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Response surface methodology based on central composite design as a chemometric tool for optimization of dispersive-solidification liquid–liquid microextraction for speciation of inorganic arsenic in environmental water samples

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ABSTRACT

Dispersive-solidification liquid–liquid microextraction (DSLLME) coupled with electrothermal atomic absorption spectrometry (ETAAS) was developed for preconcentration and determination of inorganic arsenic (III, V) in water samples. At pH=1, As(III) formed complex with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into the fine droplets of 1-dodecanol (extraction solvent) which were dispersed with ethanol (disperser solvent) into the water sample solution. After extraction, the organic phase was separated by centrifugation, and was solidified by transferring into an ice bath. The solidified solvent was transferred to a conical vial and melted quickly at room temperature. As(III) was determined in the melted organic phase while As(V) remained in the aqueous layer. Total inorganic As was determined after the reduction of the pentavalent forms of arsenic with sodium thiosulphate and potassium iodide. As(V) was calculated by difference between the concentration of total inorganic As and As(III). The variable of interest in the DSLLME method, such as the volume of extraction solvent and disperser solvent, pH, concentration of APDC (chelating agent), extraction time and salt effect, was optimized with the aid of chemometric approaches. First, in screening experiments, fractional factorial design (FFD) was used for selecting the variables which significantly affected the extraction procedure. Afterwards, the significant variables were optimized using response surface methodology (RSM) based on central composite design (CCD). In the optimum conditions, the proposed method has been successfully applied to the determination of inorganic arsenic in different environmental water samples and certified reference material (NIST RSM 1643e).

1. Introduction

Arsenic mainly occurs in two oxidation states and may form several inorganic and organic species with very different physicochemical properties. Inorganic compounds of As are more toxic than their organic forms and may be found in ground and surface water [1]. The toxicity of As(III) is 10–20 times higher than that of As(V), and its oxide has been shown to cause several types of cancer [2]. To obtain sufficient information on the toxicity and biotransformation of this element, it is necessary not only to determine the total amount but also to speciate the different oxidation states.

Several instrumental techniques have been applied for the determination of arsenic. These include inductivity coupled plasma atomic emission spectrometry (ICP-AES) [3], inductivity coupled plasma mass spectrometry (ICP-MS) [4], hydride generation atomic absorption spectrometry (HG-AAS) [5], and electrothermal atomic absorption spectrometry (ETAAS) [6]. Low concentration and matrix interference are two problems in detecting arsenic compounds. So, in spite of developments in modern analytical instruments, preconcentration processes on environmental samples are needed. For the speciation of As(III) and As(V), the separation and preconcentration methods reported in the literatures are usually based on hydride generation [7,8], liquid–liquid extraction [9], solid phase extraction

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[10–14] and coprecipitation [15,16], etc. However, the disadvantages such as time consuming, unsatisfactory enrichment factors, large organic solvents and secondary wastes limit their applications. Cloud point extraction [17,18] and liquid phase microextraction [19,20] are fairly new methods of sample preparation for the preconcentration of arsenic, and have been proved to be simple, inexpensive, fast and virtually solvent-free sample pretreatment techniques with extensive application.

In 2008, Leong and co-worker introduced dispersive-solidification liquid–liquid microextraction as a simple and efficient preconcentration and microextraction method [21]. The extraction solvent used in this technique has a low density and low toxicity, a typical example being undecanol. An aqueous sample is placed in a screw-cap glass test tube, and the disperser solvent containing extraction solvent is injected into the sample solution. A cloudy solution is formed in the test tube. The large contact surface between the sample and extraction droplets speeds up mass transfer. After centrifugation, the floated droplet is solidified in an ice bath and is easily removed for analysis. The advantages of this method are simplicity of operation, rapidity, low cost, high recovery, using low toxicity extraction solvent.

In previous studies on dispersive-solidification liquid–liquid microextraction, every single factor related is varied whilst all other factors are kept fixed at a specific set of conditions. The single-dimensional search is laborious, time consuming, and incapable of reaching the true optimum due to ignoring the interaction among variables. To resolve this problem, response surface methodology (RSM) has been proposed to determine the influence of individual factors and their interactive influences. The RSM is a statistical technique for designing experiment, building models, evaluating the effects of several factors and searching optimum conditions [22].

The aim of this work is to combine dispersive-solidification liquid–liquid microextraction with ETAAS to develop a new procedure for the determination of trace As in natural water samples. Ammonium pyrrolydine dithiocarbamate (APDC), a chelating agent which originates stable complex with a number of metals and has found numerous applications in trace element separation and preconcentration methods [23], is used to extract As(III) into the organic phase. The fact that As(V) do not react with APDC allows speciation of the inorganic trivalent and pentavalent forms of these elements [24–26]. The concentration of As(V) was calculated as the difference between the total arsenic and A(III) concentrations. Because of high volatility of arsenic, the pyrolitic graphite platform was pre-treated with palladium as the permanent modifier to prevent analyte loss [25–29]. Furthermore, experimental variables, such as the volume of extraction solvent and disperser solvent, pH, concentration of APDC, extraction time and salt effect, were assessed and optimized with the aid of response surface methodology and experimental design. A fractional factorial design (FFD) was used to screen the significant factors. Then, a central composite design (CCD) was used to conduct a second-order mathematical model relating the enrichment factor with significant independent variables. The optimum conditions were predicted by using the mathematical model and three-dimensional (3D) response surfaces that obtained from it.

2. Experimental

2.1. Instrumentation

A SpectrAA220 Varian atomic absorption spectrometer with a graphite furnace atomizer (GTA-110), a arsenic hallow cathode lamp as radiation source (Varian, Australia) at the 193.7 nm wavelength with a slit width of 1 nm, 8 mA current and deuterium background corrector, were used for measurements. The temperature program used for graphite atomizer is listed in Table 1. Integrated absorbance (peak area) was used for quantitation. A research pH-meter (model 3520, Jenway, UK) with a precision 0.001 units and a centrifuge (model Z200A, HERMLE, Germany) were employed for pH adjusting and centrifuging, respectively. Pt electrodes as an anode were connected to a DC power supply (12v, model ZCM 721, ZAG Chemie Co., Tehran, Iran) via an amperometer (150 mA, model ZCM 721, ZAG Chemie Co., Tehran, Iran) indicating the deposition current. Electrochemical experiments were performed by using a Chemie Company coulometer/electrolysis system.

Table 1
The graphite furnace temperature program for arsenic determination.

Steps	Temperature (°C)	Time (s)	Argon flow rate (L min^{-1})
Drying	85	5	3
Drying	100	10	3
Ashing	800	5	3
Ashing	800	5	3
Gas stop	800	2	0
Ramp stop and read command	2600	0.9	0
Atomization and read command	2600	2	0
Cleaning	2600	10	3

2.2. Reagents and solutions

All the reagents and standards were of analytical grade unless otherwise stated, and all the dilutions were made with high purity de-ionized water (18 MΩ cm^{-1} resistivity) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Stock standards (1000 mg L^{-1}), of As(III) and As(V), were obtained by respectively dissolving appropriate amounts of Na_3AsO_3 and $Na_3AsO_4.12H_2O$ (Fluka, Buchs SG, Switzerland) in 0.1 M HCl and storing the solutions in a refrigerator at 4 °C. The chelating agent, 2 g L^{-1} ammonium pyrrolidine dithiocarbamate (APDC) solution, was prepared daily by dissolving the appropriate amount of APDC (Merck, Darmstadt, Germany) in ethanol (Merck, Darmstadt, Germany). Other chemicals such as undecanol, 1-dodecanol and hexadecane as extraction solvent, ethanol, acetone and acetonitrile as a disperser solvent, HCl (37%), NaOH with the purity higher than 99% were purchased from Merck (Darmstadt, Germany). A palladium solution, 1000 mg L^{-1}, was prepared by the dissolution of palladium(II) nitrate (Aldrich, Milwaukee, WI, USA) in 1 mol L^{-1} hydrochloric acid solution and was used as the chemical modifier. Sodium thiosulphate and potassium iodide (Merck, Darmstadt, Germany) solution in water was used for reducing pentavalent arsenic. Water standards reference material SRM 1643e from National Institute of Standards and Technology (NIST) was employed for the validation of the proposed method.

River water samples (Haraz and Tajan, Iran), Caspian sea water, tap water and drinking water were collected in prewashed (soaked in dilute HNO_3 and rinsed with de-ionized distilled water) polytetraflouroethylene (PTFE) bottles; after adjusting the pH to 3 by adding an appropriate amount of HCl, the samples were stored at 4 °C and analyzed during 48 h from the sample collection without any previous treatment for filtration.

2.3. Treatment of L'vov platform with palladium

The chemical modifiers must be used as stabilizing agents to prevent the loss of volatile arsenic compound in the ETAAS measurement [25–27]. The literature suggests using palladium as chemical modifiers for arsenic [26,27], but this would have involved two injections in dispersive-solidification liquid–liquid microextraction procedure, one of the organic extract and the other of the aqueous solution containing the modifier. For solving this problem, Najafi et al. used palladium as a permanent chemical modifier by its electrodeposition on the L'vov platform surface [28]. Therefore, according to literatures [28,29], Pd was electrically deposited on the L'vov platform surface and was used for about 500 atomization cycles without significant reduction in analysis performance under the temperature program given in Table 1.

2.4. *Dispersive-solidification liquid–liquid microextraction procedure*

About 5 mL of aqueous solution containing 0.5 ng mL^{-1} of As (III) and 0.08 ng mL^{-1} APDC (chelating agent) with pH=1 was placed in a 10 mL test tube. The mixture of 1 mL ethanol (disperser solvent) and 30 μL 1-dodecanol (extraction solvent) was injected rapidly into the sample solution. A cloudy solution formed in the test tube. In this step, As(III) reacted with APDC and extracted into fine droplets of 1-dodecanol. After centrifugation for 2 min at 5000 rpm (2906.8 × g rcf), the organic solvent droplets were floated on the surface of the aqueous solution due to its low density. Then, the test tube was transferred into an ice bath. Floated organic solvent was solidified because of the low melting point. The solidified solvent was transferred into conical vial; it started to melt at room temperature. 20 μL of extraction solvent was manually injected into the palladium-modified pyrolitic tube graphite furnace atomic absorption spectrometer.

Sine As(V) does not react with APDC [24–26] the total inorganic arsenic could be measured after reducing the As(V) to As(III). Therefore, 1 mL of a 1% (w/v) of sodium thiosulphate solution and 1 mL of 0.5% (w/v) of potassium iodide solution were added to the sample aliquot, before acidification and incorporation of the organic solvent mixture [26,30,31]. After reduction, extraction procedure was repeated and a new measurement for total inorganic arsenic was obtained. The concentration of As(V) was calculated by subtracting the As(III) concentration from the total arsenic concentration.

2.5. *Optimization strategy*

Different parameters may affect the efficiency of arsenic extraction using DSLLME such as extraction solvent volume, disperser solvent volume, concentration of APDC, pH, extraction time and salt effect. In order to develop the dispersive-solidification liquid–liquid microextraction method for arsenic determination, it is necessary to consider and optimize these variables. In the first, half fractional factorial design as a screening design was carried out to determine which of the several experimental variables and their interactions present significant effects. Then, response surface methodology (RSM) based on central composite design (CCD) as a multivariate statistic technique was used to optimize the level of effective parameters for improving the efficiency of arsenic extraction. Design generation and statistical analysis were performed using the software package STATGRAPHICS Plus version 5.1 for windows (Rock Vill. MD, USA).

3. Results and discussion

For optimization of extraction conditions, enrichment factor (EF) was used to evaluate the extraction efficiency under different conditions. The enrichment factor was defined as the ratio between the analyte concentration in the floating phase (C_{flo}) and the initial concentration of analyte (C_o) within the sample:

$$EF = \frac{C_{flo}}{C_o} \tag{1}$$

C_{flo} was calculated from the calibration graph obtained by conventional LLE-ETAAS (extraction conditions: 5 mL standard water sample in the concentration range of 10–100 ng mL^{-1} of As, 5 mL 1-dodecanol, 5 ng mL^{-1} APDC and pH 1).

3.1. *Selection of extraction and disperser solvent*

The selection of an appropriate extraction and disperser solvent is very critical for the dispersive-solidification liquid–liquid microextraction process. The extraction solvent needed to fulfill the following requirements: it need to have a low solubility in water, high affinity to analyte, a low melting point around room temperature (in the range of 10–30 °C) and a density lower than water. The main criterion for the selection of the disperser solvent is its miscibility with water and the extraction solvent. Therefore, undecanol, 1-dodecanol and hexadecane as extraction solvent and ethanol, acetone and acetonitrile as disperser solvent were investigated. In Fig. 1 EF is shown for all combinations of dispersive and extraction solvents. Regarding the EF, the combination of 1-dodecanol as the extraction solvent and ethanol as the disperser solvent is the best and an EF higher than 135 is attainable.

3.2. *Experimental design*

3.2.1. *Screening design*

2^{6-1} fractional factorial design (FFD) was employed to screen most significant parameters among numerous parameters that may affect the DSLLME method efficiency. In that way only statistically significant variables would be studied in optimization design, therefore, the number of experiments would be reduced in the central composite design (CCD) [32]. In the FFD, the number of experiments can be reduced based on the assumption that interaction effects among three or more parameters are small compared to main effects and two-variable interaction effects [33]. The number of experiments in FFD is given by $2^{k-p}+C$, where k is the number of variables, C is the number of replicates and p a whole number that indicates how fractionated the experimental design will be. When p is zero, the experimental design is full [34]. The investigated factors and their domains are presented in Table 2. Only two levels were used so that the variables were considered as discrete values and no continuous second-order response model could be estimated. High and low levels of each variable are based on the literatures [24–26] and are donated as −1 and +1.

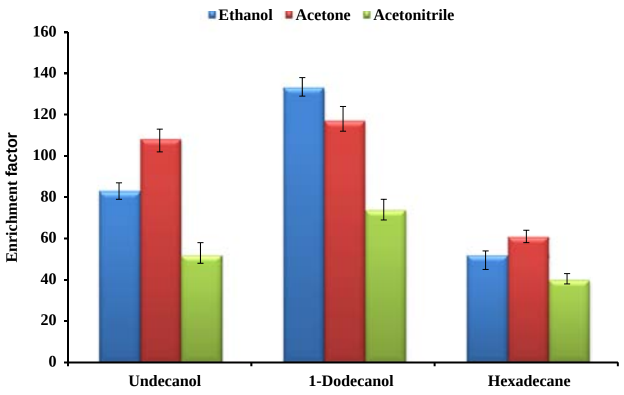

Fig. 1. Selection of extracting and dispersive solvents in DSLLME. Extraction condition: water sample volume, 5 mL; APDC amount, 0.08 ng mL^{-1}; pH=1; concentration of arsenic, 0.5 ng mL^{-1}.

Table 2
Investigated variables, their levels and symbols for FFD 2^{6-1} design.

Variables	Effect symbol	Variable levels	
		−1	+1
Volume of extraction solvent (μL)	E	30	100
Volume of disperser solvent (mL)	D	0.5	1.5
APDC Concentration (ng mL^{-1})	A	0.01	0.2
pH	P	1	6
Extraction time (min)	T	1	30
Salt concentration (w/v%)	S	0	5

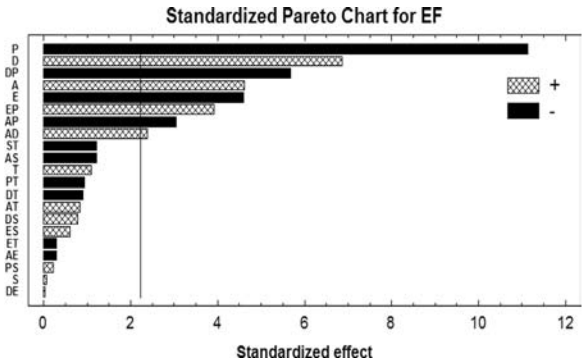

Fig. 2. Standardized (P=0.05) Pareto chart, representing the estimated effects of parameters and parameter interactions on enrichment factor.

The results obtained from half fractional factorial design (32 experiments) were evaluated by ANOVA (analysis of variance) at the 5% significance level. The pareto chart (Fig. 2) presents the results obtained from this evaluation. The length of the bars in the pareto chart is proportional to the absolute value of the standardized effects. A line in the pareto chart indicated the threshold for a test at level p=0.05 (for t_{crit}=2.23). All factors whose absolute values of the standardized effects are above critical t-value are statistically significant. Furthermore, the positive or negative sign (corresponding to a hachured or black bar filling) reveals the case when the response (enrichment factor) is enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific variable.

From the obtained results, pH, concentration of APDC, volume of extraction and disperser solvent showed statistically significant influence. Fig. 2 also reveals that the interaction of pH-APDC concentration, pH-extraction solvent volume, pH-dispersive solvent volume and APDC concentration-dispersive solvent volume appeared to have significant effect. The other variables (salt effect and extraction time) and all other interactions were not significant factors in the studied range. Therefore, extraction and disperser solvent volume, concentration of APDC and pH, as significant variables were further investigated in detail using CCD and multiple response analysis.

3.2.2. Response surface methodology

In this step, RSM was applied to fulfill following purpose: optimization of the significant factors in order to obtain the best results and obtain a predictive model which adequately represents changes in the response, depending on the input variables.

Among the standard designs used in RSM, the CCD represents a good choice because of its high efficiency with respect to the number of required runs [35]. The full fractional central composite face centered design for these four factors was applied in order to optimize the level of effective parameters for improving the sensitivity of arsenic extraction by dispersive-solidification liquid–liquid microextraction. The total number of design point needed (N) is determined by the following equation:

$$N=2^f+2f+C_p \tag{2}$$

where f is the number of variables and C_p is the number of center point [36]. Therefore, totally 30 experiments had to be run for the CCD (C_p=6). The low and high levels of these factors were as follow: extraction solvent volume (30–100 μL), dispersive solvent volume (0.5–1.5 mL), concentration of APDC (0.01–0.2 ng mL^{-1}) and pH (1–6).

Based on the results of the performed experiments the second-order polynomial equation was obtained as shown in the following equation:

$$\begin{aligned} EF=&\beta_0+\beta_1E+\beta_2D+\beta_3A+\beta_4P+\beta_{11}E^2+\beta_{12}ED+\beta_{13}EA+\beta_{14}EP\\ &+\beta_{22}D^2+\beta_{23}DA+\beta_{24}DP+\beta_{33}A^2+\beta_{34}AP+\beta_{44}P^2\\ &\beta_0=65.415;\quad \beta_1=-0.125;\quad \beta_2=182.882;\\ &\beta_3=217.047;\quad \beta_4=-12.307;\quad \beta_{11}=-0.003;\\ &\beta_{12}=0.046;\quad \beta_{13}=0.357;\quad \beta_{14}=0.045;\\ &\beta_{22}=-88.947;\quad \beta_{23}=25;\quad \beta_{24}=-1.45;\\ &\beta_{33}=-1632.89;\quad \beta_{34}=-6.052;\quad \beta_{44}=-0.038 \end{aligned} \tag{3}$$

This model consists of four main effects, six two-factor effects and four curvature effects, where the β_0 is the intercept and the β_1–β_{44} terms represent those parameters of the model which are optimized iteratively to fit, or model the data. The coefficients of determination (R^2 and adjusted-R^2) were applied to express the quality of fit of the polynomial model equation. R^2 is a measure of the amount of variation around the mean explained by the model and equal to 0.9753. The adjusted-R^2 is adjusted for the number of terms in the model. It decreases as the number of terms in the model increases, if those additional terms do not add value to the model. It is equal to 0.9523.

In Eq. (3), the positive and the negative coefficients of the main effects show that how the response changes regarding these variables. The absolute value of a coefficient shows the effectiveness of the related effect. For the graphical interpretation of the interactions, the use of three-dimensional (3D) plots of the model is highly recommended [37–40]. Therefore, the results were interpreted based on the 3D graphs obtained from the model. Fig. 3 shows 3D response surfaces and contour plots of the model. The responses were mapped against two experimental factors while the other factors are held constant at its central level.

Fig. 3a–c shows that by increasing the volume of the extraction solvent, the enrichment factor decreases. It is because of the increase in the volume of floating organic phase. Increasing the floating organic phase volume leads to decrease of concentration of arsenic in the floating phase, therefore, enrichment factor decreases. Fig. 3a, d and e shows that the efficiency increases by increasing the disperser solvent volume in the range of 0.5–1 mL. This is related to more properly dispersion of extraction solvent in aqueous solution. But from 1 to 1.5 mL the efficiency decreases. This behavior can be attributed to the increase of As–PDC complex solubility in water. In Fig. 3b, d and f, by increasing the APDC concentration: in the range of 0.01–0.08 ng mL^{-1} the enrichment factor increases, but from 0.08 to 0.2 ng mL^{-1} it decreases. In the first part, by increasing of APDC concentration, more As–PDC complex forms and extracts to organic solvent. In the second part, decrease in the extraction efficiency may be related to the extraction of the chelating agent itself, which can easily saturate the small volume of extraction solvent [41]. From Fig. 3c, e and f, it is obvious that the efficiency of extraction decreases by increasing the pH of the aqueous solution. This is because the formation of hydrophobic chelate of As(III) with APDC and subsequent extraction into organic phase decrease by increasing the pH.

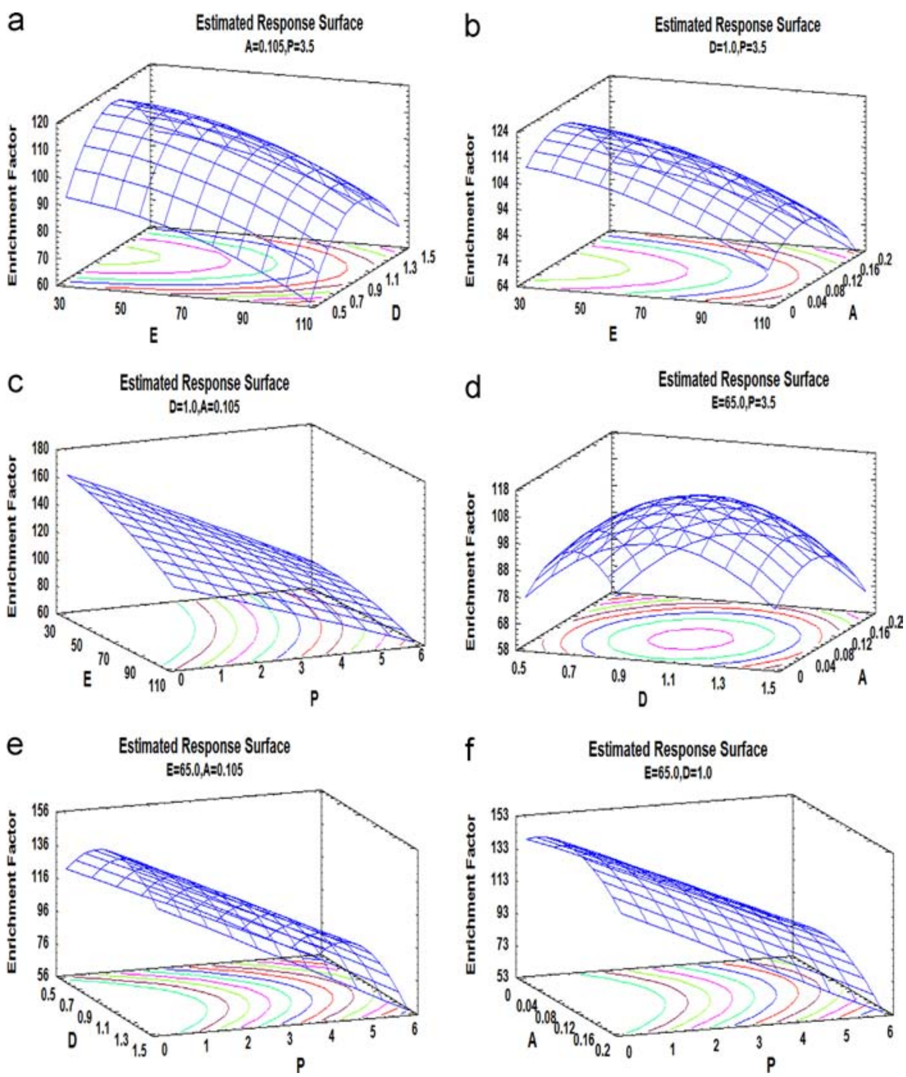

Fig. 3. Estimated response surfaces with related contours by plotting enrichment factor versus (a) extraction solvent volume (E) and dispersive solvent volume (D); (b) extraction solvent volume (E) and APDC concentration (A); (c) extraction solvent volume (E) and pH (P); (d) dispersive solvent volume (D) and APDC concentration (A); (e) dispersive solvent volume (D) and pH (P); (f) APDC concentration (A) and pH (P).

Table 3
Tolerance limits of some coexisting ions in determination of 0.5 ng mL^{-1} As in water samples using DSLLME-ETAAS.

Ion	Added as	Tolerance limits (μg mL^{-1})
Na^+	NaCl	10,000
K^+	KCl	10,000
Ca^{2+}	$CaCl_2$	2000
Mg^{2+}	$MgSO_4$	2000
Ba^{2+}	$BaCO_3$	2000
Zn^{2+}	ZnO	100
Cu^{2+}	$CuSO_4$	100
Pb^{2+}	$Pb(NO_3)_2$	20
Al^{3+}	$AlCl_3$	10
Fe^{3+}	$FeCl_3$	10
Cl^-	NaCl	10,000
NO_3^-	KNO_3	10,000
SO_4^{2-}	Na_2SO_4	10,000

After the analysis of results, the following conditions were selected as optimal working conditions to evaluate the performance of the extraction procedure for arsenic: 30 μL of 1-dodecanol as extraction solvent, 1 mL of ethanol as dispersive solvent, 0.08 ng mL^{-1} of APDC as chelating agent, pH = 1, 1 min as extraction time and 0 w/v% of salt.

3.3. *Influence of coexisting ions*

This stage was performed in order to consider the interference of some common coexisting ions in environmental water samples. The interferences are due to the competition of other heavy metal ions for chelating with APDC and their subsequent co-extraction with As(III). The concentration of arsenic was fixed at 0.5 ng mL^{-1} and different amount of foreign ions were treated according to recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount leading to recoveries of As(III) less than 90%, were given in Table 3. As can be seen, the interferences had no obvious influence on the recovery of the analyte.

3.4. *Analytical performance*

Inorganic arsenic speciation performance of the dispersive-solidification liquid–liquid microextraction method was investigated in application of this method in determining for each A(III) and As(V) solution at 0.1, 0.2, 0.3, 0.4 and 0.5 ng mL^{-1} concentrations and mixture solutions of them in water samples.

As can be seen in Fig. 4a, solutions containing only As(V) had no significant absorbance signal, because As(V) does not react with APDC therefore does not extract into the organic phase. The results of the measurements of solutions containing only As(III) after the extraction procedure (Fig. 4b) confirm the complex formation and extraction of As(III). Fig. 4c, which are for the measurements of the mixture solutions of the species before the reduction of As(V) to As(III), confirms the good separation of As(III) from As(V) in the extraction method. The results of ETAAS measurements of the mixture solutions of both species after reduction step shown in Fig. 4d also indicate the agreement of all findings with the assumption.

In the optimum conditions, a calibration curve was obtained by preconcentration series of 20 solutions according to the dispersive-solidification liquid–liquid microextraction method. The linear dynamic range (LDR) was obtained between 0.08 and 2 ng mL^{-1} with linear regression correlation coefficients greater than 0.99. The regression equation was $A = 0.782C_{As} + 0.013$, where A is the absorbance (peak area) and C_{As} is arsenic concentration in ng mL^{-1}. The limit of detection (LOD) by the recommended procedure was calculated as 0.02 ng mL^{-1} for arsenic, based on three times the standard deviation ($3S_b/m$) of the concentrations measured in 10 analytical blanks. The S_b and m are standard deviations of blank and calibration curve slope, respectively. Enrichment factor for 5 mL sample solution and relative standard deviation (RSD) for six replicate measurements of 0.5 ng mL^{-1} As was 135 and 5.3%, respectively.

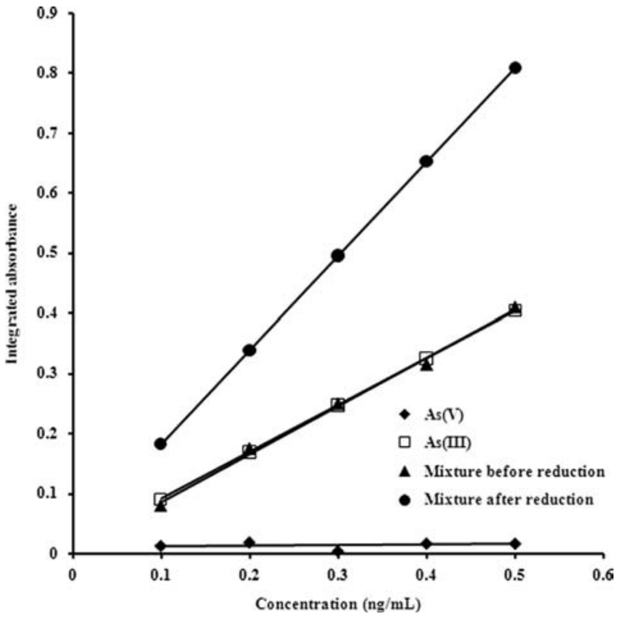

Fig. 4. Results of experiments for speciation performance, determination by ETAAS after the DSLLME process ($n=5$): (a) only As(V) solution; (b) only As(III) solution; (c) mixture of As(III) and As(V) solution before reduction procedure; (d) mixture of As(III) and As(V) solution after reduction procedure.

A comparison of the represented method with other approaches reported in the literature for speciation of arsenic in water samples by ETAAS is given in Table 4. In comparison with other preconcentration methods, the enrichment factor and the detection limit obtained by the dispersive-solidification liquid–liquid microextraction are comparable to or better than other reported methods. In comparison with Ref. [24, 25], low density, low toxicity and more environmental friendly organic solvents were used as extraction solvent in the DSLLME. Moreover, the solidification of floating organic solvent prompted the phase transferring. The higher enrichment factor and the lower detection limit in some literatures (e.g. [26]) were obtained using a large volume of sample solution during long extraction time, also these methods have higher RSD (lower precision). In general, this methodology is a simple, rapid, reproducible and low cost technique and with no requirement for complex equipment. These characteristics are key interest for routine trace analysis in laboratories.

3.5. Environmental water samples analysis

It is essential to determine the trace amount of arsenic in water samples from the environmental view point. In demonstrating the performance of the proposed dispersive-solidification liquid–liquid microextraction technique, this method was applied for the determination of As(III) and As(V) in several environmental water samples.

In order to determine As(III) and As(V) in real samples, the sample was split into two aliquots. As(III) was determined in one portion as described above, whereas the sum of As(III) and As (V) was determined in the other portion after pre-reduction of As (V) to As(III) with 1 mL of a 1% (w/v) of sodium thiosulphate solution and 1 mL of 0.5% (w/v) of potassium iodide solution [26,30,31]. The concentration of As(V) was calculated as the difference.

Except for the drinking water sample, the concentration of arsenic in the sea, rivers and tap water samples was detected. Different real samples were spiked exactly at the beginning of each procedure with As(III) and As(V) standards to assess matrix effects. The relative recoveries for above species in real water samples at spiking level of 0.5 ng mL^{-1} are listed in Table 5. The values of recoveries have confirmed the validity of the proposed method.

Table 4
Characteristic performance data obtained by using DSLLME and other techniques in determination of arsenic in water samples.

Method	LOD[a] (ng mL^{-1})	RSD[b] (%)	Enrichmet factor	Time[c] (min)	Sample consumption (mL)	Calibration range (ng mL^{-1})	Reference
CPE[d]-ETAAS	0.01	4.9	53	5	10	0.02 – 0.35	[17]
DLLME[e]-ETAAS	0.04	3.1	45	5	5	0.1 – 10	[24]
DLLME-ETAAS	0.01	3.1	115	5	5	0.06 – 2	[25]
SFDME[f]-ETAAS	0.01	8.6	1000	40	20	0.1 – 0.7	[26]
LPME[g]-ETAAS	0.05	8.6	150	7	2	0.05 – 4	[42]
DSLLME-ETAAS	0.02	5.3	135	< 3	5	0.08 – 2	This work

[a] Limit of detection.
[b] Relative standard deviation.
[c] The required time for completed extraction process.
[d] Cloud point extraction.
[e] Dispersive liquid–liquid microextraction.
[f] Solidification of floating organic drop microextraction.
[g] Liquid phase microextraction.

Table 5
Determination of inorganic As species in real and spiked water samples (Mean ± SD, $n=3$).

Sample	Sample results			Spiked recovery			
	Total As (ng mL^{-1})	As(III) (ng mL^{-1})	As(V) (ng mL^{-1})	As(III)		As(V)	
				Added (ng mL^{-1})	Recovery (%)	Added (ng mL^{-1})	Recovery (%)
Caspian sea water	0.85 ± 0.04	0.16 ± 0.01	0.69 ± 0.04	0.5	97.7 ± 4.6	0.5	96.1 ± 6.3
Haraz river water	3.29 ± 0.16	1.24 ± 0.07	2.05 ± 0.09	0.5	99.3 ± 3.8	0.5	98.3 ± 5.5
Tajan river water	1.26 ± 0.07	0.59 ± 0.03	0.67 ± 0.05	0.5	97.1 ± 5.1	0.5	98.4 ± 6.8
Tap water	0.41 ± 0.02	0.10 ± 0.01	0.31 ± 0.02	0.5	101.1 ± 1.9	0.5	99.7 ± 4.6
Drinking water	< LOD	< LOD	< LOD	0.5	99.3 ± 3.8	0.5	99.6 ± 2.8

Additionally, the accuracy of the proposed methodology was evaluated by analyzing a standard reference material (SRM) 1643e from NIST (trace elements in water); with a certified arsenic content of 60.45 ± 0.72 ng mL^{-1}. This certified value is compared to the obtained results (61.58 ± 2.84 ng mL^{-1}, $n=3$) by measuring the arsenic content in CRM with the proposed technique. As the certificate value was within the 95% confidence interval about the mean of the experimentally determined value, there is no significant difference between the values. It can be concluded that the proposed method is accurate and free from systematic errors.

4. Conclusion

This study illustrated the successful application of the dispersive-solidification liquid–liquid microextraction combined with palladium-modified tube graphite furnace atomic absorption spectrometry that allowed speciation of inorganic arsenic presented at low concentration levels in the environmental water samples. The chemometric approaches, fractional factorial and central composite design, were used to establish the optimal conditions for extraction of arsenic by DSLLME-ETAAS. The mathematical model and 3D response surfaces showed detailed effect of factors on each other and also on the extraction efficiency. This helped us to choose the best experimental conditions for the effective factors more precisely with minimal experimental trials. The resulting optimized procedure allowed for the quantification of ultra trace levels of arsenic in environmental water samples and standard reference material (SRM) 1643e (trace element in water) using DSLLME coupled to ETAAS. The main benefits of the DSLLME-ETAAS methodology for extraction and determination of arsenic were low sample consumption, minimum use of toxic organic solvent, short extraction time, rejection of matrix constituent, simplicity and high enrichment factor. Also, in comparison with DLLME this method uses different extraction solvents with lower density and toxicity.

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