

## Speciation and Determination of Trace Amount of Inorganic Arsenic in Water, Environmental and Biological Samples

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A new speciation and preconcentration method based on dispersive liquid-liquid microextraction has been developed for trace amounts of As(III) and As(V) in urine and water samples. At pH 4, As(III) is complexed with ammoniumpyrrolidine dithiocarbamate and extracted into 1-Hexyl-3-methylimidazolium hexafluorophosphate, as an ionic liquid (IL) and As(III) is determined by electrothermal atomic absorption spectrometry (ETAAS). Arsenic(V) in the mixing solution containing As(III) and As(V) was reduced by using KI and ascorbic acid in HCl solution and then the procedure was applied to determination of total arsenic. Arsenic(V) was calculated as the difference between the total arsenic content and As(III) content. The effect of various parameters on the recovery of the arsenic ions has been studied. Under the optimum conditions, the enrichment factor 135 was obtained. The proposed method was successfully applied to the determination of trace amounts of As(III) and As(V) in water and biological samples.

**Keywords:** Arsenic; Speciation; Dispersive liquid-liquid microextraction; Ionic liquid.

### INTRODUCTION

Arsenic is well known to be poisonous to organisms; however, the toxic effect of arsenic is highly dependent on its chemical forms.<sup>1-3</sup> Arsenic is a ubiquitous element in the environment originating from natural sources (geologic formations, geothermal activity and vulcanic activity) as well as human activities. Major anthropogenic sources of arsenic include wood preservatives (chromated copper arsenate), agricultural uses (monosodium methane arsonate as pesticide and disodium methane arsonate as herbicide), industrial uses (a range of arsenicals in electrophotography, catalysts, pyrotechnics, antifouling paints, pharmaceutical substances), mining and smelting. Due to its natural and anthropogenic occurrence the entire population is exposed to (low levels of) arsenic through food, water and air. The majority of arsenic speciation studies have targeted both plants and fauna of marine origin, as they are known to accumulate arsenic to relatively high levels compared to other food sources. Fish and seafood are known to contribute to the majority of ingested arsenic (75%) although it generally only constitutes a small percentage (2%) of the daily dietary intake.<sup>4-6</sup>

It has been reported that the same metal ion may pos-

sess different toxicity in its different oxidation states which are responsible for their different physico-chemical and biological activities. This indicates that it is very important to be able to measure inorganic arsenic in water sensitively and reliably. Although the above mentioned risks do not distinguish between the toxic effects of the inorganic arsenic species arsenite As(III) and arsenate As(V) individually. It is important to note that the toxicity of As(III) is greater than the toxicity of As(V).<sup>7</sup>

The term speciation analysis has often been used to indicate the analytical activity of identifying chemical species and measuring their distribution. Sometimes, it is used to indicate that a method gives more information on the form in which the element is present than other more commonly applied techniques (e.g., measuring distinct organo-mercury compounds as opposed to a total mercury determination). Thus, in order to obtain the information on toxicity and biotransformation of elements in aquatic and biological systems, the speciation of metal ions is of great importance.<sup>8,9</sup>

Since the concentrations of arsenic species in water and real samples are very low, sensitive analytical techniques are required, and so high performance liquid chro-

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matography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS),<sup>10-13</sup> inductively coupled plasma mass spectrometry (ICP-MS),<sup>14,15</sup> colorimetric<sup>16</sup> inductively coupled plasma atomic emission spectrometry (ICP-AES),<sup>17,18</sup> hydride generation and atomic fluorescence spectrometry (HGAFS)<sup>19,20</sup> electrothermal atomic absorption spectrometry (ETAAS)<sup>21,22</sup> have been recommended for this purpose. Among them, ETAAS widely applied in food, water, environmental, geological and industrial samples is probably the most common technique used for low level concentrations of both species in beverages due to its availability, simplicity, high sensitivity, speed of analysis, and minimum sample preparation. In order to achieve accurate, sensitive and reliable results at trace levels with ETAAS, preconcentration and separation steps are required prior to analyte determination.

Recently, dispersive liquid-liquid microextraction has been developed as a new mode of liquid-phase microextraction and attracted increasing attention for its simple operation, high enrichment factor, rapidness, and high extraction efficiency.<sup>23</sup> 1-Hexyl-3-methylimidazolium hexafluorophosphate as an ionic liquid was used. Ionic liquids have high ion content, high ionic conductivity, low viscosity, nonvolatility, flame resistance, good solubility for inorganic and organic compounds and good extractability for organic compounds and metal ions. Due to these properties, ionic liquids are very important and green alternative to organic solvents in classical extraction techniques.<sup>24-26</sup>

The aim of this study is to combine dispersive liquid-liquid microextraction (DLLME) with ETAAS to develop a new procedure for the speciation analysis and determination of trace amount of As(III) and As(V) in urine and water samples. Ammonium pyrrolydinedithiocarbamate (APDC), a chelating agent which forms stable complexes with a number of metals and has found numerous applications in trace element separation and preconcentration methods,<sup>27-32</sup> is used to extract As(III) into the organic phase. The fact that As(V) does not react with APDC<sup>33-38</sup> allows determination of the inorganic trivalent and pentavalent forms of arsenic.

## EXPERIMENTAL

### Materials

All chemicals used in this study, were of analytical reagent grade and were used without further purification. Ultra-pure quality water produced by a Milli-Q system (Millipore, Bedford, USA) was used throughout. All the

plastic and glassware equipments were cleaned by soaking in dilute HNO<sub>3</sub> (1+9) and were rinsed with deionised water prior to use. Arsenic standard solutions were prepared from a stock solution of 1000 mg L<sup>-1</sup> in 2% nitric acid from Fluka Switzerland (No: 39436). A 1% ammonium pyrrolidine dithiocarbamate (APDC) solution using solid APDC purchased from Sigma was prepared daily in water. A buffer solution of 0.2 mol L<sup>-1</sup> sodium acetate (Merck, Darmstadt, Germany) was used to adjust the sample pH at 4. Octyl phenyl ether (TX-100), nitric acid, nickel nitrate as a chemical modifier and potassium iodide were purchased from Merck and 1-Hexyl-3-methylimidazolium hexafluorophosphate was purchased from Sigma.

### Apparatus

The experiments were performed using a graphite furnace atomic absorption spectrometer equipped with a pyrolytic graphite tube (GFAAS 3000, Dandenong, Victoria, Australia). A hollow cathode lamp operated at a current of 8 mA and a wavelength of 193.7 nm with a spectral band width of 1 nm and deuterium background corrector was applied. All experiments were performed using a sample volume of 20 µL, injected by autosampler of GFAAS. The instrumental parameters and temperature programs for the graphite atomizer are listed in Table 1. A pH meter, Metrohm E-744 Model (Herisau, Switzerland) glass electrode was employed for measuring pH values in the aqueous phase.

### Sample preparation

Tap water samples were collected from the K. N. Toosi University of Technology and contaminated wastewater samples were collected from Tehran petrochemical, Tehran, Iran. These samples were immediately acidified with 0.1% of concentrated HCl which provided a pH lower than 2.<sup>39</sup> The samples were then filtered in the laboratory using a 0.45 µm pore size membrane filter (Macherey-Nagel, PTFE) to remove suspended solids. Urine samples were collected in a plastic container and 0.35 mL of con-

Table 1. Furnace heating program

Steps	Temperature, °C	Hold, s	Ramp, s	Argon flow rate (mL min <sup>-1</sup> )
Drying	120	20	15	300
Ashing	800	20	40	300
Atomization	2300	3	2	0
Cleaning	2500	3	1	300

centrated  $\text{HNO}_3$  was added to acidify them. The urine samples were stored at  $4^\circ\text{C}$ .

### General procedure

In a recommended procedure 1 mL of 1% (w/w) APDC solution was added to 10 mL of sample solution containing As(III)/As(V) and adjusted pH to 4 with 1 mL buffer solution in a centrifuge tube. Then, the 0.06 g of 1-Hexyl-3-methylimidazolium hexafluorophosphate was also added to the mixture and it was shaken with a vortex. After 3 min arsenic(III) was efficiently extracted and preconcentrated as As-PDC complex in ionic liquid. In order to separate the phases, the turbid solution was centrifuged for 5 min at 4000 rpm. The aqueous phase was removed with a transfer pipette then added 200  $\mu\text{L}$  of strength nitric acid solution, shaken for 1 min, and transferred to conical polyethylene tube. Finally, the amount of arsenic in a 20  $\mu\text{L}$  aliquot of the resulting solution determined by ETAAS. After that arsenic(V) in the mixing solution was reduced to As(III). For reduction experiments the samples were prepared in  $1.0\text{ mol L}^{-1}$  of HCl. KI and ascorbic acid was added to get 1% concentration in the solution and allowed to react up to 60 min at room temperature, and then the procedure was applied to determination of total arsenic. The concentration of As(V) was calculated by subtracting the content of As(III) from total arsenic content.

## RESULTS AND DISCUSSION

### Optimization of instrumental conditions for ETAAS

It was reported that successful ashing and atomization conditions should be established in order to obtain reproducible and accurate results by ETAAS. In ET-AAS method sharp and well-defined signals with a reduced background were obtained in the presence of modifiers. Therefore, a mixture of 0.2 mg Ni( $\text{Ni}(\text{NO}_3)_2$ ) and 5 mg Triton-X100 for each measurement was used. Selecting an appropriate pyrolysis temperature for removing possible organic matters resulting from microextraction process in the IL phase while preventing the pyrolysis loss of As prior to the atomization process is very important. The influence of pyrolysis temperature on the absorbance was studied within a range of 500-1000  $^\circ\text{C}$  in the presence of nickel nitrate solution. The maximum absorbance was achieved at 800  $^\circ\text{C}$ . Therefore, 800  $^\circ\text{C}$  was selected as optimal pyrolysis temperature. The maximum signal was obtained at about 2300  $^\circ\text{C}$ . It is worth noting that argon flow rate was 300  $\text{mL min}^{-1}$ .

### Effect of pH

In view of the possibility of As chelation with APDC, this reagent was used to improve affinity of the metal for the ionic liquids phase. The complexation phenomenon is strongly conditioned by the pH of solutions and subsequently affects the extraction efficiency of the As-PDC complex. Therefore, the effect of pH on analyte complexation and extraction of As-APDC was studied in the pH range of 2–10. The results illustrated in Fig. 1 show that the highest extraction efficiency was achieved in pH 4. It is well known that pH of the sample solution plays a unique role on As-chelate formation and its subsequent extraction. At pH 4 As(V) does not react with APDC, so allows speciation of the inorganic trivalent and pentavalent forms of arsenic. In this study pH value of 4 was chosen for further experiments.

### Effect of APDC concentration

The effect of APDC concentration on the extraction of As(III) was studied and the results are presented in Fig. 2. As can be seen from Fig. 2 the extraction efficiency was stable when the APDC concentration was higher than 1.0%. Therefore, the concentration of 1% (w/w) APDC was selected for the further studies.

### Optimization of amount of IL and extraction time

The variation of extraction efficiency upon IL amount was examined within the range of (0.01-0.1 g). It was observed that the extraction efficiency of the system was remarkably affected by the IL amount. Quantitative extrac-

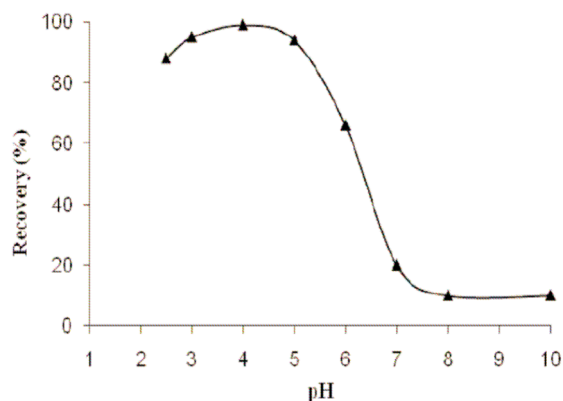


Fig. 1. Effect of pH on the recovery of arsenic. **Conditions:** Concentration of arsenic(III):  $100\text{ ng L}^{-1}$ ; amount of ionic liquid: 0.06 g; centrifugation rate: 4000 rpm; 1.0% (W/W) of APDC; sample volume: 10 mL;  $N = 3$ .

tion was observed for IL amount (1-Hexyl-3-methylimidazolium hexafluorophosphate) higher than 0.05 g. Therefore, in order to achieve a suitable pre-concentration, 0.06 g of ionic liquid was chosen as optimum leading to a final IL. The results are shown in Fig. 3. The effectiveness of As extraction under the influence of shaking and centrifugation time was studied. 3 min shaking and 5 min centrifuging (4000 rpm) were selected as optimum since complete separation occurred and no noticeable improvements on analyte extraction were observed for longer periods of time.

### Effect of sample volume

Sample volume is one of the most important parameters to be studied when real samples are analyzed by a pre-concentration technique, since it determines the sensitivity

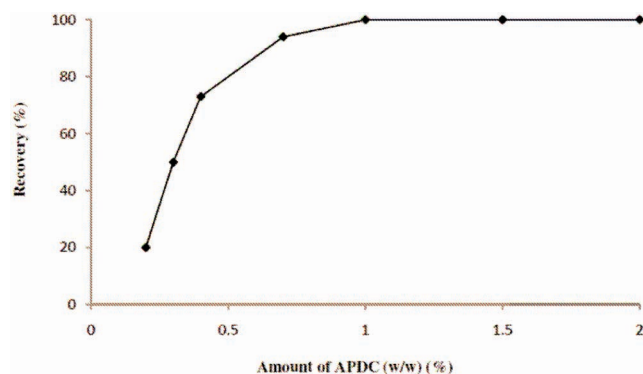


Fig. 2. The influence of APDC on the recovery of arsenic. **Conditions:** Concentration of arsenic (III):  $200 \text{ ng L}^{-1}$ ; amount of ionic liquid 0.06 g; centrifugation rate: 4000 rpm; pH = 4; sample volume: 10 mL; N = 3.

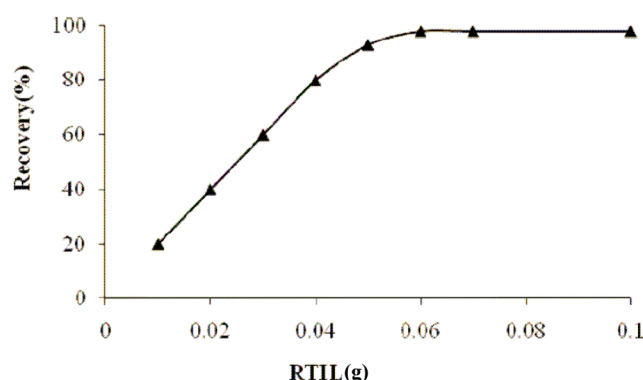


Fig. 3. The influence of amount of IL on the recovery of arsenic. **Conditions:** Concentration of arsenic(III):  $200 \text{ ng L}^{-1}$ ; 1.0% (W/W) of APDC; centrifugation rate: 4000 rpm; pH = 4; sample volume: 10 mL; N = 3.

enhancement of the method. The effect of sample volume was examined in a range of 5.0-40 mL for  $100 \text{ ng L}^{-1}$  As. It was found that the analyte could be recovered quantitatively when up to 25 mL of the sample solution was used. At higher volume the recoveries are decreased (Fig. 4). It was also noticed that higher sample volumes partially solubilized the RTIL phase, leading to non-reproducible results. Therefore the total sample volume of 27 mL can be used for pre-concentration procedure and the enrichment factor 135 was achieved.

### Analytical features

Under the optimum conditions, the calibration curve was found to be linear over the concentration  $50\text{-}400 \text{ ng L}^{-1}$  of arsenic. Peak area absorption signals were used for the calculation of the calibration curve and the precision of the method. The detection limit was found to be  $10 \text{ ng L}^{-1}$ . It was calculated by the 3s criterion, as the concentration that gives a response equivalent to three times the standard deviation (S.D.) of the blank ( $n = 12$ ). The pre-concentration factor was 135, considering the ratio of the sample volume to sample inject to ETAAS system. The relative standard deviation for  $80 \text{ ng L}^{-1}$  of arsenic was 6.5% ( $n = 12$ ).

### Interferences study

Generally, ammonium pyrrolidine dithiocarbamate is a chelating agent for many transition metals. Thus, interferences from coexisting ions should be considered. The effect of potential interferents occurring in environmental water samples on the determination of arsenic were tested using the optimized pre-concentration system. The recovery of  $60 \text{ ng L}^{-1}$  of arsenic was tested with individual interfer-

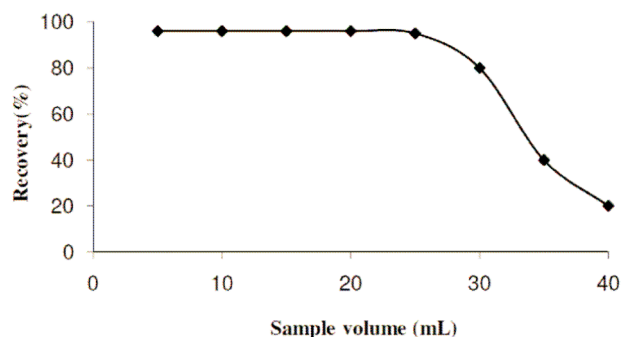


Fig. 4. The influence of sample volume on the recovery of arsenic. **Conditions:** Concentration of arsenic(III):  $100 \text{ ng L}^{-1}$ ; 1.0% (W/W) of APDC; amount of ionic liquid 0.06 g; centrifugation rate: 4000 rpm; pH = 4; N = 3.



ences added. Taking as criterion for interference the deviation of the recovery more than  $\pm 4\%$ , the obtained results showed that many ions such as  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{V}^{3+}$  could be tolerated up to at least  $2000 \mu\text{g L}^{-1}$ . High concentrations of alkali and alkaline earth metals, which are usually found in natural water, were tested.  $\text{K}^+$  up to  $3 \text{ g L}^{-1}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  up to  $2 \text{ g L}^{-1}$  and  $\text{NaCl}$  up to  $10 \text{ g L}^{-1}$  did not cause any interference.

### Application of the method

Results showed that there are no interferences from major constituents of water samples and interferences of transition metal ions; therefore we have explored feasibility of the proposed method for the determination of arsenic species in different matrices. Since no standard reference material with certified values for As(III) and As(V) are currently available, the spiked tap water, urine and waste water were prepared to demonstrate the reliability of the method for determination of As(III) and As(V). The results for this study are presented in Table 2. The recovery of spiked samples is satisfactory and was confirmed using addition method, which indicate the capability of the system in the determination of total arsenic in real samples (Table 3).

### Comparison with other methods

The comparative data from some recent studies on the determination of arsenic by the various techniques for the figure of the merits are summarized in Table 4. The detection limit and the enrichment factor of analyte ions are superior to those of preconcentration techniques. In addition, in the proposed method there is no need to use any toxic extraction solvent as dichloromethane, chloroform and carbon tetrachloride. If the selectivity of the proposed method

Table 2. Results of determination of As (III) and As (V)

Sample	Added ( $\text{ng L}^{-1}$ )		Found ( $\text{ng L}^{-1}$ ), n=3		Recovery (%)	
	As (III)	As (V)	As (III)	As (V)	As (III)	As (V)
Wastewater	-----	-----	$134.1 \pm 0.20$	$51.2 \pm 0.65$	----	-----
	60	-----	$191.5 \pm 0.91$	$52.1 \pm 1.10$	96	101
	-----	75	$131.2 \pm 0.31$	$121.7 \pm 1.52$	98	94
Wastewater	-----	-----	$187.4 \pm 0.83$	$45.8 \pm 0.55$	----	-----
	100	-----	$284.3 \pm 0.98$	$43.4 \pm 0.65$	97	95
	-----	70	$179.8 \pm 0.94$	$112.8 \pm 3.21$	96	96
Urine	-----	-----	$93.7 \pm 0.72$	$26.6 \pm 0.68$	-----	-----
	80	-----	$169.5 \pm 2.76$	$27.1 \pm 1.20$	95	102
	-----	50	$92.8 \pm 2.32$	$73.4 \pm 3.28$	99	94

Table 3. Experimental recovery of total arsenic determinations by proposed method in spiked real samples

Sample	Added ( $\text{ng/L}$ )	Found <sup>a</sup> ( $\text{ng/L}$ )	Recovery (%)
Tap water <sup>b</sup>	-----	$49 \pm 0.6$	-
	50	$101 \pm 0.5$	104
	100	$144 \pm 0.8$	95
Waste water <sup>c</sup>	----	$98 \pm 0.4$	-
	100	$197 \pm 0.8$	99
	200	$301 \pm 1.0$	101
Urine sample	----	$68 \pm 0.7$	-
	50	$116 \pm 0.7$	96
	100	$163 \pm 0.8$	95

<sup>a</sup> Mean of five determinations  $\pm$  confidence interval ( $P = 0.95$ ).

<sup>b</sup> Collected at the K. N. Toosi University of Technology.

<sup>c</sup> Tehran petrochemical wastewater

Table 4. Comparison of reported method with present method

Technique	Enrichment factor	Detection limit ( $\text{ng L}^{-1}$ )	Reference
Cloud point extraction	53	10	40
Liquid chromatography	200	150	41
Liquid phase microextraction	150	50	42
Dispersive liquid-liquid microextraction	115	10	43
Solid phase extraction	35	11	44
Dispersive liquid-liquid microextraction	135	10	This work

is compared with the previously published papers, it is obviously seen that the matrix effects with the method were reasonably tolerable by the comparison some other preconcentration techniques in literature.

### CONCLUSION

The procedure here studied takes advantage of the combination of a very simple, reliable way of preconcentrating urine and water samples for arsenic determination and speciation with the sensitive, widely available ETAAS technique. The increase in sensitivity resulting from sample preconcentration, together with the low consumption of organic solvents and possibility of speciation of the trivalent and pentavalent inorganic forms of these analytes, means the procedure can be considered an alternative to ICP-MS, since it can be used in practically all laboratories. We have highlighted the importance of arsenic speciation in studies of water chemistry due to the presence of arsenic species As(III) and As(V) with distinct toxicity. With the proposed procedures, satisfactory results of the analysis of

arsenic species in urine and water samples were obtained. The results of this study showed that the proposed method to be accurate, precise and time efficient, as just a very simple sample treatment is required.

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