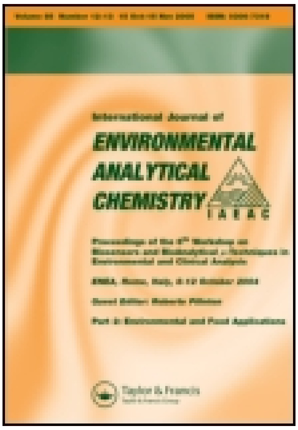

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Determination of As(III) using developed dispersive liquid–liquid microextraction and flame atomic absorption spectrometry

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The method relies on selective complexation of As(III) with a suitable chelating agent followed by dispersive liquid–liquid microextraction (DLLME) method. Flame atomic absorption spectrometry (FAAS) equipped with microsample introduction system was utilised for determination of As(III). 1-Undecanol and acetone were used as extraction solvent and disperser solvent respectively. Some effective parameters on complex formation and extraction have been optimised. Under the optimum conditions, the enrichment factor of 108 for As(III) was obtained from 9.8 mL of water samples. The calibration graph was linear in the range of 2–15 $\mu g\,L^{-1}$ with detection limits of 0.60 $\mu g\,L^{-1}$ for As(III). The relative standard deviation (R.S.D.) for ten replicate measurements of 5.00 μgL^{-1} of As(III) was 6.2%. Operation simplicity and high enrichment factors are the main advantages of DLLME for the determination of As(III) without necessity for hydride generation in water samples.

Keywords: dispersive liquid–liquid microextraction; determination of As(III); flame atomic absorption spectrometry; water analysis

1. Introduction

Arsenic is the twentieth most abundant element in the crust of earth, the fourteenth in the seawater and the twelfth in the human body. Arsenic and arsenic compounds are used in wood preservatives, glass manufacture, alloys, electronics, catalysts, food additives and veterinary chemicals [1].

Nowadays, it is well known that the occurrence of arsenic in natural waters is not just associated with the geochemical environment where it is found. Direct releasing of arsenic to the environment can occur as a result of anthropogenic activities such as petrochemical industries. Arsenic is found in crude oil in concentrations ranging from <10 to 26.2 $\mu g\,kg^{-1}$, depending on the geographical origin of petroleum [2]. Arsenic exists in nature in the oxidation states +V (arsenate), +III (arsenite), 0 (arsenic) and −III (arsine). In the aqueous environment, inorganic arsenic appears commonly in the oxidation states +V and +III as arsenous acid (As(III)), arsenic acid (As(V)), and their salts [3]. Inorganic compounds of As are more toxic than their organic ones and may be found in ground and surface waters [4]. As(III) is reported to be 25–60 times more toxic than As(V), and several hundred times more toxic than organic arsenicals (at least in the case of the mono and

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dimethylated forms). These facts indicate that it would be of priority interest to develop methods for the selective determination of As(III) [1]. The World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) have adopted a new 10 $\mu g\,L^{-1}$ (0.01 $mg\,L^{-1}$) standard for arsenic in drinking water [5].

Whereas arsenic is known as a highly toxic element and exists at trace amounts in water, numerous attempts such as hydride generation coupled to atomic absorption spectrometry (HG-AAS) [6], hydride generation coupled to atomic fluorescence spectrometry (HG-AFS) [7], inductively coupled plasma with atomic emission spectrometry (ICP-AES) [8], inductively coupled plasma-mass spectrometry (ICP-MS) [9], electrothermal atomic absorption spectrometry in graphite furnace (ETAAS) [10] and electrochemical methods [11–12] have been made to determine arsenic amounts in water.

It is well known that flame atomic absorption spectrometry (FAAS) is a less sensitive technique than flameless atomic absorption spectrometry. Nevertheless, FAAS is faster, cheaper, more reproducible and does not require expert operators [13]. So pretreatment techniques have to be used for arsenic determination to increase intensity of flame.

Hydride generation is, perhaps, the most popular sample derivatisation method used for inorganic arsenic detection [14]. However, this technique has some disadvantages. The major disadvantage of HG-AAS is that it depends upon the experimental conditions and oxidation state of As, Se, and Sb. Another disadvantage of HG-AAS is that it is a single element technique that requires labour-intensive sample preparation and analysis [15].

Other separation and preconcentration techniques for determination of arsenic in water samples include high performance liquid chromatography (HPLC) [16], capillary electrophoresis (CE) [17], ion-chromatography (IC) [18], liquid–liquid extraction (LLE) [19] solid phase extraction (SPE) [20], liquid phase microextraction (LPME) [21], co-precipitation [22] and cloud point extraction (CPE) [3]. Because these methods do not have a high enrichment factor and arsenic in these concentrations produces weak signals in flame, these methods are not used for pretreatment before arsenic determination by flame.

Arsenic's high volatility makes its determination a difficult task [23–24]. Therefore, samples contain high concentration of arsenic are necessary to introduce into nebuliser. DLLME can be an alternative method for this purpose, which was first developed by Berijani et al. [25]. DLLME has been successfully applied to the preconcentration of some certain elements prior to analysis with FAAS [26,27] and other detection techniques [28–30].

Only two attempts using DLLME have been made for arsenic measurement and both of them are coupled with ETAAS [4,31]. In these researches, DLLME is coupled by electrothermal which is a more difficult operation in comparison with FAAS.

The selection of the appropriate organic solvent is very important in the direct and continuous nebulisation of the organic extracts into the flame [26]. Since the current solvents used in DLLME have densities more than water, their nebulisation would be inefficient. Therefore, they are not suitable for the determination of arsenic by flame.

The purpose of this work is to combine DLLME with FAAS to develop a new procedure for the determination of trace As in water samples. In order to obtain lower detection limit and more effective signals, solvents with densities lesser than, or near to, water must be used. Then the solvent will be nebulised in flame system leading to high efficiency of nebulisation. As a result less solvent will be used and the detection limit of As will be decreased to lower quantities. Thus using recent operation involving DLLME which is done by solvent lighter than water [32], DLLME method was employed for the measurement of As(III).

The fact that As(V) does not react with Ammonium pyrrolidinedithiocarbamate (APDC) allows speciation of the inorganic trivalent and pentavalent forms of this element.

2. Experimental

2.1 *Apparatus*

A Shimadzu AA-670 (Kyoto, Japan) flame atomic absorption spectrometer was utilised, equipped with a 100 mm burner head, deuterium background correction and an air–acetylene flame. An arsenic hollow-cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) was used as radiation source, and it operated at 6 mA with the slit width of 0.6 nm. For arsenic detection, the wavelength was set at 193.7 nm resonance line. Air–acetylene flame was used with a fuel-oxidant ratio of 1.6 : 8. Centurion Scientific centrifuge (Model K240R, Arundel, UK) was used to accelerate the separation phase. The pH values were measured by a Metrohm pH-meter (Model 691, Herisau, Switzerland), equipped with a glass-combined electrode.

2.2 *Reagents and solutions*

All solutions were prepared with ultra pure water (Ghazi Co., Tabriz, Iran).

Stock standard solution of As(III) at the concentration of $1000\,\mathrm{mg\,L^{-1}}$ was prepared by dissolving appropriate amount of As_2O_3 (99.5%, Acros) in 1 M NaOH. The working standard solutions were prepared by serial dilutions of the stock solution with ultra pure water right before analysing them. Ammonium pyrrolidinedithiocarbamate (APDC) (analytical grade, Merck), was used as chelating agent.

The rest of the chemicals used were: 1-undecanol (for synthesis), n-hexadecane (for synthesis), 1-bromohexadecane (for synthesis), 1-dodecanol (for synthesis), butyl acetate (GR for analysis), methyl isobutyl ketone(for synthesis) as extraction solvent, acetone (suprasolv), methanol (suprasolv) and acetonitrile (suprasolv) as disperser solvent, NaCl (pro analysis) to study the effect of salt, NaOH (pro analysis), HNO_3 (65%, pro analysis), which all of them were supplied by Merck.

All the glass vessels used for the trace analysis were kept in a 10% (v/v) HNO_3 solution for at least 24 hours. Then, they were washed twice with ultra pure water and washed twice with acetone before use.

The analysed water samples for the development of the method were collected in PTFE containers. They were stored in a dark place at 4°C and analysed for 24 h after collecting them without any previous treatment or filtration.

2.3 *Microsample introduction system*

To determine the amount of a single element in FAAS, 1–4 mL of the volume of the sample solution is generally used. In the case of small sample volumes due to high dilution the concentration of elements may be less than the detection limit. To overcome this problem, it is possible to determine an element by FAAS in a microlitre sample volume (less than 100 μL) [26].

The Hamilton plug valve (distribution flow path 2-ports HVP Model 2–5, Cat. No. 86786, Hamilton, Reno, NV, USA) was used for the microsample introduction. It was coupled to the nebuliser needle by a small length of the PTFE capillary tube. A quantity of

35 μL of the collected phase was manually introduced by a micropipette (Brand Tech, Germany) into the female luer fitting (1/4 in.-28 UNF, Cat. No. 35031, Hamilton), being connected to a Hamilton plug valve.

When the female luer fitting of the plug valve was filled with the sample, the valve was switched back into the flow path and the sample was turned to the flame for monitoring arsenic. The microsample introduction system offered the opportunity to introduce a volume of above 35 μL to the flame, to provide spike-like, reproducible and interesting signal profiles.

2.4 *Dispersive liquid–liquid microextraction procedure*

A quantity of 9.8 mL of ultra pure water was placed in a 11 mL screw-cap glass test tube with conical bottom and was spiked at the level of 5 $\mu g L^{-1}$ of arsenic (III). Then 0.010 g APDC (chelating agent) was added to the sample solution and the pH was adjusted to 6.0 by 0.1 M HNO_3 solution. Reaction of arsenic ions with APDC was carried out within 20 min at 60°C. After the test tube cooled down to room temperature, 2%(w/v) NaCl was added to the cloudy solution. When salt dissolved, 1.2 mL of acetone (disperser solvent) containing 45 μL of 1-undecanol (extraction solvent) was injected rapidly into the sample solution by a 2.5-mL syringe (gastight, Hamilton, Nevada, USA). A cloudy solution (resulted from dispersion of fine droplets of 1-undecanol in aqueous sample) was formed in the test tube. In this step, As(III)-APDC complex was concentrated into the fine droplets of 1-undecanol. Then the test tube was sealed and was put upside down into the centrifuge (the bottom of conic test tube was at the top) (Figure 1(a)). The mixture was centrifuged for 5 min at 3800 rpm. After this process, the dispersed fine droplets of 1-undecanol were collected at the bottom of the conical test tube (40 ± 1 μL). The test tube was put in an ice bath upside down (Figure 1(b)). When the extracted solvent, which was collected at the bottom of conic test tube, thoroughly solidified, the test tube was set upright. Then the solidified solvent was transferred to another clean test tube (Figure 1(c,d)) and it was melted quickly. After melting solidified solvent, 35 μL of the solvent was removed using a sampler (Brand Tech, Germany) and was injected manually into the flame atomic absorption spectrometr to measure arsenic concentration. The volume of the collected phase was determined by a 50 μL microsyringe, and it was about 40 μL.

3. Results and discussion

In this research, a new method was investigated by microsample introduction system (discrete nebuliser) in order to combine it with FAAS. In this method, DLLME was improved by using solvents with less density than water or near to it so that with no necessity for hydride generation, it was possible to obtain high sensitivity and high efficiency of nebuliser. These solvents are more compatible with flame system and in the designed method, their transmission is simpler after injection.

Arsenic was chosen as an example to study the applicability of this combination. To attain a high enrichment factor, the influence of different parameters, which affect the complex formation and the extraction conditions such as type of extraction and disperser solvent and volume of them, pH, extraction time and salt addition were tested. To study

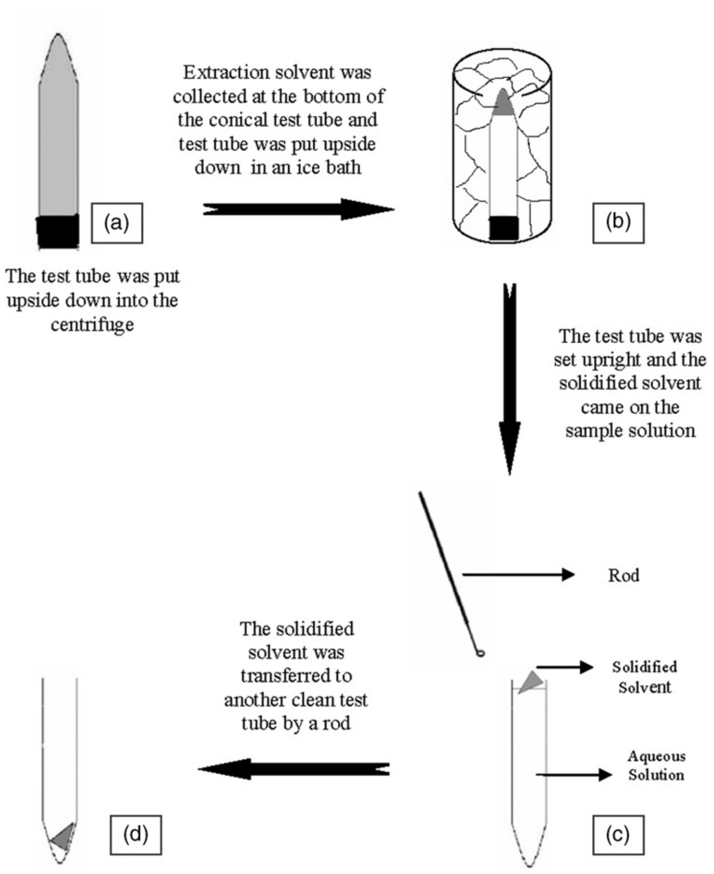

Figure 1. Schematic diagram of the proposed DLLME procedure.

these influential parameters, Equation (1) was used for the calculation of the enrichment factor:

$$EF = \frac{C_{col}}{C_0} \tag{1}$$

where EF, C_{col} and C_0 are the enrichment factor, analyte concentration in the collected phase and initial analyte concentration in the aqueous sample, respectively. C_{col} was calculated on the calibration graph which obtained from conventional LLE–FAAS (extraction conditions: 5.00 mL standard water sample in the concentration range of 1–10 mg L^{-1} of arsenic, 0.010 g APDC, pH 6.0 and T = 60°C, 5.00 mL 1-undecanol).

3.1 *Effect of the injection volume on the analytical Signal*

The investigation of the injection volume was carried out by 30 extractions in which the extraction conditions were the same as those in section 2.4 above and the concentration of arsenic was 5.0 μg L^{-1}. All of collected extraction solvents at the bottom of the 30 conical

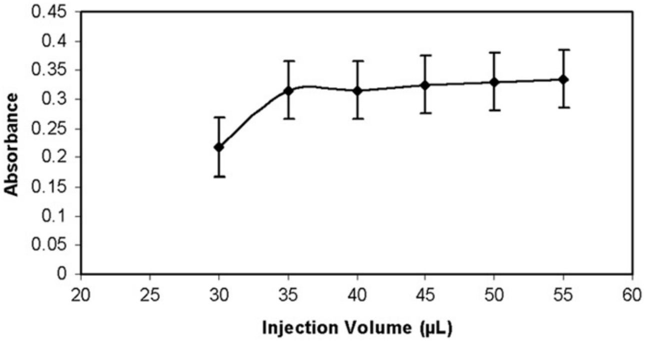

Figure 2. Effect of the injection volume on the signal height. (Extraction conditions have been mentioned in section 2.4.)

test tubes were transferred to one clean test tube. Then volumes of 30, 35, 40, 45, 50 and 55 μL of organic solvent were injected into flame.

To select the optimum injection volume, the curve of the absorbance values versus the injected volume of the standard organic extract is shown in Figure 2. The signal intensity increases by the increase of injection volume up to 35 μL and then it remains almost constant. Therefore, in all of the FAAS measurements, volumes of 35 μL of the final organic extract were introduced into the flame via a microsample introduction system.

3.2 *Influence of the extraction solvent type and volume*

The selection of the appropriate organic solvent for FAAS is limited by several essential requirements: the solvent should exhibit good nebuliser and burning characteristics, not too low boiling point and low solubility in water [26].

To increase the efficiency of nebuliser and to avoid analyte losses, an organic solvent with less density than water or near to it must be used. In DLLME, solvents with density lesser than water will be collected at the surface of water after they have centrifuged. So removing collected phase to inject it into FAAS will be very difficult or may be impossible. As a result, putting test tubes upside down in centrifuge and using solvent with a higher melting point than water will be suitable solutions. After the centrifuge process, the solvent will be solidified, and separated from water easily and it will be ready to inject into FAAS.

Therefore 1-undecanol, n-hexadecane, 1-bromohexadecane, methyl isobutyl ketone, 1-dodecanol and butyl acetate were investigated as extraction phase for the arsenic preconcentration (Table 1).

Among these solvents, methyl isobutyl ketone and butyl acetate are the most suitable solvents for FAAS. However, they are not practically used because their melting point and their solidifing point are lower than water. The results show that 1-bromohexadecane makes the flame noisy and unstable and it lessens the sensitivity of measurement. So it is not used in this process. 1-dodecanol also solidifies at room temperature and its viscosity increases during extraction process. Thus it is not suitable for this method either. So the best solvents are n-hexadecane and 1-undecanol. They have an equal enrichment factor, but working with 1-undecanol and removing it from aqueous solvent is more feasible than n-hexadecane; therefore, it is the best choice for this method.

Table 1. Properties of extraction solvents.

Solvent	Melting point (°C)	Boiling point (°C)	Density (g/cm^{-3})
1-undecanol	13–15	129–131	0.83
n-hexadecane	18	287	0.77
1-bromohexadecane	17–18	190	0.998
1-dodecanol	24	259	0.8309
Butyl acetate	−74	126	0.88
Methyl isobutyl ketone	−87.7	117–118	0.80

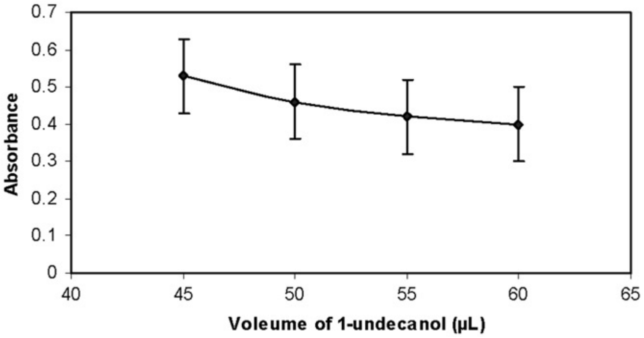

Figure 3. Effect of the volume of extraction solvent (1-undecanol) on the absorbance of arsenic obtained from DLLME. Extraction conditions: water sample volume, 9.8 mL; disperser solvent (acetone) volume, 1.20 mL; APDC amount, 10 mg; pH 6.00; As(III) concentration, 5 μg L^{-1}.

To evaluate the effect of the extraction solvent volume, solutions which contain different volumes of 1-undecanol were subjected to the preconcentration procedure. The experimental conditions were fixed and they included the use of 1.20 mL of acetone, containing different volumes of 1-undecanol (45, 50, 55, and 60 μL). By increasing the volume of 1-undecanol from 45 to 60 μL, the volume of the collected phase increases from 40 to 55 μL. Figure 3 shows the curve of the absorbance versus the volume of the extraction solvent (1-undecanol).

According to Figure 3, the absorbance decreased after increasing the volume of 1-undecanol from 45 to 60 μL, because the volume of collected phase increases. Consequently, a high absorbance was obtained at 45 μL of the extraction solvent.

In subsequent studies, 45 μL of 1-undecanol was used as the optimum volume of the extraction solvent, since the minimum volume that could be used should have been 40 μL of the collected phase.

3.3 *Influence of the disperser solvent type and volume*

The most important point for the selection of the disperser solvent is its miscibility with both organic (extraction solvent) and aqueous (sample solution) phases. For this purpose, different solvents such as acetone, acetonitrile and methanol were examined.

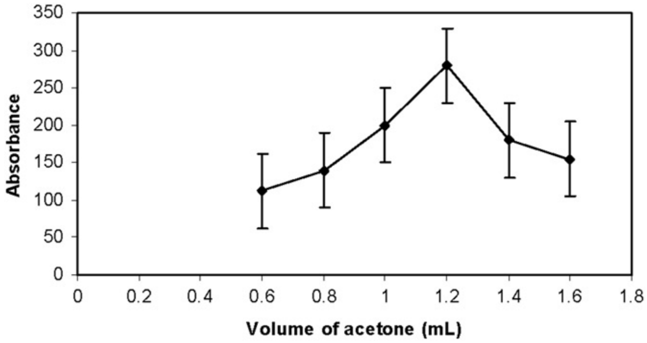

Figure 4. Effect of the volume of the disperser solvent (acetone) on the absorbance of arsenic obtained from DLLME. Extraction conditions, as with Figure 3; extraction solvent (1-undecanol) volume, 45 µL.

Solubility of 1-undecanol was very low in acetonitrile and two discrete phases were formed. When methanol was used as disperser solvent, signal intensity was equal to when acetone was used as disperser solvent. However, acetone was used as disperser solvent in all of the subsequent experiments because of its lower toxicity.

After selecting acetone as the disperser solvent, its volume should be optimised. To acquire the optimised acetone volume, various experiments were conducted using different acetone volumes (0.6, 0.8, 1.00, 1.20, 1.40 and 1.60 mL) and containing 45.0 µL of 1-undecanol. Since 1-undecanol was insoluble in water, constant volumes of the extraction solvent were collected at the bottom of the conical test tubes (40 ± 1 µL). By increasing the acetone volume to 1.20 mL, the signal height increased, but the increase of the acetone volumes from 1.20 to 1.60 mL decreased the signal height (Figure 4). Therefore, an optimal volume of 1.2 mL of acetone was chosen to achieve a better and more stable cloudy solution.

3.4 *Effect of the extraction time*

Extraction time is one the most important factors in most extraction procedures. In DLLME, extraction time is defined as the time between injecting the mixture of disperser solvent (acetone) and extraction solvent (1-undecanol) before starting to centrifuge. The dependence of signal height upon extraction time was studied within a range of 5 sec to 10 min under fixed experimental conditions. The results show that the extraction time has no significant effect on signal height. It is revealed that after formation of the cloudy solution, the surface area between extraction solvent and aqueous phase (water sample) is infinitely large. Consequently, transferring analyte from aqueous phase (water sample) to extraction solvent is fast (5 sec). Subsequently, equilibrium state is achieved quickly. Thus the extraction time will be very short.

3.5 *Salt effect*

To investigate the influence of ionic strength on DLLME performance, various experiments were performed by adding different amounts of NaCl (0–10%, w/v).

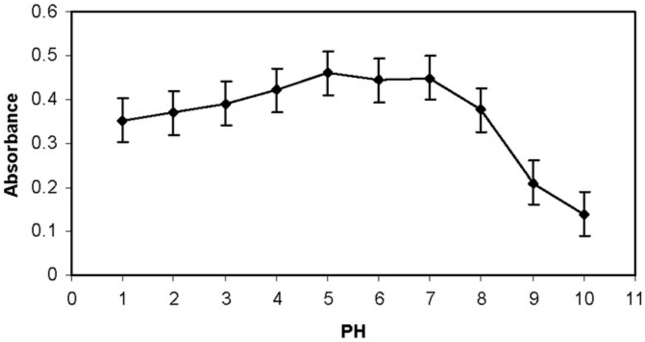

Figure 5. Effect of pH on the absorbance of arsenic obtained from DLLME. Extraction conditions, as with Figure 3; extraction solvent (1-undecanol) volume, 45 μL.

The rest of the experimental conditions were kept constant. The results obtained by altering the amount of salt confirmed that signal height increased up to 2%. Due to rising ionic strength of aqueous solution, the hydrophobic complex was easily introduced to the extraction solvent.

The results confirmed that the salt addition from 2% to 10% has no significant effect on the signal height.

3.6 *Metal-chelate formation parameters*

3.6.1 *Effect of pH*

The pH of the arsenic containing solution plays a crucial role in complex formation reaction with APDC and was studied in the range of 1–10 in steps of 1.0 through adjusting the concentration of HNO_3 or NaOH in the sample solution. Figure 5 depicted the effect of pH on the absorbance signals of As(III) using APDC as complexing reagent and 1-undecanol as the extraction solvent. It could be seen that the absorbance of As(III) increased with increasing pH from 1.0 to 5.0, remained constant with increasing pH from 5.0 to 7.0, and then decreased with further increasing pH from 7.0 to 10.0. When pH was higher than 8, As(III) absorbance was very low, indicating that extracted As(III) was very low.

The reason for this is that APDC is unstable in strong acidic solution but can be protonated in mild acidic solution, which results in forming stable As(III)–APDC complex through its two donor sulphur atoms [33]. Optimum absorption signal for arsenic(III) obtained within the pH range of 5–7. Hence, pH 6.0 was selected for complexation of As(III).

Because As(V) could not be complexed with APDC, and no As(V) could be preconcentrated, it is possible to selectively preconcentrate As(III) in the presence of As(V) [24,33,34].

3.6.2 *Influence of the APDC amount*

The influence of the amount of APDC on the extraction efficiency of 5 $\mu g\,L^{-1}$ As(III) was studied. It could be seen that the absorbance of As(III) was increased with the increase of

APDC amount from 0.25 to 10.0 mg, remained constant with the further increase of APDC amount from 10.0 to 60.0 mg. Accordingly, 10.0 mg of APDC amount (for 9.8 mL of water sample) was used to optimise other parameters.

3.6.3 *Temperature*

The equilibration temperature necessary to comprise completion of the reaction was investigated in the range of 30–90°C and optimum temperature of 60°C was selected for complex formation of As(III).

3.6.4 *Time*

Finally, the minimum required time for completion of complex formation was investigated. For this purpose, sample solutions were treated in different periods of time (5–30 min) while the other variables remained constant. Results revealed that 20 min is sufficient for complex formation of As(III) with APDC.

3.6.5 *Effect of the co-existing ions*

Most common matrix constituents of real samples such as alkali and alkaline earth elements do not react with APDC because of its selectivity. However, large amounts of metal ions which react with APDC appreciably reduce the efficiency of arsenic extraction. The effects of common coexisting ions in natural water samples on the extraction recovery of arsenic were studied. In these experiments, 9.8 mL of solutions contains 5.00 $\mu g\,L^{-1}$ of arsenic and various amounts of interfering ions were treated according to the recommended procedure. A given spices was considered to interfere if it resulted in a ±5% variation of the FAAS signal. The obtained results are given in Table 2.

3.7 *Figures of merit*

The data characteristics on the performance of the proposed method under the optimum conditions for the determination of As(III) are listed in Table 3. The calibration graph was linear in the range of 2–15 $\mu g\,L^{-1}$. The limit of detection, defined as $CL = 3SB/m$ (where CL, SB and m are the limit of detection, the standard deviation of the blank and the slope of the calibration graph, respectively), was 0.60 $\mu g\,L^{-1}$ for As(III). The relative standard

Table 2. Effect of interferents on the recovery of 5.00 $\mu g\,L^{-1}$ arsenic in water sample using DLLME-FAAS.

Interferent	Concentration/mg L^{-1}	Interferent/As (III) ratio
Na^+, K^+	5000	1000000
Ca^{+2}, Mg^{+2}	1000	200000
Zn(II), Co(II), Mn(II)	50	10000
Cu(II), Cd(II), Hg(II), Se(IV), Pb(II), Ni(II)	10	2000
Fe(III), Al(III), Cr(III)	1	200

deviation (R.S.D.) for ten replicate measurements of 5.0 μg L^{-1} As(III) was 6.2% and the square of correlation coefficient (R^2) was 0.9988. The enrichment factor was obtained 108 for As(III).

3.8 *Natural water analysis*

To test the reliability of the recommended procedure, the method was applied for determining As(III) in water from Pars Oil and Gas Company operational regions (well water and wastewater from second and third phases).

For this purpose, a volume of 9.8 mL of each sample were preconcentrated with 1.20 mL of acetone contained 45 μL of 1-undecanol according to the proposed method. The arsenic concentration in the well water and wastewater from second and third phases were determined to be 3.5 ± 0.38 and 4.6 ± 0.3 μg L^{-1} respectively (Table 4). The amounts of arsenic in samples were less than new standard for arsenic in drinking water (10 μg L^{-1}) [5]. The accuracy of the method was verified by the analysis of the samples which spiked with known amounts of arsenic. The relative arsenic recoveries from samples of well water and wastewater from second and third phases at the spiking level of 5 μg L^{-1} As(III) were 78 and 82%, respectively (Table 4). These results demonstrated that the matrices of the well water and wastewater from second and third phases samples had little effect on the DLLME method for determination of arsenic.

Table 3. Analytical characteristics of DLLME-FAAS for determination of arsenic.

Parameter	Analytical feature
Linear range (μg L^{-1})	2–15
R^2	0.9988
Limit of detection (μg L^{-1}) (3a, $n = 7$)	0.60
R.S.D. (%) ($n = 10$, 5 μg L^{-1})	6.2
Enrichment factor	108
Sample volume (mL)	9.8
Sample preparation time (min)	<3
Sample introduction volume (μL)	35

Table 4. Determination of arsenic in well water and waste water from second and third phases from Pars Oil and Gas Company operational regions and relative recovery of spiked arsenic in them.

Sample	Concentration of As^{+3}, mean ± S.D.[a] (μg L^{-1})	Added As^3 (μg L^{-1})	Found As^{+3}, mean ± S.D.[a] (μg L^{-1})	Relative recovery (%)
Well water	3.5 ± 0.38	5	7.4 ± 0.25	78
Waste water from second and third phases	4.6 ± 0.3	5	8.7 ± 0.21	82

[a] Standard deviation ($n = 3$).

Table 5. Characteristic performance data obtained by using DLLME and other preconcentration techniques for determination of arsenic in water samples.

Method	Extraction time (min)	R.S.D.[a] (%)	Enrichment factor	LOD[b] ($\mu g\,L^{-1}$)	Suitable injection volume (μL)	Reference
CPE-ET AAS[c]	25	3	36	0.04	100	[3]
OnLine CE-HG AFS[d]	80	4.2	–	0.012	10 mL	[35]
HF LPME-ET AAS[e]	10	8	78	$0.12\,ng\,mL^{-1}$	5	[33]
Coprecipitation-HGAAS[f]	20	<8	25	0.012	10 mL	[36]
DLLME-FAAS[g]	A few seconds	6.2	108	0.6	35	[Represented method]

[a] Relative standard deviation.
[b] Limit of detection.
[c] Cloud point extraction-electrothermal atomic absorption spectrometry.
[d] On-Line Capillary Electrophoresis-Hydride generation atomic fluorescence spectrometry
[e] Hollow fibre liquid phase microextraction-electrothermal atomic absorption spectrometry.
[f] Coprecipitation-Hydride generation atomic absorption spectrometry.
[g] Dispersive liquid–liquid microextraction-flame atomic absorption spectrometry.

3.9 *Comparison with other methods*

Table 5 indicates the suitable injection volume, the relative standard deviation, the limit of detection, the enrichment factor and the extraction time in the cloud point extraction (CPE) [3], On-Line Capillary Electrophoresis [35], Hollow fibre liquid phase microextraction (HF LPME) [33], co-precipitation [36] and developed DLLME (represented method) for the extraction and determination of arsenic in water samples. The comparison of the results exhibits that extraction time and the enrichment factor with a sample volume of 9.8 mL in the present method were better than those of the other methods. RSD in DLLME was relatively low. All these results demonstrate that DLLME-FAAS by microsample introduction is a sensitive, fast and reproducible technique for the preconcentration and determination of As(III) in water samples.

4. Conclusions

This investigation demonstrated that DLLME combined with FAAS without necessity to HG is a powerful tool for preconcentration and determination of trace levels of As(III) in aqueous samples. This method is easier and more accessible in comparison with previous methods.

The small volume of the collected phase (40 μL) leads to high values of the enrichment factor. The nebulisation of 35 μL organic extract of the arsenic–APDC complex into the flame provides a very smooth and spike-like signal profiles and the evolution of only a small amount of toxic gases.

In this method, the sample preparation time as well as the consumption of the toxic organic solvents is minimised without affecting the sensitivity of the method. The extraction method is simple, rapid and inexpensive. Also, this method indicated that hereinafter arsenic determination with high sensitivity is possible without necessity for hydride generation, which it was not feasible up to this time.

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