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Speciation of As(III) and As(V) in water samples by graphite furnace atomic absorption spectrometry after solid phase extraction combined with dispersive liquid–liquid microextraction based on the solidification of floating organic drop

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ABSTRACT

A solid phase extraction (SPE) coupled with dispersive liquid–liquid microextraction based on the solidification of floating organic drop (DLLME-SFO) method, using diethyldithiphosphate (DDTP) as a proper chelating agent, has been developed as an ultra preconcentration technique for the determination of inorganic arsenic in water samples prior to graphite furnace atomic absorption spectrometry (GFAAS). Variables affecting the performance of both steps were thoroughly investigated. Under optimized conditions, 100 mL of As(III) solution was first concentrated using a solid phase sorbent. The extract was collected in 2.0 mL of acetone and 60.0 μL of 1-undecanol was added into the collecting solvent. The mixture was then injected rapidly into 5.0 mL of pure water for further DLLME-SFO. 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. A mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ was used as a chemical modifier in GFAAS. The analytical characteristics of the method were determined. The calibration graph was linear in the rage of 10–100 ng L^{-1} with detection limit of 2.5 ng L^{-1}. Repeatability (intra-day) and reproducibility (inter-day) of method based on seven replicate measurements of 80 ng L^{-1} of As(III) were 6.8% and 7.5%, respectively. The method was successfully applied to speciation of As(III), As(V) and determination of the total amount of As in water samples and in a certified reference material (NIST RSM 1643e).

1. Introduction

The presence of arsenic in drinking water has reached calamitous proportions in many parts of the world. Arsenic occurs as both inorganic and organic compounds and its toxicity is strongly related to its chemical form. Consequently, it is essential to perform the speciation of this element in aqueous, geological, and biological matrices [1]. Arsenic can be found in drinking water, in the air as volatile arsines, and in soil, where it can concentrate if absorbed on the soil components [2]. The release of arsenic in the environment occurs in a variety of ways through industrial effluents, pesticides, wood preservative agents, combustion of fossil fuels, and mining activity [3]. Exposure to elevated levels of arsenic, as a class I human carcinogen, has become a global concern affecting millions worldwide. The currently recommended upper limit of arsenic in drinking water is 10 μg L^{-1} [4]. This element occurs in the natural environment in four oxidation states: As(V), As(III), As(0) and As(−III). Inorganic compounds consist of water-soluble arsenite, As(III), as the most toxic form, and arsenate, As(V), as the less toxic form, and such pollutants have been associated with many health problems such as skin lesions, keratosis (skin hardening), lung cancer, and bladder cancer [3].

Because of very low concentration of arsenic in environmental and biological samples, sensitive analytical techniques are required. Up to now, a number of analytical techniques have been developed

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for the determination of low concentration levels of arsenic, including the inductively coupled plasma mass spectrometry (ICP-MS) [5], inductively coupled plasma-optical emission spectrometry (ICP-OES) [6], hydride generation-atomic absorption spectrometry (HG-AAS) [7], hydride generation-atomic fluorescence spectrometry (HG-AFS) [8] and electrothermal atomic absorption spectrometry (ETAAS) [9]. ETAAS is still being used because it combines a fast analysis time, a relative simplicity, a cheaper cost, low sample volume requirements and low detection limits. In addition, a number of hyphenated techniques for arsenic speciation, such as ion chromatography coupled with hydride generation-inductively coupled plasma atomic emission spectrometry [10], ion chromatography [11] or high-performance liquid chromatography [12] coupled to inductively coupled plasma mass spectrometry have also been reported. However, these methods are not sufficiently sensitive for the direct determination of arsenic in water samples. In this context, the development of methods for separation and pre-concentration of arsenic are necessary [13].

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures. Liquid-phase microextraction (LPME) has emerged in these last years as a powerful tool for preconcentration and matrix separation prior to detection. A new mode of liquid-phase microextraction, namely dispersive liquid–liquid microextraction (DLLME), has been developed by Assadi and co-workers in 2006 [14]. DLLME is based on ternary component solvent systems. Here, an appropriate mixture of extraction solvent and dispersive solvent is injected rapidly into an aqueous solution, resulting in a cloudy state consisting of fine droplets of the extraction solvent dispersed in the aqueous phase, which markedly increased the contact surface between phases and reduce extraction time with the increasing enrichment factors. The advantages of the DLLME method are simplicity of operation, rapidity, low cost, high recovery and enrichment factors. Up to now, DLLME has been used for separation and preconcentration of organic and inorganic compounds from different matrices [15–17]. In conventional DLLME, the density of extraction solvent should be higher than water; the applications of DLLME in most cases were limited to water samples and the volume of the sedimented phase in some cases was dependent on the surrounding temperature. These limitations have caused some development on DLLME. The modification techniques that resulted in DLLME development include solid phase extraction combined with DLLME (SPE–DLLME) [18–20], supercritical fluid extraction combined with DLLME (SFE–DLLME) [21], DLLME based on the solidification of flouting organic drop (DLLME-SFO) [22–25] and low-density extraction solvent-based solvent terminated DLLME (ST–DLLME) [26,27].

In this work for the first time, a combination of SPE and DLLME based on solidification of flouting organic drop (SPE–DLLME-SFO) was employed as a sample-preparation method for graphite furnace atomic absorption spectrometry (GFAAS). The factors affecting the efficiency of microextraction were thoroughly studied. The applicability of the approach was demonstrated for the rapid determination of inorganic arsenic ultra trace amounts in water samples using diethyldithiphosphate DDTP as a proper chelating agent.

2. Experimental

2.1. Reagents and solutions

Ultrapure water, obtained using a Milli-Q system (Millipore, Bedford, MA, USA), was used exclusively. Stock standard solutions of arsenic(III) and arsenic(V) with a concentration of 1000 mg L^{-1} were obtained by dissolving appropriate amounts of As_2O_3 and Na_2HAsO_4 (Merck, Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. The chelating agent, DDTP with the density of 1.17 kg L^{-1} was supplied from Merck. 1-Undecanol, 1-dodecanol and 1-decanol as extraction solvent, methanol (for spectroscopy), acetone (HPLC grade) and acetonitrile (HPLC grade) as disperser solvent, NaCl (analytical grade) and HNO_3 (65%, suprapur) were obtained from Merck. A mixture of 1000 mg L^{-1} $Pd(NO_3)_2$ and 300 mg L^{-1} $Mg(NO_3)_2$ solutions, both from Merck (Darmstadt, Germany), were used as chemical modifiers. A standard reference material SRM 1643e from National Institute of Standards and Technology (NIST) was employed for the validation of the proposed method. Tap, lake, well and mineral water samples from Kermanshah (Iran), collected in PTFE containers and stored in dark at 4 °C, were used for development of the method and analyzed within 24 h of collection without any previous treatment or filtration.

2.2. Instrumentation

A Model nov AA 400 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with deuterium background correction, a transversely heated graphite tube atomizer and an MPE 60 auto-sampler was used for all measurements. An arsenic hollow cathode lamp (Analytik Jena, Jena, Germany), operated at a current of 5.0 mA and a wavelength of 193.7 nm with a spectral bandwidth of 0.8 nm was used. Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer (Part no. 407-A81.026). The instrumental parameters and temperature program for the graphite atomizer are listed in Table 1. Argon 99.999% (Roham Gas Co., Arak, Iran) was used as a protected and purge gas at a flow-rate of 2.0 L min^{-1}. Integrated absorbance (peak area) was used exclusively for signal evaluation and quantification. The pH values were measured with a Metrohm pH-meter (Model: 692, Herisau, Switzerland) supplied with a glass-combined electrode. A Hettich Zentrifugen (EBA20, Tuttlingen, Germany) was used for centrifugations.

2.3. Extraction procedure

SPE of As(III) ions from the water samples was carried out using 500-mg C_{18} sorbent (6 mL syringe barrel, Varian, Harbor City, CA, USA). The C_{18} cartridge was conditioned with 3.0 mL of acetone, water and water at pH 2.5. Into aliquots of 100 mL standard solution containing 80 ng L^{-1} As(III), prepared by diluting the stock solution with HNO_3 (0.01 mol L^{-1}), was added 20 μL of DDTP as a chelating agent and the resulted solution gently shaken for a few minutes. After complexation of As(III) ions with DDTP, the sample was loaded at a flow rate of about 20 mL min^{-1} with the

Table 1
The graphite furnace temperature program for As(III) determination.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (L min^{-1})
Inject modifier	80	5	30	2
Inject sample				
Drying	120	3	20	2
Drying	250	2	10	2
Pyrolysis	500	25	10	2
AZ[a]	500	0	6	0
Atomization	2000	0	3	0
Cleaning	2400	0	2	2

[a] Auto-zero.

aid of a vacuum pump (Rotavac, Heidolph, Germany). The cartridge was washed with 3.0 mL of water at pH 2.5 at a flow rate of 1.0 mL min^{-1} to remove the matrix interferences.

After drying the solid phase by passing air through it, the As(III) ions that reacted with DDTP were eluted with 2.0 mL acetone and collected into a 10-mL screw cap glass test tubes with conical bottom. Next, 60.0 μL 1-undecanol (extraction solvent) was added to the acetone in the test tube. Then, 5.00 mL water was rapidly injected into the test tube, using a 5.00-mL syringe (gastight, Hamilton, Reno, NV, USA). A cloudy solution was formed in the test tube (the cloudy state was stable for a long time) and the mixtures were centrifuged for 3 min at 5000 rpm. Accordingly, the organic solvent droplet was floated on the surface of the aqueous solution due to its low density. The sample vial was thereafter put into an ice bath for 5 min; at this time, the floated solvent was solidified because of the low melting point (14 °C). The solidified solvent was transferred into a conical glass sample cup where it was melted immediately. Finally, 20 μL of this organic phase using an auto-sampler was injected into the GFAAS and was submitted to the temperature program of Table 1. Total inorganic arsenic (As(III) and As(V)) was measured after reduction of As(V) with 1.0 mL of 1% (w/v) of sodium thiosulfate solution and 1.0 mL of 0.5% (w/v) of potassium iodide solution [28,29] and the concentration of As (V) was calculated by subtracting the As(III) concentration from the total As concentration.

3. Results and discussion

In the present work, SPE–DLLME–SFO combined with GFAAS was developed for the determination of inorganic arsenic in water samples. This combination lead to very high enrichment factor and could be used in complex matrices. In order to obtain a high extraction recovery and enrichment factor with the employment of SPE–DLLME-SFO, the SPE and DLLME-SFO conditions were optimized. One variable at a time optimization was used to obtain optimum conditions for SPE–DLLME-SFO procedure.

3.1. Optimization of SPE parameters

3.1.1. Effect of the flow rates and breakthrough volume

The effect of sample solution flow rate on recovery of As(III) ions was investigated in the flow rate range of 5–50 mL min^{-1}. It was found that, in the range of 5–25 mL min^{-1}, the retention of arsenic ions by the solid phase is not affected by the sample solution flow rate considerably. According to the results (results not shown), 20 mL min^{-1} was used as the best sample flow rate. On the other hand, quantitative stripping of As(III) ions from the solid phase was achieved in a flow rate range of 0.5–4 mL min^{-1}, using 2.0 mL of acetone. Thus, a flow rate of 1 mL min^{-1} was employed for further experiments.

Breakthrough volume depends on the nature of the sorbent material and the type and concentration of sample constituents. The effect of breakthrough volume (from 25 to 250 mL, containing a constant amount of As(III) ions, on enrichment factor was investigated. The results showed that an acceptable enrichment factor was observed when sample volumes were increased to 200 mL, which seemed to be the tolerated volume for breakthrough. Considering the analytical time and trace level of arsenic in water samples, 100 mL was used as the optimized breakthrough volume.

3.1.2. Sample solution pH and ionic strength effect

The pH value plays an important role to adsorption of the ions onto sorbents. The effect of pH on the complex formation and extraction of As(III) from water samples was studied in the range of 2.0–7.0 by using HNO_3 and CH_3COONa. The concentration of As(III) in water sample was 80 ng L^{-1}. The higher and lower pH values were not studied because solid phase in this pH values is not resistant. The results illustrated in Fig. 1 reveal that the absorbance remained nearly constant in the pH range of 2–3.5 and it reduced at higher pH values. For further study, a pH of 2 was selected.

The influence of ionic strength on the extraction of As(III) was studied in the sodium chloride solution with various concentrations from 0% to 5.0% (w/v). It was found (results not shown) that ionic strength has no appreciable effect upon extraction efficiency up to 5.0% w/v of NaCl. Therefore, further extractions were performed without any salt addition.

3.1.3. Effect of type and volume of the elution solvent

Since the eluent of SPE should be used as the dispersant in the following DLLME-SFO procedure, in SPE combined with DLLME-SFO, acetone, acetonitrile, and methanol were investigated as elution solvents. The SPE cartridge was eluted using 2.0 mL of each elution solvent. The results of this study are shown in Fig. 2, which clearly shows that the recovery by using acetone is higher than that for acetonitrile and methanol. Consequently, acetone was selected as the optimum elution (disperser) solvent. The volume of elution (disperser) solvent must be high enough to perform an effective elution of the complexed As(III) ions. On the other hand, it should be low enough so that it maintains the enrichment factor as high as possible. For this purpose, various experiments were performed by using different volumes of

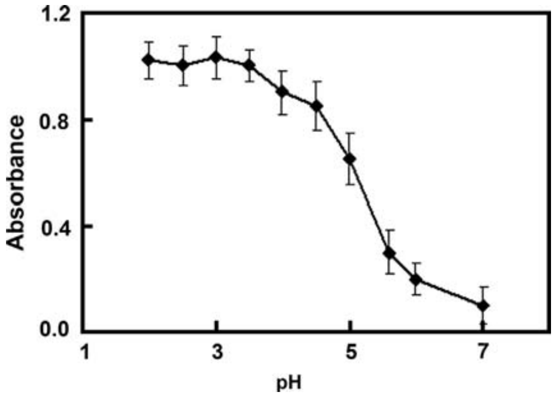

Fig. 1. Effect of pH on the absorbance of As(III) obtained from SPE–DLLME-SFO. Extraction conditions: water sample volume, 100 mL; elution or disperser solvent (acetone) volume, 2.0 mL; extraction solvent (1-undecanol) volume, 60.0 μL; concentration of DDTP, 0.02% (v/v); sedimented phase volume, 25 ± 2 μL; room temperature; concentration of As(III), 80 ng L^{-1}.

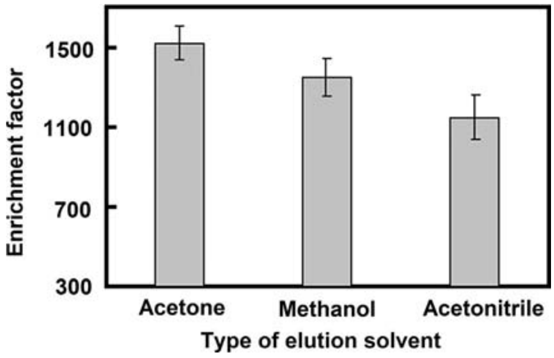

Fig. 2. Effect of type of elution or disperser solvent on the enrichment factor of As (III) obtained from SPE–DLLME-SFO. Extraction conditions: similar to those in Fig. 1, except for a sample solution pH of 2.

acetone (0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 mL). The obtained results are illustrated in Fig. 3. As seen, the acetone volumes of lower than 2.00 mL cannot elute cartridge completely and the enrichment factor decreases. Also, by using more than 2.0 mL acetone, in DLLME stage the solubility of complexed ions in water samples increases and it causes a decrease in the enrichment factor. According to the results, a volume of 2.0 mL acetone was chosen as the optimum volume of the elution (disperser) solvent.

3.1.4. *Effect of DDTP concentration*

The effect of the DDTP concentration on the enrichment factor is shown in Fig. 4. The influence of DDTP concentration was carried out in which the other experimental variables remained constant. It was found that the enrichment factor of As(III) increased with the increasing DDTP concentration from 0.002% to 0.02% (v/v) and is kept constant upon further increase in concentration. Thus, the concentration of 0.02% (v/v) of DDTP was then used in subsequent experiments.

3.2. *Optimization of DLLME parameters*

3.2.1. *Effect of the type and volume of extraction solvent*

In conventional DLLME, halogenated hydrocarbons such as chlorobenzene, chloroform, carbon tetrachloride and tetrachloroethylene are usually selected as extracting solvents because of their high density. These solvents are toxic and environmentally unfriendly. In DLLME-SFO, lower toxicity extracting solvents can be used and selecting a suitable extraction solvent is crucial in this method. It should have some properties as high affinity to analytes, low solubility in water, lower density than water, low volatility and proper melting point around room temperature. In this study, three different organic solvents were evaluated, including 1-decanol, 1-dodecanol and 1-undecanol. These solvents have melting points close to or below room temperature, and their densities are less than water. Average enrichment factor (triplicate) and standard deviation (SD) for different extraction solvents are shown in Fig. 5. The results revealed that 1-undecanol has the highest enrichment factor (1520) in comparison with the other tested solvents. Therefore, 1-undecanol was chosen for further experiments.

The influence of the volume of 1-undecanol as the extraction solvent on the enrichment factor was studied. For this purpose, different volumes of 1-undecanol (50, 60, 70, 80, 90 and 100 μL) with a fixed volume of disperser solvent were used with the same DLLME-SFO procedure. As shown in Fig. 6, by increasing the volume of 1-undecanol from 50 to 100 μL, the volume of the floating organic drop increases from 18 to 65 μL and enrichment factor decreases. It is clear that by increasing the volume of 1-undecanol, the extraction recovery increases and by further increasing the extraction solvent volume, the extraction recovery slightly decreases because of dilution effect (Fig. 6). The volume of extractant solvent has to be selected to obtain high enrichment factor and extraction recovery. In the subsequent studies, 60 μL of 1-undecanol was used as the optimal volume of the extraction solvent.

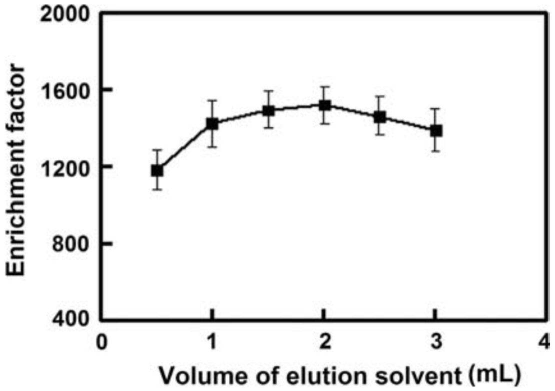

Fig. 3. Effect of volume of elution or disperser solvent on the enrichment factor of As(III) obtained from SPE–DLLME-SFO. Extraction conditions are similar to those of Fig. 2.

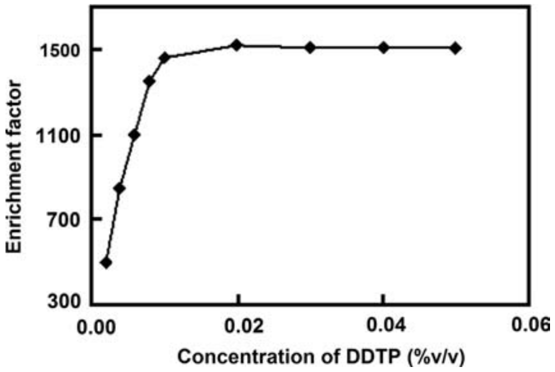

Fig. 4. Effect of concentration of DDTP on the enrichment factor of As(III) obtained from SPE–DLLME-SFO. Extraction conditions are similar to those of Fig. 2.

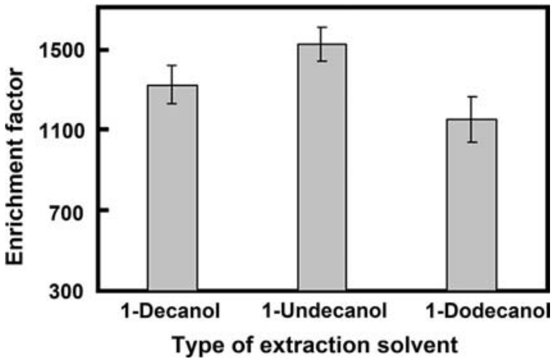

Fig. 5. Effect of the type of extraction solvent on the enrichment factor of As(III) obtained from SPE–DLLME-SFO. Extraction conditions are similar to those of Fig. 2.

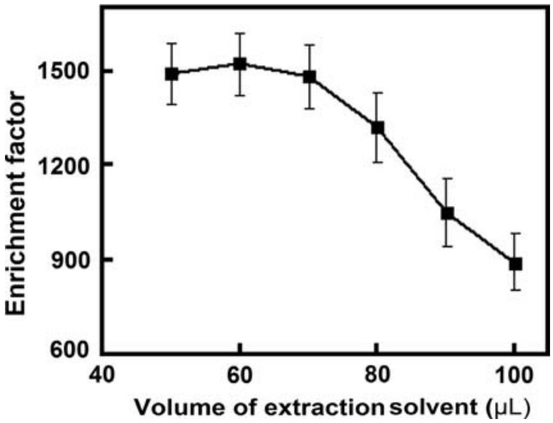

Fig. 6. Effect of the volume of extraction solvent (1-undecanol) on the enrichment factor of As(III) obtained from SPE–DLLME-SFO. Extraction conditions are similar to those of Fig. 2.

3.2.2. *Effect of the type and volume of disperser solvent*

When combining SPE with DLLME-SFO, the elution solvent of SPE should be used as disperser solvent in the DLLME-SFO stage. For this purpose, acetone, acetonitrile and methanol were used as disperser (elution) solvent. According to the results in Section 3.1.3, acetone was selected as disperser solvent and 2.0-mL volume of acetone was selected as an optimum volume of disperser solvent.

3.2.3. *Effect of the extraction time*

Extraction time is one of the most important factors in most extraction procedures. In DLLME, extraction time is defined as the time between injection mixture of disperser and extraction solvent, and starting to centrifuge. The influence of the extraction time was examined in the range of 0–60 min with the experimental conditions remaining constant. The results showed that the extraction time has no significant effect on the extraction efficiency. It was revealed that after the formation of the cloudy solution, the surface area among the extraction solvent and the aqueous phase was essentially large. Thereby, complex formation of As(III) and its transfer from aqueous phase to extraction solvent is fast. This fact was one of the advantages of the DLLME technique.

3.2.4. *Effect of coexisting ions*

Most common matrix constituents of real samples such as alkali and alkaline earth elements do not react with DDTP because of its selectivity. The effects of common coexisting ions in natural water samples on the recovery of arsenic were studied. For this purpose, according to the recommended procedure, 100 mL of solution that contains 80 ng L^{-1} of As(III) and various amounts from interfering ions, were preconcentrated and determined. A given spices was considered to interfere if it resulted in a ±5% variation of the GFAAS signal. The results obtained are given in Table 2. The results showed that interferences possess no obvious influence on the signal intensity of the analyte.

3.3. *Figures of merit of the proposed method*

The figures of merit of the proposed method, including linear range, limit of detection, reproducibility, and enrichment factor are summarized in Table 3. The calibration graph was linear in the As(III) concentration range of 0.010–0.10 μg L^{-1}. The detection limit (calculated as three times the standard deviation of 7 blank measurements, divided by the slope of the calibration curve) for the As(III) was found to be 2.50 ng L^{-1}. Concerning the reproducibility of the method, it was evaluated with 100 mL from the solution, containing the analyte ions in the As(III) concentration of 80 ng L^{-1}. The repeatability (intra-day) and reproducibility (inter-day) of method were evaluated by carrying out seven replicate extraction and determination of As(III) at a concentration level of 80 ng L^{-1} during a day (intra-day) and seven replicates at seven subsequent days (inter-day). The values of intra-day RSD and inter-day RSD were 6.8% and 7.5%, respectively. Finally, a high enrichment factor of 1520 was obtained for a 100 mL water sample.

Table 2
Effect of interferents on the recovery of 80 ng L^{-1} As(III) in water sample using SPE–DLLME-SFO–GFAAS.

Interferent	Concentration (μg L^{-1})	Interferent/As(III) ratio	Recovery (%)
Na^+	1000	12,000	96.4
K^+	1000	12,000	99.0
Li^+	1000	12,000	103.5
Ca^{2+}	500	6000	95.8
Co(II)	50	600	97.1
Se(IV)	8	100	94.0
Sb(III)	8	100	92.5
Fe(II)	50	600	104.0
Ni(II)	20	250	101.4
Zn(II)	50	600	98.8
Cd(II)	50	600	94.6
Cu(II)	50	600	95.4
Cl^-	1000	12,000	97.5
SO_4^{2-}	1000	12,000	101.5
NO_3^-	1000	12,000	102.0

Table 3
Analytical characteristics of SPE–DLLME-SFO–GFAAS for determination of As(III).

Parameter	Analytical feature
Linear range (ng L^{-1})	10–100
r^2	0.9866
Limit of detection (ng L^{-1}) (3σ, n=7)	2.5
RSD[a] % (Intra-day, n=7)	6.8
RSD % (Inter-day, n=7)	7.5
Enrichment factor	1520
Sample volume (mL)	100
Sample preparation time (min)	< 15

[a] As(III) concentration was 80 ng L^{-1} for which RSD was obtained.

3.4. *Analysis of real water samples*

To demonstrate the applicability and reliability of the proposed trace enrichment method for environmental purposes, the procedure was applied to the inorganic arsenic determination in natural water samples (well, mineral, lake and tap water). The As(III) and As(V) amounts in mineral and well water samples were less than the limit of detection. In the lake and tap water samples, As(III) and As(V) were detected and they were confirmed by spiking As (III) and As(V) into the lake and tap water samples. The concentration of As(III) and As(V) in the lake and tap water samples are shown in Table 4. Water samples were spiked with As(III) and As (V) standards to assess matrix effects. The relative recoveries of As (III) and As(V) from well, mineral, lake and tap water samples at spiking level of 20 and 30 ng L^{-1} are listed in Table 4. The quantitative results show that the method is accurate and reliable and could be applied for the determination of As in real water samples.

In addition, the accuracy of the proposed methodology was evaluated by analyzing a standard reference material (SRM) 1643e from NIST (trace elements in water), with certified arsenic content of 60.45 ± 0.72 ng mL^{-1}, and the analytical results are added to Table 4. As is obvious from Table 4, the determined value of 56.9 ± 3.0 is in satisfactory agreement with the certified value.

3.5. *Comparison of SPE–DLLME-SFO with previously reported methods*

In Table 5 are compared the performance characteristics of the proposed SPE–DLLME-SFO–GFAAS method for determination of inorganic arsenic in water samples with those of some other established methods [28,30–35]. It is clearly seen that the proposed method possesses a good sensitivity together with a suitable dynamic linear range and an improved limit of detection. The RSD values in the SPE–DLLME-SFO are low, the extraction time is relatively short and its enrichment factor is much higher than that of the previous methods. These characteristics are of great interest for the routine laboratories in the trace analysis of metal ions.

Table 4
Determination of As(III), As(V) and total As in water samples and in a certified reference material.

Sample	Spiked (ng L^{-1})		Found, mean ± S.D. (n=3) (ng L^{-1})		Total As ± S.D. (n=3) (ng L^{-1})	Relative recovery (%)	
	As(III)	As(V)	As(III)	As(V)		As(III)	As(V)
Mineral water	–	–	n.d.[a]	n.d.	–	–	–
	20	20	19 ± 0.5	21 ± 0.8	40 ± 1.3	95.0	105.0
Tap water	–	–	38 ± 1.5	55 ± 2.0	93 ± 3.5	–	–
	30	30	66 ± 2.2	88 ± 4.2	154 ± 6.4	97.0	103.5
Well water	–	–	n.d.	n.d.	–	–	–
	20	20	22 ± 1.6	21 ± 1.0	43 ± 2.6	110.0	105.0
Lake water	–	–	25 ± 2.0	33 ± 2.5	58 ± 4.5	–	–
	30	30	53 ± 3.5	68 ± 4.0	121 ± 7.5	96.3	103.0
NIST SRM 1643e	60.45 ± 0.72[b] (ng mL^{-1})		8.3 ± 0.7 (ng mL^{-1})	48.6 ± 2.3 (ng mL^{-1})	56.9 ± 3.0 (ng mL^{-1})	94.1[c]	

[a] Not detected.
[b] Certified value of total arsenic.
[c] Relative recovery of total arsenic.

Table 5
Characteristic performance data obtained by using SPE–DLLME-SFO and other preconcentration techniques for determination of As(III) in water samples.

Method	LOD (ng L^{-1})	RSD (intra-day) (%)	Enrichment factor	Sample volume (mL)	Time (min)	Linear range (ng L^{-1})	References
DLLME–ETAAS[a]	10	3.1	115	5	5	60–200	[30]
CPE–HGAAS[b]	8	3.5	60	50	> 20	30–4000	[31]
DLLME–GFAAS[c]	36	3.1	45	5	5	100–10,000	[32]
SPE–ETAAS[d]	20	3.5	250	50	–	30–600	[33]
SFDME–ETAAS[e]	9.2	8.6	1000	20	40	100–700	[28]
SPE–ETAAS[f]	4.6	3.9	300	150	~40	15–650	[34]
MSPE–CL[g]	2	2.17	80	200	–	5–5000	[35]
SPE–DLLME-SFO–GFAAS[h]	2.5	6.8	1520	100	< 15	10–100	This work

[a] Dispersive liquid–liquid microextraction–electrothermal atomic absorption spectrometry.
[b] Hydride generation atomic absorption spectrometry after cloud point extraction.
[c] Dispersive liquid–liquid microextraction–graphite furnace atomic absorption spectrometry.
[d] Solid phase extraction–electrothermal atomic absorption spectrometry.
[e] Solidification of floating drop microextraction–electrothermal atomic absorption spectrometry.
[f] Solid phase extraction–electrothermal atomic absorption spectrometry.
[g] Magnetic solid phase extraction–chemiluminescence.
[h] Solid phase extraction–dispersive liquid–liquid microextraction based on the solidification of floating organic drop–graphite furnace atomic absorption spectrometry.

4. Conclusions

In the present study, the SPE method was combined with the DLLME-SFO technique. This combination was successfully applied to extraction and preconcentration of inorganic arsenic from water samples prior to analysis by GFAAS. High preconcentration factor was obtained easily through this method and a detection limit at ng L^{-1} level was achieved with 100 mL of sample. The high-preconcentration factor and the low detection limit were the major advantages of the technique. In this method, the sample preparation time (less than 15 min) as well as the consumption of the toxic organic solvents (at microlitre level) was minimized without affecting the method sensitivity. As a conclusion, the proposed method possesses great potential in analysis of trace metal ions in real water samples.

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References

[1] S. Mazan, G. Cretier, N. Gilon, J.M. Mermet, J.L. Rocca, Anal. Chem. 74 (2002) 1281–1287.
[2] V. Arancibia, A. Lopez, M.C. Zuniga, R. Segura, Talanta 68 (2006) 1567–1573.
[3] E. Majid, S. Hrapovic, Y. Liu, K.B. Male, J.H.T. Luong, Anal. Chem. 78 (2006) 762–769.
[4] M.K. Sengupta, M.F. Sawalha, S.I. Ohira, A.D. Idowu, P.K. Dasgupta, Anal. Chem. 82 (2010) 3467–3473.
[5] C.H. Yu, Q.T. Cai, Z.X. Guo, Z.G. Yang, S.B. Khoo, Analyst 127 (2002) 1380–1385.
[6] Y.L. Feng, H. Narasaki, H.Y. Chen, L.C. Tian, Anal. Chim. Acta 386 (1999) 297–304.
[7] J.Y. Cabon, C.L. Madec, Anal. Chim. Acta 504 (2004) 209–215.
[8] P. Cava-Montesinos, M.L. Cervera, A. Pastor, M. de la Guardia, Talanta 60 (2003) 787–799.
[9] N. Campillo, P. Vinas, I. Lopez-Garcia, M. Hernandez-Cordoba, Analyst 125 (2000) 313–316.
[10] R.T. Gettar, R.N. Garavaglia, E.A. Gautier, D.A. Batistoni, J. Chromatogr. A 884 (2000) 211–221.
[11] E. Vassileva, A. Becker, J.A.C. Broekaert, Anal. Chim. Acta 441 (2001) 135–146.
[12] K. Wrobel, K. Wrobel, B. Parker, S.S. Kannamkumarath, J.A. Caruso, Talanta 58 (2002) 899–907.
[13] D. Pozebon, V.L. Dressler, J.A. Gomes Neto, A.J. Curtius, Talanta 45 (1998) 1167–1175.
[14] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[15] S. Berijani, Y. Assadi, M. Anbia, M.R.M. Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1–9.
[16] N. Fattahi, Y. Assadi, M.R.M. Hosseini, E.Z. Jahromi, J. Chromatogr. A 1157 (2007) 23–29.
[17] M. Shamsipur, M. Ramezani, Talanta 75 (2008) 294–300.
[18] N. Fattahi, S. Samadi, Y. Assadi, M.R.M. Hosseini, J. Chromatogr. A 1169 (2007) 63–69.
[19] M. Shamsipur, N. Fattahi, M. Sadeghi, M. Pirsaheb, J. Iran. Chem. Soc. 11 (2014) 249–256.
[20] X. Liu, J. Li, Z. Zhao, W. Zhang, K. Lin, C. Huang, X. Wang, J. Chromatogr. A 1216 (2009) 2220–2226.
[21] M.H. Naeeni, Y. Yamini, M. Rezaee, J. Supercrit. Fluids 57 (2011) 219–226.
[22] T. Asadollahi, S. Dadfarnia, A.M. Haji Shabani, Talanta 82 (2010) 208–212.
[23] Hui Xu, Z. Ding, L. Lv, D. Song, Y.Q. Feng, Anal. Chim. Acta 636 (2009) 28–33.
[24] C.C. Chang, S.D. Huang, Anal. Chim. Acta 662 (2010) 39–43.
[25] H. Sereshti, V. Khojeh, S. Samadi, Talanta 83 (2011) 885–890.
[26] H. Chen, R. Chen, S. Li, J. Chromatogr. A 1217 (2010) 1244–1248.
[27] P. Hashemi, S. Beyranvand, R.S. Mansur, A.R. Ghiasvand, Anal. Chim. Acta 655 (2009) 60–65.

[28] M. Ghambarian, M.R. Khalili-Zanjani, Y. Yamini, A. Esrafili, N. Yazdanfar, Talanta 81 (2010) 197–201.

[29] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, Anal. Chim. Acta 508 (2004) 99–105.

[30] R.E. Rivas, I. Lopez-Garcia, M. Hernandez-Cordoba, Spectrochim. Acta, Part B 64 (2009) 329–333.

[31] H.I. Ulusoy, M. Akcay, S. Ulusoy, R. Gurkan, Anal. Chim. Acta 703 (2011) 137–144.

[32] P. Liang, L. Peng, P. Yan, Microchim. Acta 166 (2009) 47–52.

[33] I. Lopez-Garcia, R.E. Rivas, M. Hernandez-Cordoba, Talanta 86 (2011) 52–57.

[34] H. Abdolmohammad-Zadeh, A. Jouyban, R. Amini, Talanta 116 (2013) 604–610.

[35] H. Abdolmohammad-Zadeh, Z. Talleb, Talanta 128 (2014) 147–155.