factor of 130 were obtained with 5 mL of sample. The detection limit was 1.9  $\text{ng L}^{-1}$  and the relative standard deviation for six replicate measurements of 1.0  $\mu\text{g L}^{-1}$  for As was 4.9%, 5.0% and 5.1% for As(v), As(III) and organic As species, respectively.

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## 1 Introduction

Arsenic is a toxic element and it naturally occurs in different environmental compartments under various chemical forms (species).<sup>1</sup> The toxicity of As in living organisms depends mainly on the quantity absorbed, the species and the exposure routes.<sup>2</sup> In fact, it has been found that inorganic As species are more toxic than organic ones, with methyl derivatives being thousand-fold less toxic than inorganic species.<sup>3</sup> Therefore, determination of As species is very important because of its biological and environmental effects.

Arsenic species have been determined by electrochemical, chromatographic and spectrometric techniques.<sup>4–6</sup> Although some of these techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), show high sensitivity and very low detection limits, instrumentation and maintenance costs could be still high for routine analytical laboratories. On the other hand, electrothermal atomic absorption spectrometry (ETAAS) is widely used due to its reliability, sensitivity and low cost of instrumentation. Moreover, ETAAS allows the injection of a

minimal volume of sample and organic solvents, as one of its main advantages for liquid–liquid microextraction (LLME) and preconcentration of trace elements.<sup>7</sup>

Until now, different methods have been reported for As preconcentration including LLME,<sup>8</sup> solid phase extraction (SPE),<sup>9,10</sup> dual cloud point extraction (DCPE),<sup>11</sup> coprecipitation with metal oxides,<sup>12,13</sup> etc. In LLME, metals form a complex with a suitable reagent and then they are extracted into a few microliters of solvent to be later injected into ETAAS. On the other hand, in conventional LLE, high volumes of organic volatile solvents are used, representing a source of pollution due to evaporation and the direct impact on the environment. Recently, ionic liquids (ILs) have emerged as very attractive alternatives to replace regular organic solvents because of their undetectable vapor pressure.<sup>14</sup> In fact, different As species have been determined by LLME and preconcentration methods using ILs.<sup>8,15</sup> The IL-LLME technique has been used for As determination through complexation with DDTC (sodium diethyldithiocarbamate)<sup>15</sup> and ADPC (ammonium pyrrolidinedithiocarbamate).<sup>16</sup> Interestingly, As(v) forms a highly stable complex with the molybdate anion at low pH (1.0–2.0), known as the arsenomolybdate anionic complex ( $\text{AsMo}_{12}\text{O}_{40}^{3-}$ ), which can be efficiently extracted thanks to the ion-pairing properties of some ILs.<sup>17</sup>

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Imidazolium-based ILs have been used as ion-pairing reagents for mobile phase additives in high performance liquid chromatography (HPLC). Thus, the formation of ion-pairs with analytes was observed, but the hydrogen bond formed between the imidazolium cation and its counterion also plays an important role. This effect is mainly due to charge delocalization in the imidazolium cation.<sup>18</sup> On the other hand, the positive charge of phosphonium-IL (PIL) cations is not delocalized; hence, a stronger ion-pair interaction between the cation and negatively charged molecules present in the medium can be expected. Despite some work carried out on IL-LLME using imidazolium-ILs for As preconcentration, very little has explored the capabilities of other types of ILs, such as phosphonium or pyrrolidinium.<sup>19</sup> Phosphonium-ILs have shown better properties than nitrogen cation-based ILs in some applications. One of the advantages is that PILs are more thermally stable than nitrogen cation-based ILs.<sup>20</sup> Consequently, PILs can be considered as excellent candidates for LLME, based on their ion-pairing interactions with different analytes. In fact, a recent study done by our group demonstrates the successful application of tetradecyl(trihexyl)phosphonium chloride as the ion-pairing agent for As preconcentration.<sup>8</sup> However, other phosphonium-ILs containing alternative cations or anions have not been explored yet.

The aim of this study was to investigate how the chemical structure of different PILs could affect ion-pairing reaction with the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex and how this property can be used for developing a fast, easy and sensitive LLME method for As speciation analysis in water samples. Different phosphonium-ILs were assayed for ion-pairing reaction with the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex formed between As(v) species (as arsenate) and the molybdate anion (Table 1). Two PILs with low miscibility in water sharing the same cation (tetradecyl(trihexyl)phosphonium), but differing in their anions (dicyanamide and decanoate), were selected to evaluate the influence of the type of anion on ion-pair formation. Also, the IL tributyl(methyl)phosphonium methylsulphate was tested. The performance of PILs was compared with that shown by a conventional ion-pairing agent, named cetyltrimethylammonium bromide (CTAB). The ion-pair formed between the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex and the selected PIL was extracted into a minimal volume of organic solvent, followed by As detection with the ETAAS technique.

## 2 Materials and methods

### 2.1 Instrumentation

The measurements were performed with a Perkin Elmer (Überlingen, Germany) Model 5100 ZL atomic absorption spectrometer equipped with a transversely heated graphite atomizer, an As Electrodeless Discharge Lamp (EDL), and a Zeeman-effect background correction system (conditions in Table 2). All measurements were made based on absorbance

Table 2 ETAAS instrumental and experimental conditions for As determination by the proposed LLME method

Wavelength	193.7 nm			
Spectral band width	0.7 nm			
Lamp (EDL) current	300 mA			
Injection volume	80 $\mu\text{L}$			
Matrix modifier	10 $\mu\text{g}$ Mg [ $\text{Mg}(\text{NO}_3)_2$ ] 10 $\mu\text{g}$ Pd [ $\text{Pd}(\text{NO}_3)_2$ ]			
Graphite furnace temperature program				
Step	$T$ ( $^{\circ}\text{C}$ )	Ramp time (s)	Hold time (s)	Argon flow ( $\text{mL min}^{-1}$ )
Drying 1	110	15	30	250
Drying 2	130	15	15	250
Pyrolysis 1	600	15	20	250
Pyrolysis 2	1300	10	20	250
Atomization	2300	0	3	0
Cleaning	2400	1	2	250
Optimal LLME conditions				
Working pH	1.0			
Sample volume	5.0 mL			
Mo concentration	0.084 $\text{mol L}^{-1}$			
PIL concentration	$3.4 \times 10^{-4}$ $\text{mol L}^{-1}$			
PIL used	Tetradecyl(trihexyl)phosphonium dicyanamide			
Extraction solvent	Tetrachloroethylene			
$\text{NaClO}_4$ concentration	0.5% (w/v)			
Temperature	30 $^{\circ}\text{C}$			
Heating time	5 min			
Stirring time	3 min			
Centrifugation time	5 min			

Table 1 Physicochemical properties of the PILs studied in this work<sup>20</sup>

Chemical name	Abbreviation	Density (25 $^{\circ}\text{C}$ ) ( $\text{g cm}^{-3}$ )	Viscosity (25 $^{\circ}\text{C}$ ) (mPa s)	Physical state (25 $^{\circ}\text{C}$ )	Hydrophobic/hydrophilic	Miscibility
Tetradecyl(trihexyl)phosphonium decanoate	PIL1	0.888	319	Liquid	Hydrophobic <sup>a</sup> (21%)	Non-polar/polar aprotic solvents
Tetradecyl(trihexyl)phosphonium dicyanamide	PIL2	0.898	256	Liquid	Hydrophobic <sup>a</sup> (3.1%)	Non-polar/polar aprotic solvents
Tributyl(methyl)phosphonium methylsulphate	PIL3	1.067	409	Solid	Hydrophilic	Polar solvents

<sup>a</sup> Maximum water capacity.

signals with an integration time of 3 s. A centrifuge (Luguimac, Buenos Aires, Argentina) model LC-15 was used to separate the phases during microextraction. A vortex model Bio Vortex B1 (Boeco, Hamburg, Germany) was used for mixing the reagents. A Horiba F-51 pH meter (Kyoto, Japan) was used for pH determination and a thermostated bath (Vicking, Buenos Aires, Argentina) model Masson Digital for heating and keeping the temperature stable. Also, an ultrasound bath (40 kHz and 600 W) with temperature control (Test Lab, Buenos Aires, Argentina) was employed.

## 2.2 Reagents

Stock standard solutions of inorganic As(v) and As(III) species 1000 mg L<sup>-1</sup> as sodium arsenate dibasic heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) (99.998%) (Sigma-Aldrich, Milwaukee, WI, USA) and sodium (meta)arsenite (NaAsO<sub>2</sub>) (99%) (Fluka, Buchs, Switzerland), respectively, were prepared in 0.1 mol L<sup>-1</sup> HCl. Disodium methylarsenate (CH<sub>3</sub>AsNa<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O) (MMA, 98%) (Fluka) and dimethylarsinic acid (C<sub>2</sub>H<sub>7</sub>AsO<sub>2</sub>) (DMA, 98.6%) (Fluka) stock standard solutions (1000 mg L<sup>-1</sup>) were prepared with ultrapure water and stored at 4 °C in amber-coloured HDPE bottles. Working solutions were prepared by diluting these stock solutions.

A 1000 mg L<sup>-1</sup> palladium nitrate solution [Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O] (Fluka) and 1000 mg L<sup>-1</sup> magnesium nitrate solution [Mg(NO<sub>3</sub>)<sub>2</sub>] (99%) (Merck, Darmstadt, Germany) were prepared and used as chemical modifiers (Table 2). These solutions were prepared in 0.1% (v/v) HNO<sub>3</sub> (Ultrex® II Mallinckrodt Baker, Phillipsburg, NJ, USA). A 15% (w/v) ammonium molybdate tetrahydrate (>99%) (Fluka) solution was prepared in ultrapure water. Hydrochloric acid (37% (w/w)), chloroform, trichloroethylene, tetrachloroethylene, dichloromethane, toluene and carbon tetrachloride were from Merck. Potassium peroxodisulfate (>99%) (Sigma-Aldrich) was used as the oxidant. A 0.075 mol L<sup>-1</sup> cetyltrimethylammonium bromide (99%) (Merck) solution was prepared in ultrapure water. Tetradecyl(triethyl) phosphonium decanoate (95%) (PIL1), tetradecyl(triethyl) phosphonium dicyanamide (95%) (PIL2) and tributyl(methyl) phosphonium methylsulphate (95%) (PIL3) were from Sigma-Aldrich. Diluted solutions at 0.085 mol L<sup>-1</sup> were prepared by weighing accurate amounts of each IL in toluene, with the exception of (PIL3) that was prepared directly in ultrapure water. Sodium perchlorate monohydrated (>99%) (Merck) was employed to evaluate the effect of ionic strength. Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). All bottles for storing samples and standard solutions and the glassware were washed in 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> for 24 h and later rinsed with ultrapure water.

## 2.3 Sample collection and conditioning

Several types of water samples including tap water, river water, bottled mineral water and rainwater were analyzed in this work. For tap water sample collection, domestic water was allowed to run for 20 min and a volume of 1000 mL approximately was collected in a beaker. Tap water samples were analyzed

immediately after sampling. Bottled mineral water samples were obtained from a local store. Rainwater samples were collected during a rain episode occurred in Mendoza city (Argentina) in cleaned HNO<sub>3</sub>-washed HDPE bottles, rinsed three times with the sample prior to collection. River water was collected in amber bottles, filtered and kept at 4 °C until the analysis was performed. All samples were filtered with 0.45 μm pore size PTFE membrane filters (Millipore Corporation, Bedford, MA, USA).

## 2.4 General LLME procedure with phosphate interference elimination

For the development of the LLME procedure, 5 mL of water sample (or 1.5 μg L<sup>-1</sup> As(v) standard solution for optimization) were placed in a centrifugation tube along with 50 μL of 10 mol L<sup>-1</sup> HCl, 500 μL of a 0.12 mol L<sup>-1</sup> ammonium molybdate solution and 250 μL of 10% (w/v) NaClO<sub>4</sub>. The solutions were allowed to stand for 10 min at 30 °C to ensure the complete formation of the AsMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> complex. Then, 500 μL of 1-butanol:chloroform (1 : 3) were added to the sample solution and the mixture was stirred at constant vortex stirring for 3 min. The 1-butanol:chloroform organic phase extracts only the PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> complex (formed between phosphate and molybdate), but not AsMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>. After stirring, the sample solution was centrifuged at 1200 rpm during 5 min and the 1-butanol:chloroform organic phase was separated and discarded using a Pasteur transference pipette. The upper aqueous upper phase was added with 20 μL of 0.085 mol L<sup>-1</sup> PIL (prepared in toluene) and the resulting system was sonicated for 5 min in an ultrasonic bath. Finally, 80 μL of tetrachloroethylene (extraction solvent) were added to the sample solution. After 3 min of shaking time with a vortex, centrifugation at 1200 rpm for 5 min was applied for separation of the enriched phase. The upper aqueous phase was manually removed with a transfer pipette, and the PIL-containing enriched phase was directly injected into ETAAS for As determination under the conditions given in Table 2.

## 2.5 Determination of total inorganic As

Oxidation of As(III) to As(v) species was performed before the elimination of phosphate interference and the preconcentration step. A 5 mL-aliquot of water sample was treated with 0.5% (w/v) potassium peroxodisulfate solution at room temperature for 5 min and total inorganic As (now as As(v)) was determined as described earlier. Thus, the concentration of As(III) was obtained by the difference between total inorganic As and As(v) concentration. As(v) species was determined directly in the acidified sample according to the extraction procedure described in Section 2.4.

## 2.6 Determination of total As

Total As was determined over another 5 mL-aliquot of water sample by means of a strong oxidation with a 0.5% (w/v) potassium peroxodisulfate solution at 90 °C for 30 min. After the oxidation process, the samples were treated as mentioned in Section 2.4 for As(v) determination. Finally, the total

concentration of organic As species was obtained by the difference between total As and total inorganic As concentration.

### 3 Results and discussion

#### 3.1 ETAAS conditions for As determination in PIL-containing matrices

In order to obtain Gaussian-shape peaks for As determination in the presence of the organic extraction phase, pyrolysis and atomization temperatures of the graphite furnace program were initially optimized. The effect of matrix modifiers was evaluated to reduce spectral interference and increase analytical accuracy. These initial studies were performed over a  $100 \mu\text{g L}^{-1}$  As(v) standard solution prepared in chloroform with 10% (w/v) of each PIL. A volume of  $40 \mu\text{L}$  of the prepared solution was injected into the graphite furnace after addition of  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Pd}(\text{NO}_3)_2$  used as matrix modifiers. Different mass ratios of these matrix modifiers were evaluated:  $2.5 \mu\text{g Mg} + 2.5 \mu\text{g Pd}$ ,  $5.0 \mu\text{g Mg} + 5.0 \mu\text{g Pd}$  and  $10 \mu\text{g Mg} + 10 \mu\text{g Pd}$ . Optimal signals were obtained with the  $10 \mu\text{g Mg} + 10 \mu\text{g Pd}$  mass ratio. The selected matrix modifiers contributed significantly to obtain high sensitivity and Gaussian-shape absorbance peaks, with a reduction of the background signal.

The influence of pyrolysis temperature on As absorbance was studied in detail within a range of  $600$  to  $800 \text{ }^\circ\text{C}$  (pyrolysis step 1) and  $1000$  to  $1400 \text{ }^\circ\text{C}$  (pyrolysis step 2). The optimum pyrolysis temperatures were  $600 \text{ }^\circ\text{C}$  and  $1300 \text{ }^\circ\text{C}$ , respectively. Once the pyrolysis temperatures were selected, the effect of atomization temperature on As absorbance was studied in the range of  $2100$  to  $2300 \text{ }^\circ\text{C}$ . The optimum atomization temperature was  $2300 \text{ }^\circ\text{C}$ . With this temperature program was possible to obtain well-defined peaks with good reproducibility, even in the presence of the matrix provided by the organic extraction phase. Moreover, these conditions for As determination by ETAAS were also confirmed when the highest sensitivity was obtained under the final LLME conditions discussed later in this work.

#### 3.2 Formation of the arsenomolybdate complex and ion-pairing reaction with PILs

Initially, the Mo : As molar ratio was evaluated in order to ensure the total formation of the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex. Therefore, the following Mo : As molar ratios were assayed:  $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5$  and  $4.2 \times 10^6$ . The  $4.2 \times 10^6$  Mo : As molar ratio was chosen as it ensured the formation of the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion. In fact, the need of high Mo : As molar ratios for complete formation of the complex has been already reported in previous studies:  $7.6 \times 10^4$ ,<sup>21</sup>  $9.0 \times 10^6$ ,<sup>22</sup>  $2.5 \times 10^5$ .<sup>23</sup> Likewise, it is well known that arsenate and molybdate anions form a stable and negatively charged complex  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  under acidic conditions. Consequently, the pH is a very important factor to form the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex. When molybdate is in acidic medium, a polymerization process occurs until the  $\text{Mo}_7\text{O}_{24}^{6-}$  anion is obtained. This process occurs in the pH range of 1.0 to 6.5 under different polymerization degrees of Mo. When this polymer is formed, As(v) is included inside its

structure, forming the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion. Only As(v) forms the molybdoheteropoly acid and As(III) remains inert. Once the heteropoly acid is formed it is stable, but it can dissociate in a neutral solution. Thus, an appropriate pH value must be chosen to keep the complex stable. Moreover, it has been found that the extraction of heteropoly acid compounds in organic solvents is influenced by pH.<sup>24</sup> In this work, the pH was evaluated changing the concentration of HCl from  $0.05$  to  $2.0 \text{ mol L}^{-1}$ . The results showed that the highest extraction of As was obtained with  $0.1 \text{ mol L}^{-1}$  HCl (Fig. 1) for each PIL studied. Analyte extraction was 17%, 53%, 65% and 80% for CTAB, PIL1, PIL2 and PIL3, respectively. On the other hand, As extraction decreased for HCl concentrations higher than  $0.1 \text{ mol L}^{-1}$ . This behavior could be attributed to the higher protonation of  $\text{AsO}_4^{3-}$  at lower pH, thus inhibiting the formation of the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex.<sup>25</sup>

It has been established that the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion is able to form ion-pairs with different positively charged species.<sup>26</sup> Likewise, it has been demonstrated that ILS have high capacity for ion exchange and ion-pairing reactions.<sup>27</sup> In fact, in a previous study done by our group, the IL tetradecyl(trihexyl) phosphonium chloride was used for ion-pairing reaction with the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion.<sup>8</sup> In this work, other PILs (PIL1, PIL2 and PIL3) were evaluated. The extraction efficiency achieved with these reagents was compared with that obtained with a common ion-pairing agent such as CTAB, in an attempt to understand the mechanisms involved in ion-pair formation with PILs. Thus, considering that the ion-pair is formed with the phosphonium counterpart, PIL concentration was evaluated in the range of  $1.5 \times 10^{-4}$  to  $3.0 \times 10^{-3} \text{ mol L}^{-1}$ . As shown in Fig. 2, the best results were obtained with  $3.4 \times 10^{-4} \text{ mol L}^{-1}$  for each PIL studied in this work. The analyte extraction decreased for IL concentrations beyond  $3.4 \times 10^{-4} \text{ mol L}^{-1}$ . On the other hand, when the CTAB concentration was increased, no significant changes were observed in As(v) extraction efficiency.

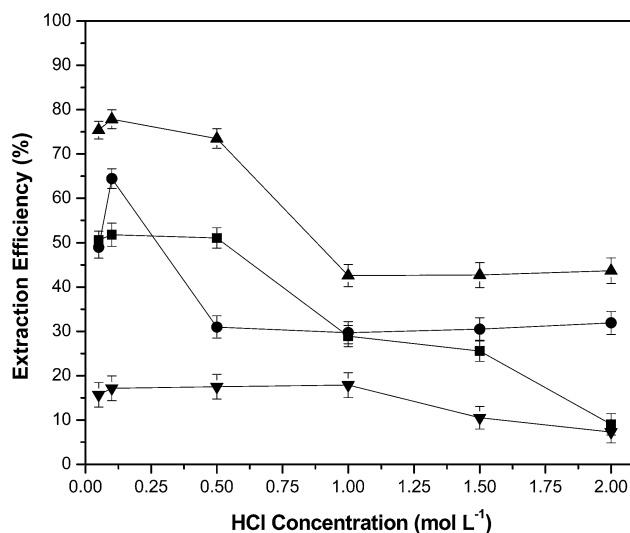


Fig. 1 Influence of HCl concentration on the extraction efficiency of As(v) using (▲) PIL3, (●) PIL2, (■) PIL1 and (▼) CTAB as ion-pairing agents. Experiments were done at  $25 \text{ }^\circ\text{C}$ . Other conditions were as mentioned in Table 1.

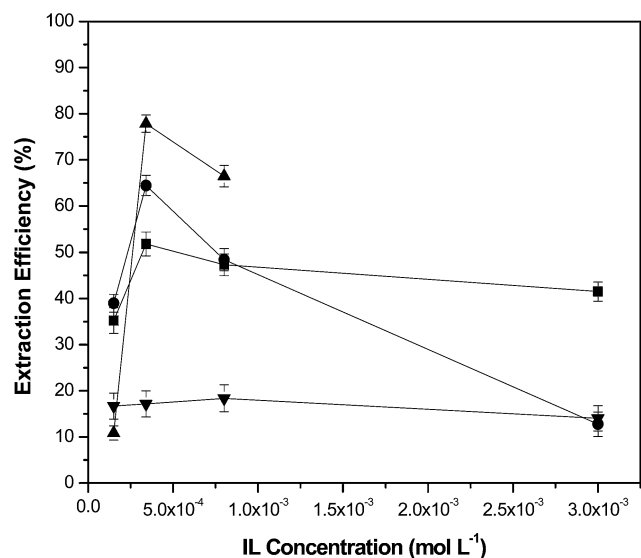


Fig. 2 Effect of the concentration of (▲) PIL3, (●) PIL2, (■) PIL1 and (▼) CTAB on ion-pair formation and extraction of As(v) with the developed LLME method. Temperature of experiments was set up to 25 °C and HCl concentration was 0.1 mol L<sup>-1</sup>. Other conditions were as detailed in Table 1.

Although CTAB is more soluble than PILs, meaning that a higher concentration of cations would be expected in solution for the ion-pairing reaction, the extraction efficiency was lower with CTAB. This could be attributed to the capability of PILs to form stronger ion-pairs with the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion than that formed with CTAB. Thus, the high localization of the positive charge occurring in PIL cations compared to the CTAB cation would lead to a stronger attraction between PIL cations and the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion.

It has to be pointed out that PIL1 and PIL2 contain the same cation but differ in the anion. Interestingly, the highest extraction efficiency was obtained with the PIL containing the smallest anion. This was the case of dicyanamide –  $\text{N}(\text{CN}_2)^-$  (PIL2 with 66% As extraction) with respect to decanoate  $\text{C}_9\text{H}_{19}\text{COO}^-$  (PIL1 with 51% As extraction). At this point of our study the highest extraction efficiency was achieved with PIL3. This is possible due to the large solubility of PIL3 as compared to those of PIL1 and PIL2, which ensures a higher concentration of PIL3 cations in solution for ion-pair formation. Moreover, PIL3 contains the smallest cation among the PILs studied; hence, the ion-pair formation with PIL3 would be favored if steric effects are considered. Consequently, two factors could influence the ion-pair formation between PILs and the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion: the solubility in water and the size of the PIL cation. Finally, a concentration of  $3.4 \times 10^{-4}$  mol L<sup>-1</sup> IL was chosen for further studies.

The effect of temperature on the formation of the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex was also evaluated in this work. In order to explore a possible influence of the temperature on complex formation, and hence, on the extraction efficiency too, the following temperatures were evaluated: 20, 30, 50, 70 and 90 °C. Tubes containing As(v) and ammonium molybdate solutions

were stirred and placed in a thermostated bath for 5 min. The tubes were cooled down in an ice-water bath and the LLME procedure described in Section 2.4 was developed. The results showed that the highest As extraction efficiencies for each PIL assayed as the ion-pair agent were obtained at 30 °C. At this temperature, As extraction efficiencies were 85%, 81% and 70% for PIL3, PIL2 and PIL1, respectively.

### 3.3 Influence of the extraction solvent

Molybdenum heteropoly acids can be partially extracted into organic solvents containing oxygen atoms, such as ethers, ketones, alcohols, aldehydes and esters. However, they are not extracted in solvents not containing oxygen atoms which are very useful for LLME procedures, such as carbon tetrachloride or chloroform.<sup>24</sup> On the other hand, the formation of ion-pairs with PILs could make feasible the efficient extraction of the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex in several solvents, because the polarity of the ion-pair formed is expected to be lower than that of the complex. In order to evaluate the influence of the extraction solvent, five different solvents were assayed including, chloroform, trichloroethylene, tetrachloroethylene, dichloromethane and carbon tetrachloride. These solvents were chosen considering that density and solubility in water could be appropriate for LLME. The solvent density must be high enough to allow its separation from the aqueous phase after the centrifugation step. Furthermore, the solubility in water must be very low in order to extract the less polar species and to avoid losses of the extraction phase by dissolution in the aqueous medium. The solubility in water of the solvents under study is as follows: 1.8 g 100 mL<sup>-1</sup> (dichloromethane) > 0.8 g 100 mL<sup>-1</sup> (chloroform) > 0.1 g 100 mL<sup>-1</sup> (trichloroethylene) > 0.08 g 100 mL<sup>-1</sup> (carbon tetrachloride) > 0.015 g 100 mL<sup>-1</sup> (tetrachloroethylene). The efficiencies of ion-pair formation and the different extraction processes were evaluated for each solvent–PIL combination. Specific results were obtained depending on the type of PIL and solvent. Therefore, according to the results shown in Fig. 3(a), the highest extraction efficiencies were: 80% (chloroform) for PIL3, 100% (tetrachloroethylene) for PIL2 and 52% (chloroform) for PIL1. Furthermore, in the case of PILs sharing the same cation (PIL1 and PIL2), the highest extraction efficiency was obtained with the less soluble solvent and the highest soluble IL in water. The combination of the above-mentioned factors determines the formation of the ion-pair between PILs and the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  complex, it is favored when the more polar PIL is chosen, while maximum extraction efficiency is obtained with the solvent that is less soluble in water. On the other hand, ion-pairs formed with less polar PILs could be better extracted in organic solvents. As a result medium polarity PIL2 with tetrachloroethylene was the best combination to obtain the highest extraction efficiency with the proposed LLME method.

The extraction phase volume is a critical parameter since it affects the extraction efficiency and the enhancement factor. The effect of tetrachloroethylene volume was evaluated between 30 and 200  $\mu\text{L}$ . Recoveries for different extraction volumes of tetrachloroethylene are shown in Fig. 3(b). The highest

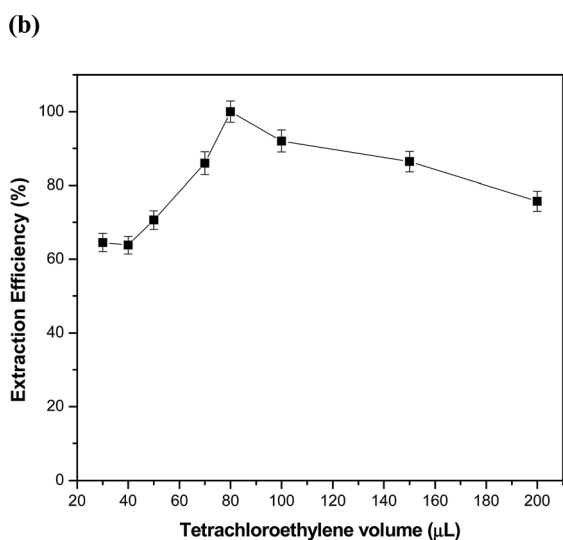
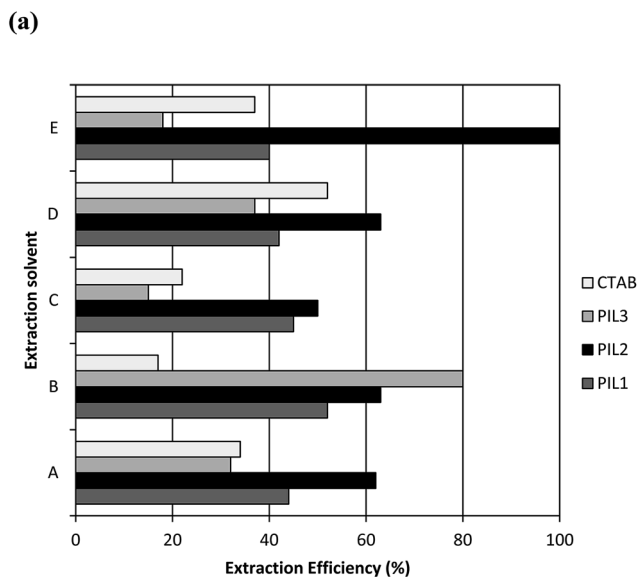


Fig. 3 (a) Extraction performance of different solvents at optimum extraction conditions and (b) effect of tetrachloroethylene volume on As(v) extraction. (A) Dichloromethane, (B) chloroform, (C) trichloroethylene, (D) carbon tetrachloride, (E) tetrachloroethylene. The optimized conditions are detailed in Table 1.

extraction efficiency was obtained with 80 μL. Extraction volumes as low as 30 μL were not sufficient to form a biphasic system due to partial solubilization of tetrachloroethylene in the aqueous media. On the other hand, extraction volumes as high as 200 μL exceeded the maximum volume allowed for sample introduction into the graphite furnace of ETAAS. Thus, a tetrachloroethylene volume of 80 μL was selected for further development.

### 3.4 Effect of ultrasound on the microextraction process

Ultrasound has been used in LLME for several purposes, including analyte mass transfer from aqueous phase to organic phase by decreasing the equilibrium time and the enhancement

of the extraction efficiency.<sup>28</sup> Due to these reasons, it was decided to evaluate the effect of ultrasound both on the ion-pair formation with PILs and their extraction into the organic solvent phase. It was found that 5 min of ultrasound was the minimal time required during ion-pair formation to obtain the highest extraction efficiency. The extraction efficiency increased from 51% (with vortex stirring) up to 62% for PIL1 when ultrasound was applied. Likewise, extraction efficiency with PL2 increased from 64% up to 92%. The results indicate that ultrasound really speeds up the formation of ion-pairs by increasing the chances of interactions between PIL cations and the  $\text{AsMo}_{12}\text{O}_{40}^{3-}$  anion in solution. Moreover, three ultrasound times were evaluated for the extraction step: 1, 3 and 5 min. However, the use of ultrasound did not show significant differences with respect to the extraction efficiency achieved with 3 min of vortex stirring. Therefore, 5 min of ultrasound for the ion-pair formation step and 3 min of vortex stirring for the extraction step with the organic solvent were applied in this study.

### 3.5 Ionic strength evaluation

The effect of the ionic strength on LLME efficiency was evaluated by preparing solutions with concentrations of  $\text{NaClO}_4$  within the range of 0.5–5% (w/v). Fig. 4 shows the variation of As extraction efficiency when the ionic strength was modified in the sample solutions. For PILs containing the same cation, *i.e.*, tetradecyl(trihexyl)phosphonium, the extraction behavior was very similar. The highest extraction efficiency (100%) was achieved with PIL2 at 0.5% (w/v)  $\text{NaClO}_4$  followed by a marked decrease. On the other hand, the extraction efficiency was almost constant for PIL3 up to 3% (w/v)  $\text{NaClO}_4$ , with a slight decrease after that concentration. Similar results have been reported for other IL-DLLME systems.<sup>29–31</sup> Finally, the ionic

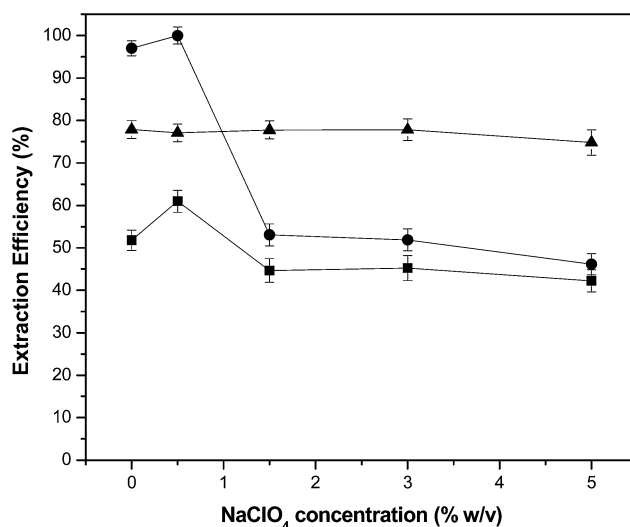


Fig. 4 Effect of ionic strength on As(v) extraction efficiency upon (▲) PIL3, (●) PIL2 and (■) PIL1 assayed in this work. Other conditions were as mentioned in Table 1.

strength was adjusted with 0.5% (w/v) NaClO<sub>4</sub> for the LLME procedure.

### 3.6 Effect of sample volume on As microextraction

Sample volume is an important variable since it affects the frequency of analysis, the preconcentration factor and the consumption index of preconcentration methods. Therefore, the effect of sample volume on analyte extraction was evaluated for three different volumes: 5, 10 and 15 mL. The results showed that a sample volume of 5 mL was optimum for analysis. When the volume was higher than 5 mL, the extraction efficiency of the analyte decreased significantly due to the change caused in analyte distribution as a consequence of a higher aqueous-to-organic solvent volume ratio. Therefore, a volume of 5 mL of sample was selected.

### 3.7 Study of potential interference

The effect of potential interference that might occur in the samples under study was evaluated in this work. Ions commonly present in water samples, *i.e.*, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>, were included in this study. Therefore, the influence of these ions on As determination and detection was evaluated using a 1.5 μg L<sup>-1</sup> As(v) standard solution containing different concomitant ions in the concentrations at which they usually occur in water samples. A concomitant ion was considered to interfere when an analytical signal variation of ±5% was observed. With the exception of PO<sub>4</sub><sup>3-</sup>, it was found that none of the ions caused interference up to 100 mg L<sup>-1</sup>. However, in the case of PO<sub>4</sub><sup>3-</sup>, a strong interference effect was observed for concentrations from 1 mg L<sup>-1</sup>. Analyte extraction decreased from 100% to 60% and 10% with 5 and 500 mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>, respectively. This interference effect can be explained by the formation of a Keggin-type polyoxometalate (PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>) between the PO<sub>4</sub><sup>3-</sup> anion and molybdate under the same conditions that AsMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> is formed.<sup>32</sup> In order to eliminate the interference caused by PO<sub>4</sub><sup>3-</sup>, a procedure for selective extraction of the PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> complex using a 1-butanol-chloroform (1 : 3) mixture was followed before the preconcentration step.<sup>33</sup> The solvent mixture permitted the selective extraction of PO<sub>4</sub><sup>3-</sup>, while As(v) remained in the aqueous sample solution for the preconcentration step. By this procedure, As(v) was fully recovered and PO<sub>4</sub><sup>3-</sup> was tolerated even at concentrations as high as 5 mg L<sup>-1</sup>. Moreover, As(III), MMA(v) and DMA(v) species do not form anionic complexes with the molybdate anion and they were not extracted into the 1-butanol:chloroform phase.

### 3.8 Analytical performance

Since the best results were obtained when PIL2 was used as the ion-pairing agent, this IL was applied for LLME development to determine As and its species in water samples. Under the optimized conditions mentioned in Table 2, a calibration linear range was obtained for As concentrations up to 4 μg L<sup>-1</sup>. The detection limit (LOD), calculated based on the signal at intercept and three times the standard deviation of the calibration curve, was 1.9 ng L<sup>-1</sup>. The relative standard deviation (RSD) for

six replicate measurements of 1.0 μg L<sup>-1</sup> As was 4.9%, 5.0% and 5.1% for As(v), As(III) and total As organic species, respectively.

Furthermore, the analytical sensitivity for As determination was enhanced by a factor of 130. The enhancement factor was obtained from the ratio of the calibration curve slopes for As(v) with and without application of the extraction/preconcentration step. The calibration curve without preconcentration was obtained by direct injection of As(v) standard solutions at different concentrations into ETAAS. The extraction recovery (ER%) or extraction efficiency was calculated using the following equation:

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

where  $m_{IL\text{phase}}$  is the final mass of the analyte in the final organic phase and  $m_{aq}$  is the initial mass in the aqueous phase.  $C_{IL\text{phase}}$  and  $C_{aq}$  are the final and the initial As concentrations respectively.  $V_{IL\text{phase}}$  and  $V_{aq}$  are the final and the initial volume of the organic and aqueous phases, respectively.<sup>34</sup> The extraction efficiency under the optimal conditions was 100%. Also, the consumption index (CI) is an important parameter for the characterization of a preconcentration analytical methodology. It can be described by the following equation:

$$CI = \frac{V_s}{EF}$$

where  $V_s$  is the volume of sample in mL consumed to achieve the EF value.<sup>35</sup> The CI obtained for the proposed methodology was 38 μL. Regarding the frequency of analysis, the whole preconcentration procedure lasts for 22 min per individual sample including complex formation, ion-pair formation, vortex stirring, centrifugation, phase separation and measurement by ETAAS. However, since it is possible to treat as many samples as can be placed in the centrifugation equipment, the real frequency of analysis was at least 40 samples per hour based on the centrifugation equipment used in this work.

Finally, a comparison of the proposed method with others reported for preconcentration of As is shown in Table 3. The developed methodology has a LOD that is comparable or better than other methods reported for As determination in water samples. Moreover, the frequency of analysis was superior too. Therefore, the proposed method can be considered as a fast and high performance alternative for As speciation analysis, bringing remarkable analytical advantages, such as low detection limits and high sample throughput.

### 3.9 Validation study and determination of As species in water samples

For the validation study, the developed LLME method was applied to a standard reference material (SRM), natural water NIST SRM 1643e "Trace elements in water", with a declared As concentration of 60.45 ± 0.72 μg L<sup>-1</sup>. The SRM was submitted to the same procedure developed for PO<sub>4</sub><sup>3-</sup> elimination from sample solutions. Since the certified concentration value in the SRM was higher than the upper limit of the linear range

Table 3 Comparison of the developed methodology with others reported for As species determination in water by ETAAS<sup>c</sup>

Method	IL	Speciation analysis	LOD (ng L <sup>-1</sup> )	EF	RSD (%)	Sample volume (mL)	Calibration range (μg L <sup>-1</sup> )	Analysis frequency (h <sup>-1</sup> )	CI (μL)	Ref.
DSLLME-ETAAS	<sup>a</sup>	Yes	20	135	5.3	5	0.08–2.0	20	37	37
SPE-HG-ETAAS	<sup>a</sup>	Yes	1.0	38	6.3	2	0.01–0.5	6	53	38
IL-DLLME-ETAAS	[BMIM][NTf <sub>2</sub> ]	Yes	13	255	4.9	5	0.1–7.5	<sup>b</sup>	19	39
IL-DLLME-ETAAS	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	Yes	10	135	6.5	27	0.05–0.4	<sup>b</sup>	200	40
SPE-ETAAS	<sup>a</sup>	Yes	20	250	3.5	50	0.03–0.6	<sup>b</sup>	200	41
IL-DLLME-ETAAS	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	Yes	10	208	4.6	10	0.025–1.0	<sup>b</sup>	24	16
IL-LLME-ETAAS	[P <sub>6,6,6,14</sub> ][Cl]	Yes	2.0	125	4.1	5	0.01–3.8	30	40	8
SPE-HGAAS	<sup>a</sup>	Yes	11.0	35	2.4	250	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	10
CP-HGAAS	<sup>a</sup>	Yes	12.0	25	3.1	50	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	12
CP-ETAAS	<sup>a</sup>	Yes	50.0	75	4.3	2	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	13
IL-LLME-ETAAS	[P <sub>6,6,6,14</sub> ][dca]	Yes	1.92	130	4.9	5	0.01–4.0	40	38	This work

<sup>a</sup> IL not used. <sup>b</sup> Not reported. <sup>c</sup> DSLLME: dispersive-solidification liquid–liquid microextraction; IL-DLLME: ionic liquid dispersive-liquid–liquid microextraction; SPE: solid phase extraction; CP: coprecipitation; [BMIM][NTf<sub>2</sub>]: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide; [C<sub>6</sub>MIM][PF<sub>6</sub>]: 1-hexyl-3-methylimidazolium hexafluorophosphate; [P<sub>6,6,6,14</sub>][Cl]: trihexyl(tetradecyl)phosphonium chloride; [P<sub>6,6,6,14</sub>][dca]: trihexyl(tetradecyl)phosphonium dicyanamide.

Table 4 Determination of As species in water samples and analyte recovery study (95% confidence interval; *n* = 6) with the optimized methodology

Sample	As(v)			As(III)			OrgAs		
	Added (μg L <sup>-1</sup> )	Found μg L <sup>-1</sup>	Recovery <sup>b</sup> (%)	Added (μg L <sup>-1</sup> )	Found (μg L <sup>-1</sup> )	Recovery <sup>b</sup> (%)	Added (μg L <sup>-1</sup> )	Found (μg L <sup>-1</sup> )	Recovery <sup>b</sup> (%)
Bottle water	0	0.06 ± 0.01 <sup>a</sup>	—	0	<LOD <sup>a</sup>	—	0	<LOD <sup>a</sup>	—
	0.5	0.57 ± 0.03	102	0.5	0.49 ± 0.03	98	0.5	0.48 ± 0.03	96
	1	1.03 ± 0.08	97	1	0.99 ± 0.05	99	1	0.94 ± 0.05	94
Rain water	0	<LOD <sup>a</sup>	—	0	<LOD <sup>a</sup>	—	0	<LOD <sup>a</sup>	—
	0.5	0.48 ± 0.03	96	0.5	0.46 ± 0.04	92	0.5	0.52 ± 0.04	104
	1	0.93 ± 0.05	93	1	0.97 ± 0.05	97	1	0.95 ± 0.06	95
River water 1	0	3.20 ± 0.16 <sup>a</sup>	—	0	1.60 ± 0.08 <sup>a</sup>	—	0	<LOD <sup>a</sup>	—
	0.5	3.74 ± 0.17	108	0.5	2.13 ± 0.12	106	0.5	0.47 ± 0.04	94
	1	4.16 ± 0.20	96	1	2.62 ± 0.13	102	1	1.02 ± 0.06	102
River water 2	0	4.70 ± 0.25 <sup>a</sup>	—	0	2.40 ± 0.13 <sup>a</sup>	—	0	<LOD <sup>a</sup>	—
	0.5	5.22 ± 0.27	104	0.5	2.87 ± 0.15	94	0.5	0.51 ± 0.03	102
	1	5.73 ± 0.30	103	1	3.39 ± 0.21	99	1	0.93 ± 0.05	93
Tap water	0	0.08 ± 0.01 <sup>a</sup>	—	0	<LOD <sup>a</sup>	—	0	<LOD <sup>a</sup>	—
	0.5	0.54 ± 0.04	92	0.5	0.53 ± 0.03	106	0.5	0.47 ± 0.04	94
	1	1.09 ± 0.06	101	1	0.94 ± 0.05	94	1	1.09 ± 0.06	109

<sup>a</sup> Initial concentration. <sup>b</sup> 100 × [(found – initial)/added].

achieved by the proposed methodology, a 120-fold dilution was made before the analysis. Using the methodology developed in this work, As concentration was found to be 60.38 ± 0.95 μg L<sup>-1</sup>. This result did not indicate a significant difference for a value of *p* < 0.01.

Finally, the proposed method was applied to different kinds of water as it is indicated in Table 4. The results showed that concentrations were under 10 μg L<sup>-1</sup> As, which is accepted as

the maximum residual level for drinking water by WHO.<sup>36</sup> The recovery percentages were close to 100% in bottle water and rain water. The concentrations were in the range of <LOD–4.7 μg L<sup>-1</sup> for As(v), <LOD–2.4 μg L<sup>-1</sup> for As(III) and <LOD for As-organic species. Our results were in good agreement with those previously reported by other authors for water samples with similar matrices.<sup>37–39</sup>



## 4 Conclusions

The capabilities of different PILs as ion-pairing agents have been studied in this work. Our results demonstrate the great potential that PILs have for LLME due to the high extraction efficiencies achieved with PILs compared to other common ion-pairing agents, such as CTAB. Since the positive charge of cations is not delocalized in their molecules, stronger ion-pair interactions can be expected to occur with PILs. Moreover, the influence of cation structure of the PIL chosen to develop the LLME method should be considered, as steric effects might regulate ion-pairing mechanisms. Therefore, the performance of PILs in LLME would be defined by the formation of strong and low polar ion-pairs which can be efficiently extracted from aqueous sample solutions into a finely dispersed organic solvent.

The application of PILs as ion-pairing agents has allowed the development of a novel LLME method with ETAAS detection for As speciation analysis in water samples. Arsenate was selectively complexed with the molybdate anion, followed by ion-pairing reaction with PILs and extraction of the formed ion-pair into a few microliters of an organic solvent. The sample treatment with a 1-butanol : chloroform mixture eliminated a possible interference effect caused by the presence of phosphate in the samples. After optimization of the method, a 100% extraction efficiency and 130-fold sensitivity enhancement factor were obtained with PIL2 and only 5 mL of sample. Finally, the LLME method was successfully applied for As speciation analysis in different water samples and it can be considered as an interference-free, cost-effective and environmentally friendly alternative, due to the low volume of sample and reagents required for the analysis.

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