Ionic liquid as ion-pairing reagent for liquid–liquid microextraction and preconcentration of arsenic species in natural waters followed by ETAAS

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A simple and highly efficient microextraction methodology was developed for arsenate [As(v)], arsenite [As(iii)] and organic arsenic (*i.e.*, DMA and MMA) preconcentration and determination based on the novel use of tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) as an ion-pairing reagent. As(v) species was selectively separated by forming As(v)-molybdate heteropoly acid [As(v)-MHPA] complex with molybdenum, followed by ion-pairing reaction with CYPHOS® IL 101 and microextraction in chloroform. Arsenic detection was performed by electrothermal atomic absorption spectrometry (ETAAS). Under optimum conditions, the analyte extraction efficiency was 99% and yielded a preconcentration factor of 125 with only 5.00 mL of sample. The detection limit was 0.002 μg L^{-1} as As(v). The relative standard deviation (RSD) for six replicate measurements at 1.5 μg L^{-1} of As were 4.1%, 4.9% and 5.0% for As(v), As(iii) and total organoarsenicals, respectively. The proposed methodology was successfully applied for As speciation analysis in several types of water samples.

Introduction

Arsenic has a complex chemistry,[1,2] mobility and toxicity in environmental and biological systems, which are strongly dependant on chemical nature of its species.[3] Therefore, the sole evaluation of total arsenic concentration in a sample does not fulfil our understanding about the toxicological risk of this element in environmental and biological studies. Thus, speciation analysis of arsenic becomes highly necessary.[4]

A number of hyphenated techniques, involving chromatography coupled to elemental detectors, have been used for determination of arsenic species. Likewise, non-chromatographic techniques based on different approaches involving, solid phase extraction (SPE),[5] liquid–liquid extraction (LLE) with organic solvents,[6] ion pair-SPE, *etc.*,[7] have also been employed for arsenic species separation and preconcentration. However, some disadvantages arise from the application of this class of techniques, such as large volumes of toxic and expensive solvents, complex equipment, large volume of wastes and reduced frequency of analysis.[8] On the other hand, liquid–liquid microextraction techniques (LLME) effectively overcome these difficulties by reducing organic solvent consumption as well as allowing sample extraction and preconcentration to be performed in a simple and single step.[9]

Recently, the use of modern solvents known as ionic liquids (ILs), which are composed entirely of ions (anions and cations) and remain liquid over a wide range of temperatures, has become an attractive tool for developing novel separation procedures.[10] Since arsenate species could selectively react with molybdate ions to form As(v)-molybdate heteropoly acid [As(v)-MHPA] complex, this yellow compound has been used in the past for colorimetric determination of arsenic in water samples.[11] Moreover, the capabilities of this charged complex as an ion-pairing reagent have been studied.[12]

The aim of this work was the development of a novel analytical methodology based on environmental benign solvents, such as ILs, for simple and highly selective determination of As species. Tetradecyl(trihexyl)phosphonium chloride ionic liquid (CYPHOS® IL 101) was assessed for ion-pairing with As(v)-MPHA complex. The method was designed to distinguish between inorganic As(v) and As(iii), from organic arsenic species. The effect of experimental parameters on LLME efficiency such as, As(v) complexation with MHPA reagent, ion-pair formation, including type and volume of solvent, volume of ILs, acidity, salt addition and extraction time were studied and optimized. The proposed method was particularly useful for obtaining information about arsenic speciation in water samples of different origins.

Experimental

Instrumentation and reagents

The measurements were performed with a Perkin Elmer (Uberlingen, 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 1). Stock standard solutions of As(v), As(iii), DMA and MMA were prepared as previously described.[4] CYPHOS® IL 101 was kindly donated by Prof. Ullastiina Hakala (University of Helsinki, Finland) and supplied by CYTEC (Canada). A solution containing 15% (w/v) $(NH_4)_6Mo_7O_{24}$. $4H_2O$ >99% (Fluka, Buchs,

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Table 1 ETAAS conditions for As determination in IL-enriched phase

Instrumental				
Wavelength				193.7 nm
Spectral band width				0.7 nm
Lamp (EDL) current				300 mA
Injection (manual) volume				40 μL
Matrix modifier				5 μg $Pd(NO_3)_2$ 3 μg $Mg(NO_3)_2$
Graphite furnace temperature program				
Step	*T*/°C	Ramp Time/s	Hold Time/s	Argon flow rate/mL min^{-1}
Drying	110	1	30	250
Drying	130	15	30	250
Pyrolysis	600	10	10	250
Pyrolysis	800	5	10	250
Atomization	2300	0	3	—
Cleaning	2400	1	2	250

Switzerland) was prepared. Hydrochloric acid and chloroform from Merck (Darmstadt, Germany) were used. Potassium peroxodisulfate >99% (Sigma-Aldrich, Milwaukee, WI, USA) was used as oxidant.

Sample collection and conditioning

For tap water sampling, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a beaker. Bottled mineral water was a commercial product. River, sea and groundwater samples were collected in cleaned bottles rinsed three times with ultrapure water prior to collection. All samples were filtered through acid cleaned 0.22-μm pore size membrane filters (Millipore Corporation, Bedford, MA, USA) and analyzed within 24 h.

Extraction and determination of As(v) species

A volume of 5 mL of sample, or standard solution containing 1.5 μg L^{-1} of As(v), was placed in a 10 mL graduated glass centrifuge tube with 50 μL hydrochloric acid (37% w/w), 500 μL 0.12 mol L^{-1} $(NH_4)_6Mo_7O_{24}$ and 10 μL 10% (v/v) CYPHOS® IL 101 (in chloroform) solution. The mixture was shaken for 1 min. The resulting homogenous solution was added with 80 μL of chloroform and shaken for 2.5 min, forming a cloudy solution that was centrifuged at 900 rpm (136 × g) for 5 min. After this process, the organic phase containing CYPHOS® IL 101–As(v)-MHPA ion pair is observed at the bottom of conical test tube while the upper aqueous phase was removed with a transfer pipette. The final organic phase (~40 μL) was manually injected with a syringe into the graphite tube of ETAAS instrument (full conditions in Table 1). Calibration was performed against aqueous standards submitted to the same preconcentration procedure. Likewise, blank solutions were analyzed in the same manner as standard and sample solutions.

Extraction and determination of total inorganic As species

Specific oxidation of As(III) to As(v) species was performed following the procedure described by Hata *et al.*,[13] with a slight modification. A volume of 50 mL of sample solution was placed in a digestion flask adds and dissolves 0.25 g of $K_2S_2O_8$ to oxidize arsenite to arsenate. Thus, oxidation occurs immediately after dissolving the oxidizing agent. No heating should be applied in order to avoid As-containing organic species to be oxidized too. Total inorganic As was determined by following the same procedure indicated above for As(v) species.

Extraction and determination of total arsenic

A 50 mL-volume of sample was added to 0.25 g potassium peroxydisulfate in a digestion flask and kept boiling on a heating plate for 30 min. After complete oxidation, total arsenic concentration was evaluated by following the same procedure as described for As(v) species.

Results and discussion

Study on As detection by ETAAS in IL-containing matrix

In this work, arsenic was determined in the presence of the IL organic matrix by direct injection of that phase into the graphite furnace of ETAAS instrument. It is widely known that trace element detection by ETAAS in an organic-rich phase can carry some drawbacks if sufficient matrix elimination is not achieved. Therefore, pyrolysis and atomization temperatures were carefully optimized in order to obtain the highest absorbance-to-background signal ratio. Two modifiers, $Pd(NO_3)_2$ and $Mg(NO_3)_2$, were investigated. The matrix modifier made significant contribution to obtain high sensitivity, sharp and well defined absorption peaks and a reduced background. This was obtained by injecting 3 μg $Mg(NO_3)_2$ and 5 μg $Pd(NO_3)_2$ into the graphite furnace. Finally, all analyte measurements were performed with this mixture. Optimal pyrolysis and atomization temperatures were 800 °C and 2300 °C, respectively (Table 1).

Formation of As(v)-molybdate heteropoly acid

In this work, the reaction between As(v) and molybdate ion is proposed as an attractive tool to reduce polarity of As(v) species due to higher size-to-charge ratio of As(v)-MHPA formed. Thus, the separation of As species by the LLME procedure involved previous formation of As(v)-MHPA. Different variables that typically could influence As(v)-MHPA formation, *i.e.* pH, acid concentration, molybdate concentration, and salt addition, were studied. The concentration and type of acid plays an important role on heteropoly acid formation and subsequent extraction.[14] The formation of As(v)-MHPA complex was studied using nitric acid and hydrochloric acid within a range of 0.1 to 2 mol L^{-1}. The optimal results were achieved when 0.1 mol L^{-1} HCl was used for conditioning the medium. Molybdenum concentration was studied within an interval of 1.35×10^{-5} to 1.35×10^{-2} mol L^{-1}. The lowest molybdenum concentration for total As(v) reaction was 1.35×10^{-3} mol L^{-1} and no further changes were observed at higher values. These results were similar to those reported by Wadelin and Mellon[11] and Sounderajan *et al.*[6]

Role of Investigation of ion-pairing capabilities of CYPHOS® IL 101 in the microextraction procedure

The choice of CYPHOS® IL 101 was motivated by its reduced solubility in aqueous medium, which could strongly determine a high volume ratio between sample solution and extractant phase. The studies involved the extraction of As(v)-MHPA by the sole application of CYPHOS® IL 101. However, significantly high IL volumes were required to develop the procedure with limited extraction efficiency (~50%). A different role of CYPHOS® IL 101 on As(v)-MHPA extraction was considered based on possible ion-pairing reaction of phosphonium-containing salts and surfactants with some anions.[15,16] Therefore, our experiments were focused on evaluating ion-pairing capabilities of IL followed by extraction of As(v)-MHPA-CYPHOS® IL 101 ion pair with a common organic solvent, such as chloroform.

In ion pair extractions, concentration of ion pairing reagent plays an important role, because it affects the distribution of counter ions, therefore influencing the extraction efficiency.[17] Different amounts of CYPHOS® IL 101 were tested, while maintaining constant the other parameters. The experiments were performed varying the amount of the IL in 5 mL of a 1.5 μg L^{-1} As(v) standard solution. The study of CYPHOS® IL 101 amount was not only useful for evaluating ion pair formation, but also to determine a possible increment of background levels during ETAAS measurements. The effect of CYPHOS® IL 101 amount on analyte absorption is shown in Fig. 1 along with the background level observed for each case. Arsenic absorption increased when CYPHOS® IL 101 amount was varied from 0.5 to 20 μL, and it remained constant at higher volumes. A background increase was observed for high amounts of the IL as a consequence of major amounts of organic material injected into the graphite tube of ETAAS instrument. The best results were observed when 1 μL of CYPHOS® IL 101 was used. Thus, As(v)-MHPA-CYPHOS® IL 101 molar ratio was 1 : 30, which represents a 10-fold molar excess of the IL as compared to the minimal theoretical ratio (1 : 3) needed to form the ion pair. The reason for this could be attributed to the fact that equilibrium displacement towards total ion pair formation occurs when an excess of IL is in solution.

Selection of type and volume of extraction solvent

The selection of extraction solvent was made based on higher density than water, good extraction capability of compounds and relatively low solubility in aqueous medium. Chloroform, carbon tetrachloride and trichloroethylene were compared in this methodology. A series of sample solutions with and without CYPHOS® IL 101 were assayed using 100 μL of each extraction solvent. Poor analyte recoveries (~20%) were observed when CYPHOS® IL 101 was not added to sample solutions. On the other hand, As recovery was significantly enhanced when CYPHOS® IL 101 was present (79%, 72% and 94% for trichloroethylene, carbon tetrachloride and chloroform, respectively). Therefore, the above results demonstrate that CYPHOS® IL 101 is needed to form a hydrophobic ion pair with As(v)-MHPA, which is subsequently extracted into a microvolume of solvent. Chloroform was selected for the next experiments.

The volume of the extractant phase is critical in LLME procedures as it conditions both extraction efficiency and enrichment factor. The minimal volume of extractant was investigated within a range of 30–200 μL of chloroform. As shown in Fig. 2, the final volume of chloroform was lower than the initial one, which was attributed to its partial solubility in aqueous medium. In fact, an approximately linear relationship between these two magnitudes was observed. On the other hand, the variation of As recovery with extractant volume did not follow a linear behavior and the highest recovery was observed for 80 μL of chloroform. Extractant volumes lower than 30 μL were not suitable due to total solubilization of chloroform in aqueous medium. Therefore, the addition of 80 μL of chloroform was very convenient not only to achieve optimal extraction efficiency, but also to perform a one-step injection of analyte into the graphite tube as the final phase volume was about 40 μL. The addition of more than 80 μL of chloroform, and since the injection volume was kept constant at 40 μL, led to lower sensitivity due to dilution effect caused by this solvent.

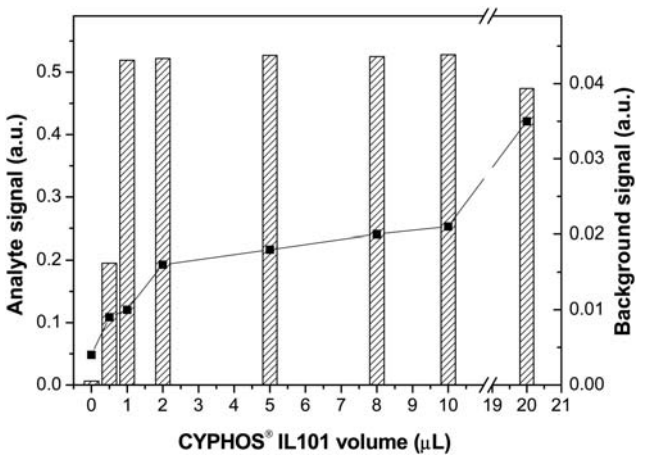

Fig. 1 Effect of CYPHOS® IL 101 amount on (▨) As recovery and (■) background level. Other conditions were as shown in Experimental section.

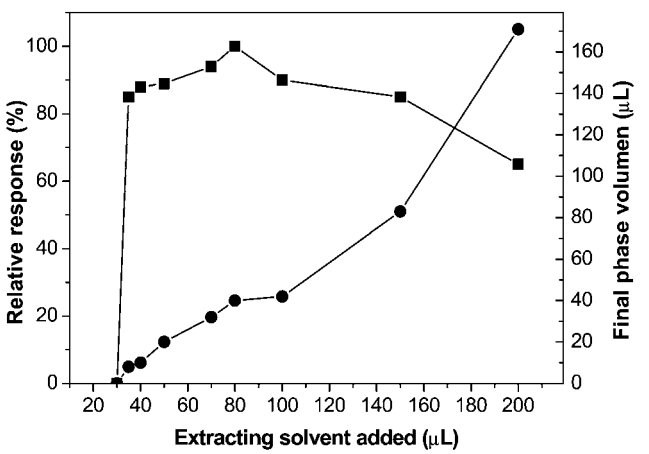

Fig. 2 Evaluation of extractant solvent volume on As recovery (■). Resulting final volume of extractant phase is also indicated (●). Other conditions were as shown in Experimental section.

Time-dependant processes during As species microextraction

Different mechanical approaches were evaluated for efficiently mixing sample solution and extractant phase. Thus, sonication and a vortex shaker were applied during 2.5 min. The highest recovery was achieved with vortex-based shaking rather than sonication.

The time involved during two different steps was evaluated: time for ion pair formation with the IL and extraction time with solvent. Therefore, three different approaches were evaluated: (1) shaking time after IL addition was varied (0.5–10 min) and shaking time after chloroform addition was constant (2 min); (2) shaking time for chloroform was changed and the one for IL was constant (1 min); and both, (3) IL and chloroform were added together shaking this mixture for different time. For first approach, the results showed that As(v)-MHPA-CYPHOS® IL 101 ion pair formation is a fast process as the highest and constant extraction efficiency was reached in only 1 min. The extraction time, involving addition of extractant solvent and complete phase separation, was studied in the range of 0.5 to 10 min. A minimal extraction time of 2.5 min was thus required. Moreover, simultaneous addition of IL and chloroform before shaking the system led to the longest time for the process (10 min).

Influence of ionic strength and potential interfering species

Ionic strength effect was studied with sodium chloride as a salting out agent. No effects on the enrichment factor and analyte recovery were observed within 0–5% (w/v) interval.

To study potential interferences, several anions and cations at the concentration levels at which they may occur in the samples under study, were added to a 1.5 μg L^{-1} As solution and the procedure was followed as described early. Analyte recovery was not influenced by Fe^{3+}, Cd^{2+}, Ca^{2+}, Mn^{2+}, Na^{+}, K^{+} and Mg^{2+} cations [between 150 and 15 000-fold concentration (in μg L^{-1}) higher than that of As(v)]. Other elements, such as V, Cr, Si, Sn and Sb, could react with molybdate ions to form molybdate heteropoly acid complexes. However, these elements are normally present at low concentrations in water samples. Thus, an excess of molybdate was used to effectively form the heteropoly complex with As(v) (As/Mo molar ratio = 10^5) yielding a quantitative extraction [at least 500-fold concentration (in μg L^{-1}) higher than that of As(v)]. Anions, such as Cl^{-}, NO_3^{-} and SO_4^{2-} [between 1500 and 25 000-fold concentration (in μg L^{-1}) higher than that of As(v)] did not cause any adverse effects on analytical signal. The value of the reagent blank signal was not modified by the presence of potentially interfering ions. Chloroform is not expected to cause interferences on As absorption signal as it is removed during drying step in ETAAS measurement.[18]

Phosphate was tolerated up to 4.5 mg L^{-1} without significantly changing As recovery. However, higher concentrations of PO_4^{3-} ions could be easily tolerated by separating this interference from the sample with anion-exchange resins. In fact, other authors have reported the application of weakly basic anion exchangers (*e.g.* Dowex Marathon WBA) for selective separation of As(v) and PO_4^{3-} in the pH interval of 2 to 7.[19] Selectivity of the resin towards these anions decreases by increasing hydrated ionic radius.[20]

Analytical performance

The calibration graphs for ETAAS determination of As was linear at levels near the detection limit and up to at least 3.8 μg L^{-1}, with a correlation coefficient of 0.991. The limit of detection (LOD), calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve, was 0.002 μg L^{-1}. The relative standard deviation (RSD)

Table 2 Characteristic performance data obtained by using the proposed method and others reported for As determination in water samples

Method	Species	LOD/ng L^{-1}	RSD (%)	EF[a]	Sample volume/mL	Calibration range/μg L^{-1}	Analysis frequency/h^{-1}	CI/μL	Ref.
LLE-ETAAS	As/V; As(III)	200	0.4	20	200	5-100	44	10,000	6
SPE-ICP-OES[b]	As/V; As(III)	50	5.7	100	30	0.3–30	n.r.[c]	300	24
CPE[d]-ETAAS	As/V; As(III)	10	5	52.5	10	0.02–0.35	40	190	16
LLME-ETAAS	As/V; As(III); OrgAs	2.0	4.1	125	5	0.01–3.8	30	40	This work

[a] EF: calculated based on slope ratio of calibration graph after and before the microextraction procedure. [b] ICP-OES: Inductively coupled plasma optical emission spectrometry. [c] n.r.: Not reported. [d] CPE: Cloud point extraction.

Table 3 Analytical selectivity for inorganic As species determination (95% confidence interval, $n = 6$)

	As/V			As(III)		
As/V/As(III) ratio	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)[a]	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)[a]
20	3	2.99 ± 0.09	100	0.15	0.14 ± 0.01	93
2.5	1	0.98 ± 0.03	98	0.4	0.39 ± 0.02	97
1	1	1.00 ± 0.04	100	1	0.99 ± 0.04	99
0.5	1	0.99 ± 0.04	99	2	1.98 ± 0.07	99
0.05	0.15	0.14 ± 0.01	93	3	2.99 ± 0.09	100

[a] 100×(found/added).

Table 4 Results of As speciation analysis in water samples (95% confidence interval, $n = 6$)

	As/V			As(III)			OrgAs		
Sample	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)[b]	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)[b]	Added/μg L^{-1}	Found/μg L^{-1}	Recovery (%)[b]
Sea water	0	0.67 ± 0.03[a]	—	0	< 0.002	—	0	< 0.002	—
	1	1.68 ± 0.07	101	0.25	0.23 ± 0.02	94	0.25	0.24 ± 0.02	96
	2	2.61 ± 0.10	98	0.50	0.49 ± 0.04	97	0.50	0.50 ± 0.04	101
Bottle mineral water	0	0.11 ± 0.01[a]	—	0	< 0.002	—	0	< 0.002	—
	1	1.11 ± 0.05	100	0.25	0.24 ± 0.02	95	0.25	0.23 ± 0.02	94
	2	2.09 ± 0.08	99	0.50	0.50 ± 0.03	98	0.50	0.48 ± 0.04	96
Ground water	0	27.5 ± 1.0[a]	—	0	5.00 ± 0.39[a]	—	0	< 0.002	—
	1	27.6 ± 1.1	97	0.25	4.86 ± 0.37	93	0.25	0.24 ± 0.02	96
	2	29.5 ± 1.1	100	0.50	5.31 ± 0.40	97	0.50	0.49 ± 0.04	98
Tap water	0	1.10 ± 0.05[a]	—	0	< 0.002	—	0	< 0.002	—
	1	2.06 ± 0.09	98	0.25	0.24 ± 0.02	97	0.25	0.24 ± 0.02	95
	2	3.10 ± 0.13	100	0.50	0.50 ± 0.04	99	0.50	0.49 ± 0.04	97
River water	0	5.84 ± 0.23[a]	—	0	4.94 ± 0.38[a]	—	0	< 0.002	—
	1	6.57 ± 0.25	96	0.25	4.88 ± 0.37	94	0.25	0.24 ± 0.02	95
	2	7.60 ± 0.28	97	0.50	5.33 ± 0.40	98	0.50	0.49 ± 0.04	97

[a] Initial concentration. [b] 100 x [(found - initial)/added].

for six replicate measurements of the overall procedure applied to 1.5 μg L^{-1} of As was 4.1%, 4.9% and 5.0% for As(v), As(III) and As-organic species, respectively. The enrichment factor (EF) was obtained from the slope ratio of calibration graph after and before the microextraction procedure. An enrichment factor of 125 was obtained under optimum experimental conditions.

The extraction recovery (ER%) was calculated using eqn (1):

$$\mathrm{ER}\% = \frac{m_f}{m_0} = \frac{C_f \times V_f}{C_0 \times V_0} \times 100 \quad (1)$$

where m_f and m_0 are the mass of analyte in the final organic phase and the initial aqueous solution, respectively. Similarly, C_f and C_0 represents As concentration, while V_f and V_0 are the volumes of the phases involved.[21]

The extraction recovery was 99% under optimal conditions. Furthermore, the frequency of analysis was at least 30 samples per hour considering the possibility of treating as many samples as can be placed in the centrifugation equipment. 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 (Table 2). Our method presents a higher enrichment factor and lower detection limit than those methods developed for As preconcentration and determination in water samples. Moreover, a high enrichment factor was obtained with a reduced volume of sample.

Selectivity and determination of As species in different water samples

To assay the reliability of the proposed method several solutions containing As(v) and As(III) were analyzed by the LLME procedure. The results (Table 3) indicate that selective determination of As species at trace levels is feasible. A similar procedure was developed with As-organic species commonly found in water samples (MMA and DMA). The determination of total As was performed by initial oxidation of As-organic species to As(v). All results were compared with *t*-test and good recovery percentages were obtained. The accuracy of the proposed method was evaluated by analyzing a standard reference material, NIST SRM 1643e "Trace Elements in Water", with a reported As content of 60.45 ± 0.72 μg L^{-1}. Using the proposed methodology the total As content determined in this SRM was 60.39 ± 1.26 μg L^{-1}.

Finally, the proposed LLME methodology was applied for determining inorganic As species and total As-organic species in different types of water samples. The results are shown in Table 4. Concentration levels were in the range of 0.11–27.5 μg L^{-1} for As(v), <0.002–5.0 μg L^{-1} for As(III) and <0.002 μg L^{-1} for total As-organic species. The ground water and river water were diluted before analysis. Moreover, the levels observed in this work were not significantly different to those reported by Tuzen *et al.*[22] and Chamsaz *et al.*[23]

Conclusions

An efficient LLME method based on the novel application of the IL CYPHOS® IL 101, as an ion-pairing reagent, to determine As(III), As(v) and total As-organic species in several types of water samples, is presented in this work. Sensitive determination of As species was performed *via* separation and preconcentration of As(v)-MHPA-CYPHOS® IL 101 ion pair, which has been demonstrated is formed by this study. Our work shows the great potential that ILs have, not only for direct separation of elemental species, but also as real derivatizing agents for highly efficient extraction (~99%) and preconcentration. The LLME approach associated with ETAAS detection can be proposed as a low organic solvent consuming extraction technique, which turns it into a low cost and environmentally friendly tool for elemental speciation studies.

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