



Preconcentration and speciation of arsenic in water specimens by the combination of solidification of floating drop microextraction and electrothermal atomic absorption spectrometry

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ABSTRACT

A simple solidification of floating drop microextraction procedure for preconcentration and speciation of trace amounts of As(III) and As(V) in water samples has been proposed prior to electrothermal atomic absorption spectrometry (ETAAS). In this method, a free microdroplet of organic solvent is floated on the surface of aqueous solution while being agitated by a stirring bar placed on the bottom of the sample vial. The determination of As(III) was achieved by selective formation of the As(III)–pyrrolidine dithiocarbamate complex in the presence of 0.1 M HCl while As(V) forms a weak complex with the ligand in the same pH conditions. Total inorganic As(III, V) was extracted similarly after reduction of As(V) to As(III) with potassium iodide and sodium thiosulfate and As(V) concentration was calculated by difference. Pd(NO₃)₂ was used as a chemical modifier in ETAAS. Some important extraction parameters such as the type of organic solvent, solvent volume, sample stirring rate, sample solution temperature, salt addition and the exposure time on the extraction recovery were investigated and optimized. Under the optimized extraction conditions, the detection limit of 9.2 pg mL⁻¹ and suitable precision (RSD < 8.6%), along with enhancement factor of 1000 for As were achieved. The developed method was applied successfully to speciation of As(III), As(V) and determination of the total amount of As in water samples.

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1. Introduction

Arsenic contamination in our natural water supply is a worldwide problem and has become a challenge for the world's scientists. The presence of it in natural water is related to the process of leaching from the arsenic containing source rocks and sediments [1].

Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [2]. This element occurs in the natural environment in four oxidation states: As(V), As(III), As(0) and As(–III). The mobility and toxicity of arsenic are determined by its oxidation state [3]. Regarding inorganic arsenic, As(III) is appreciably more toxic than As(V) [4]. Therefore, the development of sensitive and accurate methods for speciation and preconcentration of trace amounts of As(III) and As(V) is necessary. Up to now, a battery of analytical techniques has been employed in determination of the low concentration levels of As, such as the electrothermal vaporization

inductively coupled plasma mass spectrometry [5], electrothermal atomic absorption spectroscopy [6–8], hydride generation-atomic absorption spectroscopy [9] and hydride generation-atomic fluorescence spectrometry [10,11]. As well as a number of hyphenated techniques for arsenic speciation, such as ion chromatography coupled with hydride generation-inductively coupled plasma atomic emission spectrometry [12,13], ion chromatography [14,15] or high-performance liquid chromatography [16] coupled to inductively coupled plasma mass spectrometry were reported.

Liquid-phase microextraction (LPME) has emerged in these last years as a powerful tool for preconcentration and matrix separation prior to detection. It is a simple, inexpensive, fast and effective pretreatment technique [17,18]. However, it should be noted that the overwhelming majority of research works done on LPME have been concentrated on the analysis of organic analytes yet their potential for preconcentration of inorganic analytes has been recognized [19–21]. The importance of arsenic detection is a well-recognized fact that is emphasized by the extensive studies carried out in this area, as illustrated in a recent issue of *Spectrochimica Acta part B* (Vol. 64 (1), 2009) entirely dedicated to miniaturized preconcentration methods for ultra-trace analysis of inorganic elements such as As [22–24].

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Nowadays, a new mode of liquid-phase microextraction (LPME) named solidification of floating drop microextraction (SFDME) has been proposed as a high-performance, powerful, rapid and inexpensive microextraction method [25,26]. In this technique, some microliters of the suitable organic solvent (the organic solvent must have a melting point near room temperature in the range of 10–30 °C) are delivered to the surface of the solution containing analytes and solution is stirred for a desired time. Then sample vial is cooled by inserting it into an ice bath for 5 min. The solidified organic solvent is transferred into a suitable vial and melted; then, a fraction of it is injected into an analysis instrument.

The aim of this work is to develop the SFDME combined with the electrothermal atomic absorption spectrometry for the speciation and determination of trace amounts of As(III) and As(V) in water samples. The main parameters influencing the extraction efficiency such as the type of organic solvent, solvent volume, sample stirring rate, sample solution temperature, salt addition and the exposure time were investigated and optimized.

2. Experimental

2.1. Reagents and standard solutions

A stock standard As(III) solution (1.0 mg mL⁻¹) was prepared by dissolving 0.1320 g As₂O₃ (Merck, Darmstadt, Germany) in the appropriate amounts of KOH (Merck). The solution was diluted to 100 mL with ultrapure water. Ultrapure water used was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

As(V) stock standard solution (1.0 mg mL⁻¹) was prepared from Na₂HAsO₄·7H₂O (Merck). Working standard solutions were obtained by step dilution of the stock standard solution. Ammonium pyrrolidine dithiocarbamate (APDC) was obtained from Merck and its working solution (1300 mg L⁻¹) was prepared by dissolving appropriate amounts of this reagent in ethanol (Merck). The organic extractant was 1-undecanol (Merck). The pH was adjusted with 0.1 mol L⁻¹ hydrochloric acid solution before use. Sodium thiosulfate and potassium iodide (Merck) were added for the reduction of As(V) to the trivalent state in sample solutions in order to determine total As. A chemical modifier solution (500 mg L⁻¹) for ETAAS was prepared by diluting Pd (NO₃)₂ stock solution (10.0 ± 0.2 g L⁻¹, Merck) in ultrapure water.

2.2. Apparatus

2.2.1. Electrothermal atomic absorption spectrometry

Measurements were carried out on a GBC atomic absorption spectrometer (Avanta PM, Australia) equipped with a GF 3000 graphite furnace atomizer and a Pal 3000 furnace autosampler. Deuterium background correction was employed to correct non-specific absorbance. An arsenic hollow cathode lamp from GBC was employed as the radiation source and operated at 8 mA with a spectral bandwidth 1.0 nm. Integrated absorbance was used as signal in quantitative measurements. Aliquots of 10 µL of Pd modifier and 10 µL of sample and calibration solutions were directly injected into the graphite tube and submitted to the temperature program as shown in Table 1. Argon 99.999% (Roham Gas Co., Tehran, Iran) was used as a protected and purge gas at a flow-rate of 3.0 L min⁻¹.

2.2.2. Microextraction system

Stirring of the solution was carried out on a Heidolph MR 3001 K magnetic heater-stirrer (Kelheim, Germany) using a 12 mm × 4 mm stirring bar. A simple water bath placed on the heater-stirrer was employed to control the temperature of the sample solution. Two 25 µL microsyringes (Hamilton, Bonaduz, AG

Table 1
Instrumental parameters for As determination.

Spectrometer parameter				
Wavelength (nm)				193.7
Slit width (nm)				1.0
Lamp current (mA)				8.0
Step	Temperature (°C)	Time (s)	Gas flow (L min ⁻¹)	
			Ramp	Hold
Graphite atomizer				
Pre-warming	50	1	2	3.0
Inject step	Inject sample	–	–	3.0
Drying I	120	10	15	3.0
Drying II	400	20	10	3.0
Pyrolysis	1000	10	5	3.0
Gas stop step	1000	0	1	0
Atomization	2200	0.9	1.2	0
Cleaning	2600	1	2	3.0

Switzerland) were employed for the addition of the APDC solution and organic solvent into the sample solution.

2.3. Microextraction procedure

Into aliquots of 20 mL standard solution containing 1 µg L⁻¹ As(III) that was prepared by diluting the stock solution with HCl (0.1 mol L⁻¹), 50 µL of APDC (130 mg L⁻¹) was added and the resulted solution was kept in a water bath at 45 °C for 20 min while the stirrer was on. Then, 15 µL of the 1-undecanol as an organic solvent was placed on the surface of the sample solution by a microsyringe. The primary experimental results showed that 1-undecanol has the required conditions for the extraction of the analyte [25,26]. Therefore, 1-undecanol was selected as extraction solvent in the further studies.

As the sample solution flowed around the organic drop continuously, the trace chelated As with APDC, were extracted into the extraction solvent. After a desired period of extraction, the sample vial was placed into a beaker containing ice pieces and the organic solvent was solidified after 5 min. Then, the solidified solvent was transferred with a spatula into the conical vial and melted quickly at the room temperature. Finally, 10 µL of extractant plus 10 µL of Pd(NO₃)₂ as a chemical modifier was injected simultaneously into the graphite furnace tube by means of the autosampler.

Total inorganic As (As(III) and As(V)) was measured after reduction of As(V) with 1 mL of 1% (w/v) of sodium thiosulfate solution and 1 mL of 0.5% (w/v) of potassium iodide solution [27,28] and the concentration of As(V) was calculated by subtracting the As(III) concentration from the total As concentration. Calibration was performed against aqueous standards and subjected to the same SFDME procedure. A blank was prepared following the same procedure as described above, and then it was measured parallel to the samples and calibration solutions.

3. Results and discussion

3.1. Optimization of the graphite furnace heating program

Arsenic is one of the relatively volatile elements, so a certain loss of arsenic may occur during the ashing stage. To reduce interferences and to increase sensitivity and accuracy, the use of a chemical modifier has become indispensable for the stabilization of volatile elements during the pretreatment step [29]. In the present work, Pd(NO₃)₂ was used as the chemical modifier. According to many reports, the mechanism of palladium modifier activity involves the formation of PdAs. The palladium–arsenic compounds have melting points between the range of 900 and 1100 °C [30].

Also, the ramp and the time of the drying step were optimized to attain a smooth and complete evaporation/removal of the liquid part of each sample without sputtering. In the present work, the drying temperatures were set at 120 and 400 °C with the ramp mode for 10 and 20 s, respectively. The optimal pyrolysis (1000 °C) and atomization (2200 °C) temperatures were chosen mainly on the basis of the obtained signals.

3.2. Optimization of extraction conditions

The initial object was to optimize all the parameters which could affect and control the performance of As extraction from the aqueous samples. These included the concentration of HCl, the ligand to metal ratio, salt addition, stirring rate, temperature, organic solvent volume and the extraction time. The effects of each parameter on the extraction process were examined and the results are as follows.

3.2.1. Effect of acid concentration

The influence of the concentration of HCl on the selective extraction of As(III) was investigated (at the presence of APDC) in the range of 0.02–1 mol L⁻¹ (Fig. 1). It was found that the As(III) could be efficiently extracted into organic solvent when the HCl concentration was in the range of 0.05–0.2 mol L⁻¹. Similar results were reported in the research literature [31]. Thus 0.1 mol L⁻¹ HCl was then selected for the further studies.

3.2.2. Effect of amounts of APDC

The influence of the molar ratio of APDC to As(III) on the extraction efficiency of As(III) was also examined. It was found that the absorbance signal of As(III) increased with the increase of APDC to As(III) ratio of 0 to 25 (Fig. 1) and kept constant with further ratios. Thus molar ratio of 25 was then used in subsequent experiments.

3.2.3. Effect of salt addition

The extraction efficiency of As(III) as a function of NaCl concentration was investigated and the results are shown in Fig. 2. The extraction efficiency gradually increases (Fig. 2) as the salt concentration increases in the range of 0–4 mol L⁻¹. Thus, further extractions were carried out with a NaCl concentration of 4 mol L⁻¹.

3.2.4. Effect of stirring rate

Sample agitation is another important parameter having a great role in its ability to enhance extraction efficiency and to reduce extraction time [32,33]. In this extraction method, the stirring speed has a direct influence on both the shape of the droplet and the mass transfer characteristic in the aqueous sample. The effect

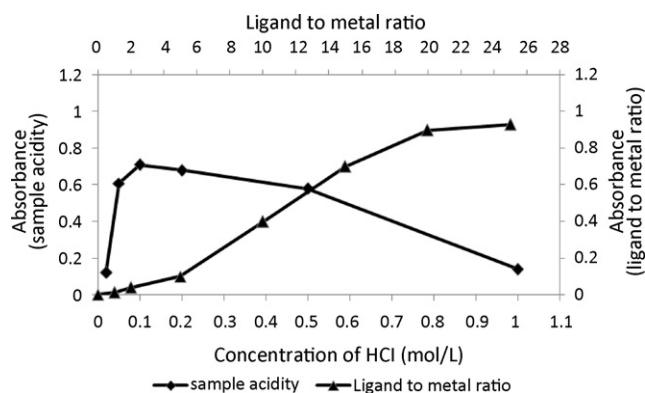


Fig. 1. Effect of HCl concentration and ligand to metal ratio on the extraction efficiency. Conditions: organic solvent volume, 10 μ L; sample volume, 20 mL containing 1 μ g L⁻¹ of analyte; extraction time, 30 min and without salt addition.

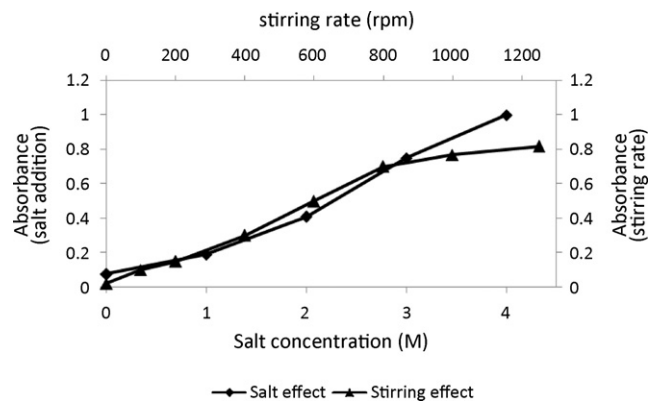


Fig. 2. Effect of salt concentration and stirring rate on the extraction efficiency. Conditions: organic solvent volume, 10 μ L; HCl concentration, 0.1 mol L⁻¹; sample volume, 20 mL containing 1 μ g L⁻¹ of analyte; ligand to metal ratio, 25; extraction time, 30 min.

of the stirring rate on the extraction efficiency of As(III) in the range of 0–1250 rpm was investigated. The results showed that the absorbance increased by increasing the stirring rate (Fig. 2). This is in agreement with the expected behavior of the solvent microextraction based on the penetration theory of mass transfer of a solute. Thus, a sample stirring rate of 1250 rpm was selected in this work.

3.2.5. Sampling temperature

In a liquid–liquid extraction, temperature has an influence on both equilibrium and mass transfer. This process facilitates the mass transfer of the analytes from the sample to the organic solvent and thus increases the efficiency of the extraction. The experimental results showed that the extraction efficiency increases by rising the sample temperature up to 45 °C though at higher temperatures the extraction efficiency would decrease. This result may be due to the decreasing of distribution ratio of As(III)–APDC complex at higher temperatures (Fig. 3). Thus, the temperature of solution was adjusted to 45 °C for further experiments.

3.2.6. Effect of solvent volume

The effect of a solvent's volume on the extraction efficiency of As(III) was evaluated. The solvent's volume is a key parameter affecting the extraction kinetics and also the preconcentration factor. It was found that the signal intensity of As(III) increased by increasing the solvent volume up to 15 μ L (Fig. 3) because the rate of the analyte transport into a microdrop is directly related to the interfacial area between the two liquid phases. However, at larger

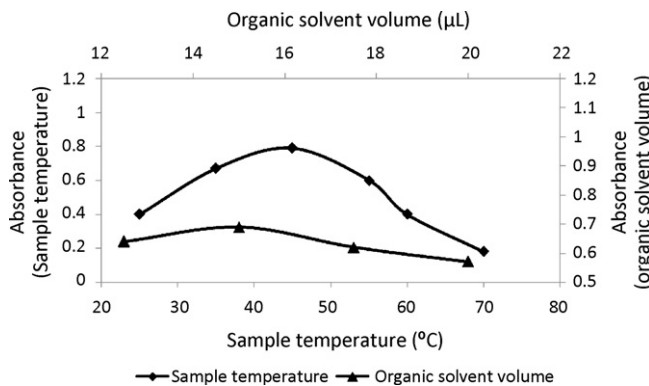


Fig. 3. Effect of temperature and organic solvent volume on the extraction efficiency. Conditions: HCl concentration, 0.1 mol L⁻¹; ligand to metal ratio, 25; sample volume, 20 mL containing 1 μ g L⁻¹ of analyte; extraction time, 30 min and salt concentration, 4 mol L⁻¹.

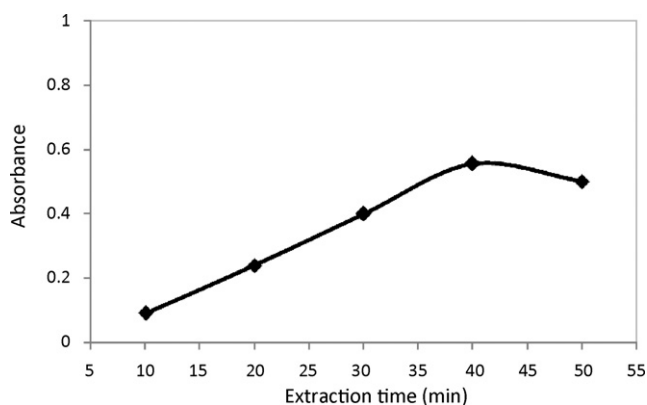


Fig. 4. Effect of extraction time on the extraction efficiency. Conditions: organic solvent volume, 15 μL ; HCl concentration, 0.1 mol L^{-1} ; ligand to metal ratio, 25; sample volume, 20 mL containing 1 $\mu\text{g L}^{-1}$ of analyte and salt concentration, 4 mol L^{-1} .

volumes due to the dilution effect, concentration of an analyte in the organic phase will decrease. Thus, a solvent volume of 15 μL was used for all subsequent extractions.

3.2.7. Effect of extraction time

For a quantitative analysis as well as increasing the precision of the LPME method, it is necessary to allow a sufficient mass transfer into the drop, this guarantees the equilibrium between the aqueous and organic phases has been achieved. The effect of the extraction time on the extraction efficiency was examined and found to be in the range of 10–50 min with the constant stirring speed of 1250 rpm. The results are illustrated in Fig. 4. One can see, the analytical signals increased when the extraction time was increased from 10 to 40 min. The extraction time profile indicates that the equilibrium between both phases was reached after 40 min and thus the extraction time of 40 min was selected in the present study. Although the extraction time was relatively long, the sheer smallness of the developed LPME system lends itself to extraction in parallel. In the present work six samples were extracted all together using a multi stirrer, but much higher parallelization is feasible.

3.3. Selectivity of the method

The potential interferences in the present system were investigated. The interferences are due to the competition between other heavy metal ions for chelating with APDC and their subsequent co-extraction with the As(III). The concentration of As was fixed at 1 $\mu\text{g L}^{-1}$ and possible interferences were evaluated using the following concentrations: 500 $\mu\text{g L}^{-1}$ for Co^{2+} , Ni^{2+} , Fe^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and 5000 $\mu\text{g L}^{-1}$ for K^+ , Na^+ , Ca^{2+} . The interference effect was evaluated considering the difference between the absorbance signal of As both in the presence and, in the absence of the elements studied. A relative error of three times the standard deviation of measurements (i.e. 5% concentration) was considered tolerable.

The obtained results showed that interferences had no obvious influence on the signal intensity of the analyte.

3.4. Analytical performance

The detection limit of the proposed method for As under the optimized temperature program of a graphite furnace and the extraction conditions, that were calculated according to the three times of the standard deviation of the blank signals was 9.2 ng L^{-1} . The linear dynamic range (LDR) was obtained between 100 and 700 ng L^{-1} with a correlation coefficient of 0.999 and the relative standard deviation (RSD) was 8.6%. In order to calculate the enhancement factor, analytical curves with and without the pre-concentration step were obtained. Under the optimum extraction conditions, the enhancement factor could be as high as a 1000-fold and the extraction recovery was calculated to be at 60%.

A comparison between the figures of merit for the proposed SFDME method and some of the published methods for extraction and determination of As are summarized in Table 2. It clearly shows that our proposed method has a good sensitivity and precision with a suitable dynamic linear range. Also, the obtained detection limit by this method is better than those obtained by other methods [34–36]. Accordingly, the main advantages of our proposed method includes high sensitivity with a good precision, its promptness, the low consumption of an organic solvent, it is low in cost and the simplicity of operation.

Table 2
Comparison of the proposed method with other methods applied for the determination of As.

Ions	Method of extraction/detection system	LDR ^a (ng mL^{-1})	DL ^b (ng L^{-1})	RSD %	EF	Reference
As(V)	CPE ^c /ETAAS	0.02–0.35	10	4.9	52.5	[34]
As(III), As(V)	AC ^d suspension/ETAAS	Up to 100	4000	4.0	200	[35]
As(III), As(V)	PLE/HPLC-UV-HG-AFS	–	10–35 ng g^{-1}	5.3–7.1	–	[36]
As(III)	SFDME/ETAAS	0.1–0.7	9.2	8.6	1000	Proposed method

^a Linear dynamic range.

^b Detection limit.

^c Cloud point extraction.

^d Activated carbon.

Table 3
Analytical results (mean \pm SD., $n = 3$) for As(III) and As(V) in different samples.

Sample	Spiked (ng mL^{-1})		Found (ng mL^{-1})		Relative recovery (%)	
	As (III)	As(V)	As (III)	As(V)	As (III)	As(V)
Tap water ^a	–	–	0.06 \pm 0.006	0.23 \pm 0.04	–	–
	0.20	0.20	0.25 \pm 0.05	0.44 \pm 0.05	95.0	105.0
Well water ^b	–	–	ND ^c	ND	–	–
	0.20	0.20	0.21 \pm 0.04	0.18 \pm 0.03	105.0	90.0

^a Tap water (Karaj, Iran).

^b Well water (Karaj, Iran).

^c Not detected.

3.5. Real sample analysis

It is absolutely essential to determine the trace amounts of As in water samples from the environmental view point. In demonstrating the performance of the present method, different water samples were utilized for separation and determination of As(III) and As(V). The analytical results along with the extraction efficiency for the spiked samples are listed in Table 3. As can be seen, the recoveries for the spiked samples were within the acceptable range of 90–105%. The quantitative results show that the method is accurate and reliable and could be applied for the determination of As in real samples.

4. Conclusions

In the present study, the results show a very promising technique for the determination of arsenic in a variety of samples at ng L^{-1} levels without the need for any sophisticated devices. It has some outstanding advantages such as its extremely high sensitivity and being relatively free from interferences; the procedure is very simple, low cost and benefits from a very low detection limit. Using the proposed method, As can be determined with a very high sensitivity and relatively good reproducibility in aqueous samples such as tap and well water.

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