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Analytica Chimica Acta 651 (2009) 57-63

Contents lists available at ScienceDirect



Analytica Chimica Acta



journal homepage: www.elsevier.com/locate/aca

Optimization of cloud point extraction and solid phase extraction methods for speciation of arsenic in natural water using multivariate technique

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ARTICLE INFO

Article history: Received 20 May 2009 Received in revised form 31 July 2009 Accepted 31 July 2009 Available online 8 August 2009

Keywords: Arsenic speciation Cloud point extraction Solid phase extraction methods Multivariate technique Electrothermal atomic absorption spectrometry

1. Introduction

Arsenic (As) is widely distributed in the environment, water, soils, sediments and rocks in its different forms $(As^{3+}, As^{5+} and organic species)$ [1]. The As is carcinogenic and may cause lung, bladder, liver, renal and skin cancer [2–6]. Knowledge of the speciation of As in natural water is important because the bioavailability, physiological and toxicological effects of As depend on its chemical form. Thus, it is most decisive to determine As species rather than the total amount of As in water samples [7–10].

In general, some direct instrumental techniques, such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), can only yield total amount of As [11]. In order to obtain the data about its chemical form, preliminary species separation and preconcentration are required before measurement by a sensitive detection technique [12–15]. For the speciation of inorganic As, the separation and pre-concentration methods reported in the litera-

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ABSTRACT

The simple and rapid pre-concentration techniques viz. cloud point extraction (CPE) and solid phase extraction (SPE) were applied for the determination of As^{3+} and total inorganic arsenic (iAs) in surface and ground water samples. The As^{3+} was formed complex with ammonium pyrrolidinedithiocarbamate (APDC) and extracted by surfactant-rich phases in the non-ionic surfactant Triton X-114, after centrifugation the surfactant-rich phase was diluted with 0.1 mol L^{-1} HNO₃ in methanol. While total iAs in water samples was adsorbed on titanium dioxide (TiO₂); after centrifugation, the solid phase was prepared to be slurry for determination. The extracted As species were determined by electrothermal atomic absorption spectrometry. The multivariate strategy was applied to estimate the optimum values of experimental factors for the recovery of As^{3+} and total iAs by CPE and SPE. The standard addition method was used to validate the optimized methods. The obtained result showed sufficient recoveries for As^{3+} and iAs (>98.0%). The concentration factor in both cases was found to be 40.

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ture are usually based on hydride generation, solid phase extraction (SPE), cloud point extraction, co-precipitation, ion exchange, chromatography and capillary electrophoresis [16,17]. Among them, the cloud point extraction (CPE) technique was used for the extraction of As species (As³⁺ and As⁵⁺), based on the phase separation of non-ionic surfactants in aqueous media [18–26]. For the determination of total inorganic As (iAs), the enrichment on solid phase (sorbent) from liquid phase (sample solution) is used [27–33]. These sample pre-concentration methodologies are simple, low cost, environmental friendly and provides high pre-concentration factor.

Several means of optimization can be used for the extraction of metals from different matrices, but these methods are time-consuming, because they required the study of each variable separately. Procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical and effective and allow more than one variable to be optimized simultaneously [34-36]. Among the different groups of designs, Plackett-Burman design (PBD), introduced in 1946 by Plackett and Burman [37] allow us to discover the most significant variables for a certain system with only few experiments [38,39]. They are used as a screening method in order to select the variables that have influence on a system but they do not give the optimum value for each variable. In order to obtain the optimum values for each significant variable involved in a certain system, central composite designs are frequently used for second-order RS modeling within k factor experiments [40].

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The aim of present study was to optimize and improve the CPE and SPE methods using multivariate technique for the determination of As³⁺ and iAs in natural water (surface and ground water). The accuracy of these methodologies has been validated by standard addition method. Total As contents were also determined in studied water samples and validated by a certified reference material of water (SRM 1643e). The optimized methodologies were applied for the determination of As³⁺ and iAs in surface and ground water samples of southern parts of Pakistan.

2. Experimental

2.1. Reagents and materials

The ultrapure water obtained form ELGA lab water system (Buchs, UK) was used throughout. The extracting solutions were prepared from analytical grade reagents and were checked for possible trace metal contamination. The stock standard solution of As³⁺ at a concentration of 1000 mg L⁻¹ was prepared by dissolving of As₂O₃ Merck (Darmstadt, Germany) in 1 M KOH and adjusting the pH to 7.0 with 50% HCl. Working standard solutions were prepared by stepwise diluting the stock solutions just before use. While the working standard solutions for total As were prepared by dilution of certified standard solution (1000 mg L⁻¹), obtained from Fluka (Buchs, Switzerland) in 0.2 M HNO3. Triton X-114 Sigma was used as the non-ionic surfactant. Ammonium pyrrolidine dithiocarbamate (Fluka) was used as the chelating agent to form the hydrophobic metal complexes. A 0.1% (w/v) of APDC solution was prepared by dissolving suitable amount of APDC in ultrapure water. Titanium (IV) dioxide (Merck, 99%, 0.5 µm) was utilized as a sorbent. The chemical modifiers $Mg(NO_3)_2$ stock standard solution, 2000 mg L^{-1} , prepared from Mg(NO₃)₂ (Merck), and Pd stock standard solution, 3000 mg L⁻¹, was prepared from Pd 99.999% Aldrich (Milwaukee, WI, USA). The working solution of modifiers was prepared by diluting 10 mL of each stock solution in 100 mL. The standard reference materials SRM 1643e (water) was purchased from National Institute of Standards and Technology (Gaithersburg, MD, USA). The pH of the sample solution was adjusted with 0.1 M HCl (Merck).

2.2. Instrumentation

A thermostatic water bath maintained at the desired temperatures (Gallankamp, Germany) was used to study temperature effects on cloud point extraction. The phase separation was assisted with a centrifuge ROWKA Laboratoryjna type WE-1, nr-6933 (Mechanika Phecyzyjna, Poland). Mechanical shaker (Gallankamp, England) was used for shaking. A pH meter (Ecoscan Ion 6, Kuala Lumpur, Malaysia) was employed for pH adjustments. A global positioning system iFinder GPS (Lowrance, Mexico) was used for marking the sampling locations. A programmable ultrasonic bath model No. SC-121TH (Sonicor, Deep park, NY, USA) was used for incubation with temperature ranging from 0 to 80 °C and intensification frequency 35 kHz.

The As³⁺ in CPE enriched micelle mediated phase and preconcentrated iAs contents were determined by a double beam Perkin Elmer model A Analyst 700 (Norwalk, CT, USA) atomic absorption spectrophotometer, equipped with a graphite furnace HGA-400, auto sampler AS-800 and deuterium lamp for background correction. Single element hollow cathode lamp of As operated at 7.5 mA was used as energy source. The arsenic signal was isolated at 193.7 nm with a spectral bandwidth of 0.7 nm and atomization was achieved in a pyrocoated graphite tube with integrated platform. The WinLab 32 software was used to acquire and process analytical data. The graphite furnace heating program was set for total As and iAs analysis as: drying, ashing, atomization and cleaning as temperature °C/(ramp time in s/holding time in s) (80–120/1/30, 300–600/10/20, 2200–2400/0/5 and 2400–2800/0/2), respectively. Whereas, for As³⁺ as (80–120/15/45, 550/160/20, 2000–2200/0/5 and 2200–2600/0/2), respectively. For all determinations, argon (200 mL min⁻¹) was used as a purge gas except during the atomization step. The 10 μ L of (standard or sample volume) and 10 μ L modifier (5 μ g Mg (NO₃)₂ + 3 μ g Pd) were injected to electrothermal graphite atomizer.

2.3. Sampling and pretreatment

The water samples of different origin (surface and ground water) were collected in 2007 on alternate month from 30 sampling sites of each ecosystem of Sukkur, Sindh (southern part of Pakistan) with the help of Global positioning system (GPS). The sampling network was designed to cover a wide range of determinates of whole district including surface and ground water sources. From each sampling site, a fresh surface water samples (canal) were collected from main stream of five to six different sampling points at the depth of 20–30 cm. Whereas, the ground water samples (tube well, depth > 60 m) and hand pump (depth > 15 m) were collected. The samples were collected in Van Dorn plastic bottles (1.5 L capacity) and were kept in well stoppered polyethylene plastic bottles previously soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. All water samples were stored in insulated cooler containing ice and delivered on the same sampling day to laboratory for the analysis of As³⁺ and iAs, to avoid risk of transformation of species as reported elsewhere [41].

2.4. Analytical procedures

2.4.1. Determination of total As

Total As was determined in surface (canal) and ground (hand pump and tube well) water samples pre-concentrated five times at 70 °C on an electric hot plate. The concentrated water samples were filtered and kept at 4 °C till further analysis. For accuracy certified reference sample of water (SRM 1643e), with certified value of total As was treated as described in our previous work [42,43].

2.4.2. Cloud point extraction of As^{3+}

The As³⁺ was determined by CPE, using a complexing reagent, APDC and resulted complex was entrapped in Triton X-114. To optimize CPE, six replicate of sub-samples (1–2 mL) of canal water, spiked with and without known standards taken in PTFE tubes (25 mL in capacity). The pH was set in the range of (2–6), added 0.001–0.01% (w/v) APDC and 0.05–0.2% (v/v) Triton X-114 to the content of the tubes and heated in a thermostatic water bath at 20–60 °C for 5–15 min. The mixture was centrifuged at 4000 rpm for phase separation (5 min) and then cooled in an icebath for 10 min to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was carefully removed with a pipette. For the formation of surfactant-rich phase, added 0.5 mL of 0.1 M HNO₃ in methanol, to reduce its viscosity before ETAAS determination at optimum condition as reported in Section 2.2.

2.4.3. Determination of total inorganic arsenic

The factorial design was carried out to determine the optimal experimental conditions for total inorganic arsenic (iAs) by solid phase extraction using TiO_2 as adsorbent. To optimize the different analytical variables, six replicate of a sub-sample of canal water in volume ranged (10–50 mL) were taken in flasks (100 mL in capacity), with and without spiking known amount of analyte and added solid TiO_2 (10–30 mg) separately. Then adjusted the pH

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Table 1	
Variables and levels used in the factorial design for As ³⁺ and total iAs.	

Variables	Symbol	Low (-)	High (+)
Surfactant (%)	S	0.05	0.2
Complexing agent (%)	С	0.001	0.01
рН	Р	2	6
Incubation time (min)	Ι	5	15
Temperature (°C)	Т	20	60
Volume of sample (mL)	V	1	2
Total inorganic arsenic (iAs)			
Mass of adsorbent (mg)	Μ	5	30
Temperature (°C)	Т	20	60
рН	Р	1	4
Ultrasonic exposure time (min)	U	5	15
Volume of sample (mL)	V	10	50

(1-4) using 0.5 M HCl (Table 1). The flasks were placed inside the ultrasonic water bath and were subjected to ultrasonic energy at 35 kHz for different ultrasonic exposure time interval (5–15 min). The temperature range of ultrasonic water bath was 20–60 °C. The sample solutions were centrifuged, to separate the solid residue, then added 5 mL of ultrapure water and placed in ultrasonic bath for 2 min to form slurry. Then slurry with modifier was injected into a graphite tube by an autosampler. The same procedure was applied for blank.

2.4.4. Estimation of As^{5+}

The concentration of As^{5+} could not be determined directly according to the above analytical procedure, but its concentration was calculated as the difference of iAs and As^{3+} .

2.5. Procedure used in the factorial design

2.5.1. The fractional factorial design test

For the evaluation of six and five factors for As^{3+} and iAs, at two levels Plackett–Burman designs with only 16 and eight experiments were described instead of the $2^6=64$ and $2^5=32$, respectively, required for full factorial designs. The Plackett–Burman matrix shown in Tables 2a and 2b, where the low (–) and high (+) levels are those specified in Table 1. The resulting values for both experiments (1–16) and (1–8) being of six replicates of each. The experimental data were evaluated with the help of Minitab 13.2 (Minitab Inc., State College, PA, USA) and STATISTICA computer program 2007.

2.5.2. Optimization plan

For optimization of proposed methods (CPE and SPE), a central 2^3 +star orthogonal composite design with 6 degrees of freedom

Table 2a

Design matrix and the results of As^{3+} %extraction (n=6).

Experiments	A(S)	B (<i>C</i>)	C (P)	D (1)	E (<i>T</i>)	F (V)	%Recovery
1	+	_	_	_	+	_	50.2 ± 1.20
2	+	+	_	_	_	+	71.1 ± 2.40
3	+	+	+	_	_	_	54.9 ± 3.30
4	+	+	+	+	_	_	67.1 ± 1.50
5	-	+	+	+	+	_	98.9 ± 0.95
6	+	_	+	+	+	+	47.2 ± 1.40
7	-	+	_	+	+	+	70.4 ± 1.60
8	+	_	+	_	+	+	25.7 ± 2.70
9	+	+	_	+	_	+	45.6 ± 1.80
10	-	+	+	_	+	_	42.4 ± 1.30
11	-	_	+	+	_	+	28.5 ± 1.45
12	+	_	_	+	+	_	41.5 ± 2.20
13	-	+	_	_	+	+	46.6 ± 1.30
14	-	_	+	_	_	+	23.5 ± 2.10
15	-	_	_	+	_	_	33.5 ± 1.70
16	-	-	-	-	-	-	26.5 ± 1.15

Table 2b				
Design matrix and	the results	of iAs %ext	raction	(n=6).

Experiments	A (<i>M</i>)	B (U)	C (P)	D (<i>T</i>)	E (<i>V</i>)	%Recovery
1	+	_	_	+	_	98.8 ± 1.80
2	+	+	_	_	+	82.0 ± 2.14
3	+	+	+	-	-	60.0 ± 1.78
4	-	+	+	+	_	54.0 ± 2.84
5	+	-	+	+	+	72.0 ± 3.50
6	-	+	-	+	+	62.0 ± 1.55
7	-	-	+	-	+	40.0 ± 1.90
8	-	-	-	-	-	55.0 ± 2.20

Table 3a

Central 2³ +star orthogonal composite design (n = 16) for the set of (S), (C) and (P) in As³⁺.

Experiments	A (S)	B (<i>C</i>)	C (P)	(%) recovery
1	a S ⁰	_b c ⁰	cp ⁰	98.8 ± 1.40
2	_	_	_	35.2 ± 1.20
3	+	_	_	39.5 ± 2.40
4	-	+	_	39.7 ± 1.60
5	+	+	_	62.5 ± 3.10
6	_	_	+	25.0 ± 2.50
7	+	_	+	28.5 ± 1.80
8	-	+	+	97.5 ± 2.20
9	+	+	+	51.4 ± 1.90
10	$-S^{1}$	_b c ⁰	cp ⁰	32.0 ± 2.80
11	+s ²	_b c ⁰	cp ⁰	66.7 ± 2.30
12	_a s ⁰	$-c^{1}$	cp ⁰	42.0 ± 1.75
13	_a s ⁰	+c ²	cp ⁰	68.4 ± 1.45
14	_a s ⁰	_b c ⁰	$-p^1$	18.0 ± 5.80]
15	_a s ⁰	_b c ⁰	+p ²	38.5 ± 4.50
16	a S ⁰	hC0	c P ⁰	98.8 ± 2.50

Factors: 3, replicates: 6, design: 8, runs: 16, center points (total): $2^3 s^1 = -0.001\%$, $s^2 = 0.25\%$, $_a s^0 = 0.125\%$ $_b c^0 = 0.006\%$, $c^1 = -0.002\%$, $c^2 = 0.005\%$ $_c p^0 = 4.50$, $p^1 = 0.63$, $p^2 = 7.3$.

and involving 16 experiments were performed [44,45]. In present work the statistically significant variables (S, C and P) and (M, U and P) of CPE and SPE, respectively, were regarded as factors for optimization experiment (Tables 3a and 3b).

2.5.3. Calibration and sensitivity

Calibration and standard addition graphs were obtained for As^{3+} and iAs from the quantification limit up to $20 \ \mu g \ L^{-1}$ (seen in Table 4). The limit of detection (LOD) was defined as LOD = 3 s m⁻¹, where s is the standard deviation corresponding to 10 blank injections and m is the slope of the calibration graph. The LOD values

Table 3b Central 2^3 +star orthogonal composite design (n = 16) for the set of (M), (U) and (P) in total iAs.

Experiments	A (<i>M</i>)	C (P)	D (<i>T</i>)	%Rrecovery
1	_a m ⁰	_b u ⁰	cp ⁰	99.2 ± 2.60
2	-	_	-	32.0 ± 2.50
3	+	-	-	41.0 ± 2.30
4	-	+	-	35.2 ± 1.90
5	+	+	-	62.4 ± 1.40
6	-	-	+	38.3 ± 2.20
7	+	-	+	46.6 ± 1.60
8	-	+	+	34.2 ± 1.40
9	+	+	+	86.7 ± 2.70
10	m ¹	bp ⁰	ct ⁰	12.5 ± 3.40
11	+m ²	bp	ct ⁰	48.6 ± 4.20
12	_a m ⁰	P^1	ct ⁰	22.2 ± 2.80
13	_a m ⁰	+p ²	ct ⁰	68.8 ± 5.22
14	_a m ⁰	_b p ⁰	$-t^1$	22.7 ± 1.50
15	_a m ⁰	bp ⁰	+t ²	57.4 ± 1.20
16	_a m ⁰	bn 0	ct ⁰	99.5 ± 1.44

Factors: 3, replicates: 6, design: 8, runs: 16, center points (total): $2^3 m^1 = 3.18 mg$, $m^2 = 36.8 mg$, $_am^0 = 20 mg$, $_bp^0 = 2.5$, $p^1 = -0.02$, $p^2 = 5.02$, $_ct^0 = 40 \circ C$, $t^1 = 6.36 \circ C$, $t^2 = 73.6 \circ C$.

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Table 4

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Comparative data of Analytical characteristics of the SPE and CPE method for total inorganic arsenic (iAs) and As³⁺.

	Concentration range ($\mu g L^{-1}$)	slope	Intercept	Correlation coefficient (r)	$LOD/LOQ(\mu gL^{-1})$	Precision	^a EF
iAs [27]	0.10-5.0	-	-	0.9997	0.03/0.10	2.4% (<i>n</i> = 5)	20
This work	0.5–20	0.056	0.035	0.9998	0.02/0.066	<2.3% (<i>n</i> =6)	40
As ³⁺ [25]	0.1-20	0.008	0.02	0.998	0.04/0.13	3.0% (<i>n</i> = 11)	36
This work	0.2–20	0.278	0.152	0.999	0.03/0.11	<2.3% (<i>n</i> =6)	40

^a Enrichment factor.

Table 5

The results for tests of addition/recovery for As³⁺ and total iAs determination in water samples.

Sample	Species	Added concentration (۱	$\mu g L^{-1}$) Mean \pm Std ($\mu g L^{-1}$)	%Recovery		
Canal water, $n = 6$	As ³⁺	0.00	4.50 ± 0.10	-		
		2.5	6.94 ± 0.15	99.1		
		5.0	9.37 ± 0.21	98.6		
		10.0	14.3 ± 0.25	98.9		
	Total iAs	0.00	8.30 ± 0.15	-		
		2.5	10.6 ± 0.20	98.4		
		5.0	13.1 ± 0.26	98.8		
		10.0	18.1 ± 0.28	98.5		
Validation for total arsenic ($\mu g L^{-1}$)						
Certified value of SRM 1643e		Found values $\bar{x} \mp (ts/\sqrt{n})$	%Recovery (% RSD)			
60.45 ± 0.72 Paired <i>t</i> -test: <i>t</i> _{experiment} = 0.12,	c _{ertical} = 2.26 at 9	58.0 ± 1.65 95% confidence limit (<i>n</i> = 6)	97.4 (2.80)			

were 0.031 and 0.02 μ g L⁻¹ for As³⁺ and iAs, respectively. The comparative data of analytical characteristics (seen in Table 4) showed that other parameters of SPE and CPE viz. correlation coefficient (*r*), LOD/LOQ, precision and enrichment factor of present study was comparatively better than previously reported works [25,27].

To check the accuracy of the methodologies, spiking was performed in six replicate at three concentration levels (5, 10 and $20 \,\mu g \, L^{-1}$) of As³⁺ and iAs, for both methods separately (Table 5). The accuracy of total As was also checked by using standard reference material SRM 1643e (Table 5).

3. Results and discussion

3.1. Optimization of experimental variables

Considering the CPE procedure, six factors [volume of surfactant (*S*), mass of complexing agent (*C*), pH (*P*), incubation time (*I*), temperature (*T*) and volume of samples (*V*)] were selected to optimize the %recovery of As³⁺ (Table 2a). In same way, the variables chosen for iAs were mass of adsorbent (*M*), temperature (*T*), pH (*P*), ultrasonic exposure time (*U*) and volume of sample (*V*) with its %recovery as analytical responses by factorial designs are shown in Tables 2a and 2b. The data of both methods were evaluated by analysis of variance (ANOVA) and visualized by using standardized ($p \sim 95.0\%$) effects in Pareto chart (Figs. 1 and 2). The inference tests showed that the results produced at a minimum *t*-value (95.0% confidence interval) were 2.2 and 2.8 for As³⁺ and iAs, respectively. A factor is significant, when the *t*-value for certain factor is higher than the minimum observed *t*-values.

3.2. Estimated effects of variables for As^{3+} and iAs

As results shown in Pareto chart (Fig. 1) and Table 2a, the *S*, *C* and *P* are significant factor for CPE of As^{3+} . The %recovery of As^{3+} was found 47.2% in experiment 6, at (–) level of *C*, with optimum values of other variables. The pH of the sample solution was the next critical variable evaluated for its effect on the CPE of As^{3+} . It was observed that the %recovery of As^{3+} was about 45.6% at low (–) level of pH (experiment 9), with maximum level of other two

significant variables, C and S. Whereas, the optimum recovery of As^{3+} (98%) was observed in experiment 5, at (+) levels of *C*, *P*, *I* and *T*, while at (-) levels of S and V (Table 2a). It can be seen in experiment 4, *T* at (-) level produced 67.1% recovery of As^{3+} , while at (+) level in experiment 5, optimum recovery of As^{3+} was obtained. The most significant interaction between two variables was seen for A and C, while least relation was observed between variable B and D as shown in Pareto chart (Fig. 1).

For iAs the *M*, *T* and *P* were observed as the significant factors for optimum %recovery using SPE method. The maximum recovery of iAs (98.8%) was obtained in experiment 1, where *M* and *T* were at (+) levels, while *P* at (-) level. The two variables *M* and *T* at low level (-) shows that the recovery was only 40% in experiment 7, although C and E were at maximum levels. The two order interaction between A and C was found to be the most significant, whereas, least was obtained between A and E as shown in Pareto chart (Fig. 2).



Fig. 1. Pareto chart (As^{3+}) of the fractional factorial experimental design for the analysis of the variables: (*S*) surfactant (Triton X-114); (*C*) complex (APDC); (*P*) pH; (*I*) incubation time; (*T*) temperature; (*V*) volume.

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Fig. 2. Pareto chart (As total) of the fractional factorial experimental design for the analysis of the variables: (M) mass of TiO₂; (U) ultrasonic exposure time; (P) pH; (T) temperature; (V) volume.

3.3. Optimization by central composite design for As^{3+} and iAs

Having screened out the variables that did not have significant effect on the response of As^{3+} using six variables, the remaining three factors *C*, *S* and *P* were optimized to provide the maximum recovery. A central 2^3 +star orthogonal composite design with six degrees of freedom and involving 16 experiments was performed, to optimize these three variables. The variables that were shown to be insignificant by Plackett–Burman design were taken at fix values, volume of sample (2 mL), incubation time (10 min) and temperature (room temperature ~30 °C). The experimental field definition for this design is given in Table 1, while Table 3a shows the central composite design together with the %response obtained for As^{3+} for six replicate.

It was observed that at low level (-) of C, the recovery of As³⁺ was 28.5% (experiment 7) while it was 97.5% at (+) level (experiment 8, Table 3a). This step was not consistent with previous work, who reported that 0.01% of APDC might be preventing the micelle formation and the extraction efficiency [25]. Whereas, high (+) level of surfactant (at experiment 9, Table 3a), showed 40.4% of As³⁺ recovery, indicated that high amount of the surfactant increased the volume of the surfactant-rich phase that is acquired after centrifugation of the analyte. Therefore, the high amount of surfactant needed more solvent to reduce the viscosity, resulting in a loss of sensitivity. The surfactant volume > 0.12% (w/v), deteriorating the ETAAS signal. The pH is considered as third important factor for metal-chelate formation [46], the results indicated that high recovery of As³⁺ was obtained at pH > 2 (experiments 2 and 7), while, at average value (cp⁰), pH 4.5, the maximum recovery is seen (experiment 16, Table 3a). The study of estimated three dimension (3D) surfaces response for variables [S-P] and [C-P] was estimated by quadratic equation, indicated that the maximum %recovery of As³⁺ was observed at optimum values of complexing agent (0.007%), Triton X-114 (0.12%) and pH (4.5) as shown in Fig. 3a and b. As reported by Sun and Yang [47], that inorganic species of As⁵⁺ not frequently react with APDC, therefore, the interference of As⁵⁺ was negligible [26]. The estimated pH 4.5 for CPE procedure by central composite design was provided better results than previous study [25].

The central composite design matrices together with the response were also employed for iAs (Tables 2b and 3b). The M was a significant factor for %recovery of iAs by SPE method, which has a strong interaction between *T* and *P*. So, these three factors were optimized to provide the maximum recovery of iAs. A



Fig. 3. Three dimension (3D) surface response for %recovery of As^{3+} by CPE: (a) interaction b/w (pH-Triton X-114) and (b) interaction b/w (pH-APDC).

central 2^3 +star orthogonal composite design with 6 degrees of freedom, involving 16 experiments were performed to optimize these variables. The factors that were shown to be insignificant by SPE method were taken at fix values, *V* (20 mL) and *U* (10 min). The optimized study showed that the maximum %recovery of iAs was achieved at average concentration of *M* ($_{a}m^{0}$), as shown in experiment 1 and 16 (Table 3b). It was also reported in literature that, the high amount of TiO₂ may damages the graphite tube [25]. For further work, the optimum concentration (20 mg) of TiO₂ was chosen as a sorbent in the subsequent experiments. The other two significant variables D and C showed that optimum recovery of iAs was obtained at average level of both factors, 40 °C and 2.5, respectively.

Our experimental data is consistent with literature reported work that the adsorptions of ions on amphoteric oxides, such as TiO_2 , proceeds when the pH of the solution is lower than the isoelectric point of the oxide [23]. The estimation of three dimension

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Fig. 4. Three dimension (3D) surface response for %recovery of total As by TiO₂-slurry method: (a) interaction b/w (pH-mass of adsorbent) and (b) interaction b/w (temperature-mass of adsorbent).

(3D) response surfaces for each pair of variables, [T-M] and [P-M] were calculated by quadratic equation indicated that, M, T and P were 17.6 mg, 40.7 °C and 2.1, respectively, were required for maximum %recovery of iAs [Fig. 4a and b]. The estimated values of three significant variables are provided higher recovery of iAs than literature reported work [27].

3.4. Interference study

To evaluate the selectivity of the proposed methods for determination of trace levels of As^{3+} and iAs, the effect of typical potential interfering ions was investigated. The metallic ions, Na^+ and Cl^- (1000 mg), Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} and PO_4^{3-} (100 mg of each), Cu^{2+} , Co^{2+} , Se^{4+} , Ni^{2+} , Fe^{3+} , Al^{3+} and $Zn^{2+}(1.0 \text{ mg of each})$ were added to 1000 mL of sub-sample of surface and ground water separately

Table 6
Foreign ions effect on the % recoveries of 5.0 μgL^{-1} of As^{3+} and total iAs.

Ion	Concentration added, mg L ⁻¹	%Recovery of total iAs	%Recovery of As ³⁺
Na ⁺	1000	98	95
K+	100	99.2	98
Ca ²⁺	100	96	95
Mg ²⁺	100	97	94
Cu ²⁺	1.0	99.3	100
Co ²⁺	1.0	108	112
Ni ²⁺	1.0	110	117
Fe ³⁺	1.0	96	94
Al ³⁺	1.0	97	95
SO_4^{2-}	100	101	102
PO_4^{3-}	100	103	105
Cl-	1000	95	96

and subjected to corresponding methods. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than \pm 5%. The tolerance limits of various foreign ions are given in Table 6. These results demonstrated that excess amounts of common cations and anions do not interfere on the determination of trace quantities of As³⁺ and iAs while nickel and copper have positive effect (2–3%).

4. Applications

It is very important and necessary to determine trace amounts of As species in water samples. The optimized methods were employed for the determination of trace amounts of iAs and As³⁺ in 180 water samples of each involving canal, hand pump and tube well collected from south-west part of Pakistan. For comparative purposes total arsenic was also determined in all understudied water samples. The mean concentrations of different species of As expressed as $\bar{x} \mp ts/\sqrt{n}$, (n = 180 for each sampling origin) are shown in Table 7. The water bodies (especially underground) of studied area are seriously contaminated with As due to frequently use of pesticides and insecticides in agricultural lands as well as use of untreated waste water sewage sludge for dressing the agricultural land [47]. Due to unavailability of certified reference material of water for inorganic As species, therefore, standard addition method was used for validation and optimization of both methods.

The two set of six replicate sub-samples of a canal water, spiking with standard solution at three concentration levels $(2.5-10 \,\mu g \, L^{-1})$ of As³⁺ and iAs and applied both methods, CPE and SPE, respectively. The %recovery calculated as:

%recovery =
$$\frac{C_{\text{after spiking}}}{C_{\text{initial}} + C_{\text{spiked}}} \times 100$$

Table 7

Sample	Species	$Mean \pm Std (\mu g L^{-1})$
Canal water sample, <i>n</i> = 180	Total As Total iAs As ³⁺ As ⁵⁺	$\begin{array}{l} 8.90 \pm 2.80 \\ 8.40 \pm 4.10 \\ 4.80 \pm 2.60 \\ 3.60 \pm 1.70 \end{array}$
Hand pump water sample, <i>n</i> = 180	Total As Total iAs As ³⁺ As ⁵⁺	$\begin{array}{c} 62.0 \pm 41.0 \\ 58.0 \pm 33.6 \\ 24.5 \pm 13.50 \\ 33.7 \pm 13.60 \end{array}$
Tube well water sample, <i>n</i> = 180	Total As Total iAs As ³⁺ As ⁵⁺	$\begin{array}{c} 38.8 \pm 24.0 \\ 36.7 \pm 22.2 \\ 22.2 \pm 12.3 \\ 14.5 \pm 8.40 \end{array}$

The recoveries for As³⁺ and iAs spiked in the canal water samples studied were found to be >98% (Table 5), indicating no interference encountered from these sample matrices.

The obtained results showed significant differences among the concentration of different species of As in three sampling origins. All this provides evidence that anthropogenic and geological environment play a key role in the distribution of inorganic As species in understudy water bodies [48]. The concentration of iAs in three studied origins was obtained in increasing order: canal < tube well < hand pump (Table 7). The concentration of total As in canal, hand pump and tube well water samples was observed in the ranges of 6.10–11.7, 14.8–103 and 21.0–62.8 µg L⁻¹, respectively. Whereas, iAs was analyzed by SPE method was 5-10% lower than total As, indicated the less availability of organic As in surface and ground water, our results are consistent with other study [49]. The elevated level of all species in ground water samples (hand pump and tube well) might be due to the geological conditions [50]. But, in canal water samples the ratio of As³⁺ contents were higher than ground water samples (hand pump and tube well, Table 7), most probably due to anthropogenic contaminations [51].

5. Conclusions

The proposed cloud point extract and solid phase extraction methodologies for the determination of As³⁺ and iAs, respectively, were successfully optimized by multivariate technique. The detection limits and enrichment factors of As³⁺ and iAs were better than reported procedures [25,27]. The estimated values of three significant variables for CPE of As³⁺ were calculated from 3D surface response by quadratic equation to be found as [pH (4.5), C (0.007%)]and S(0.12%)]. Whereas for SPE of iAs were estimated as [pH (2.1), M(17.6 mg) and $T(40.7 \circ \text{C})$]. The synchronized foreign ions interferences and influence of organic compounds in environmental water sample using modifier $(Pd + Mg (NO_3)_2)$ show that the method is suitable for complicated matrix solutions. Speciation of arsenic in surface and ground water plays an important role in understanding arsenic exposure to human and animal health effects.

Acknowledgements

This work was supported by Higher Education Commission (HEC), Islamabad (Grant No. 20-1246/R&D/9) and we are gratified to Young Welfare Society Mughalabad (YWSM) Pakistan for their assistance in sampling.

References

- [1] M. Hall, Y. Chen, H. Ahsan, V. Slavkovich, A. van Geenc, F. Parvez, J. Graziano, Toxicology 225 (2006) 225-233.
- [2] J.A. Baig, T.G. Kazi, M.B. Arain, A.Q. Shah, R.A. Sarfraz, H.I. Afridi, G.A. Kandhro, M.K. Jamali, S. Khan, J. Hazard. Mater. 167 (2009) 745-751.
- [3] J.C. Igwe, A.A. Abia, Afr. J. Biotechnol. 5 (2006) 1167-1179.
- [4] M. Berg, S.P. Caroline, T.K.T. Pham, H.V. Mickey, L. Sampson, M. Leng, S. Samreth, D. Fredericks, Sci. Total Environ. 372 (2007) 413-425.
- [5] D. Chakraborti, M.M. Rahman, K. Paul, U.K. Chowdhury, M.K. Sengupta, D. Lodh, C.R. Chanda, K. Saha, S. Mukherjee, Talanta 58 (2002) 3-22.
- [6] M.V. Aldrich, J.R. Peralta-Videa, J.G. Parsons, J.L. Gardea-Torresdey, Sci. Total Environ. 379 (2007) 249-255
- [7] M. Prasenjit, B. Chandrajit, M.A. Bikash, J. Hazard. Mater. (2007) 420-426.

- [8] T. Ahmad, M.A. Kahlown, A. Tahir, H. Rashid, Arsenic an emerging issue, experiences from Pakistan, in: 30th WEDC International Conference, Vientiane, Lao PDR 2004
- [9] B. Sharestha, Drinking water quality: future directions for UNICEF in Pakistan Consultancy Report 2 of 3, Water Quality, SWEET Project, UNICEF Pakistan, Islamabad, 2002
- [10] L. Pei, L. Rui, Anal. Chim. Acta 602 (2007) 32-36.
- [11] J.A. Baig, T.G. Kazi, M.B. Arain, H.I. Afridi, G.A. Kandhro, R.A. Sarfraz, M.K. Jamali, A.Q. Shah, J. Hazard. Mater. 166 (2009) 662–669.
- [12] H.G. Seiler, A. Sigel, H. Sigel, Handbook on Metals in Clinical and Analytical Chemistry, Marcel Dekker, New York, 1994
- [13] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I. Afridi, A. Shah, Chemosphere 70 (2007) 1845-1856.
- [14] J. Michon, V. Deluchat, R.A. Shukry, C. Dagot, J. Bollinger, Talanta 71 (2007) 479-485
- [15] S. Wang, C.N. Mulligan, Environ. Geochem. Health 28 (2006) 197-214.
- [16] S. Hirata, H. Toshimitsu, Anal. Bioanal. Chem. 383 (2005) 454-460.
- [17] R. Murata, T. Shimizu, N. Uehara, Bunseki Kagaku 54 (2005) 831-836.
- [18] A. Sanz-Medel, M.R.F. Conzalez, M.L. Fernandez-Sanchez, Spectrochim. Acta Part B 54 (1999) 251-287.
- [19] M.A. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, Appl. Spectrosc. Rev. 40 (2005) 269-299 [20] M.G. Pereira, M.A.Z. Arruda, Microchim, Acta 141 (2003) 115–131.
- [21] J.R. Chen, K.C. Teo, Anal. Chim. Acta 450 (2001) 215-222.
- [22] J. Chen, K.C. Teo, Anal. Chim. Acta 434 (2001) 325-330.
- [23] E.K. Paleologos, D.L. Giokas, S.M. Tzouwara-Karayanni, M.I. Karayannis, Anal. Chim. Acta 458 (2002) 241-248.
- [24] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernandez, Talanta 51 (2000) 123-129.
- [25] A. Tang, G. Ding, X. Yan, Talanta 67 (2005) 942-946. [26] Q. Zhang, H. Minami, S. Inoue, Anal. Chim. Acta 508 (2004) 99-105.
- [27] L. Zhang, D. Ishi, K. Shitou, Y. Morita, A. Isozaki, Talanta 68 (2005) 336–342.
- [28] L. Zhang, Y. Morita, K. Yoshikawa, A. Isozaki, Anal. Sci. 23 (2007) 365-369.
- [29] Z. Wang, Z.M. Ni, D.R. Qiu, T.Y. Chen, G.Y. Tao, P.Y. Yang, J. Anal. Atom. Spectrom. 19 (2004) 297-300.
- [30] P. Cava-Montesinos, M.L. Cervera, A. Pastor, M.D. Guardia, Talanta 62 (2004) 173 - 182
- [31] M.J. Cal-Prieto, M. Felipe-Sotelo, A. Carlosena, J.M. Andrade, P. Lopez-Mahia, S. Muniategui, D. Prada, Talanta 56 (2002) 1-51.
- [32] I. Nukatsuka, Y. Shimizu, K. Ohzeki, Anal. Sci. 20 (2004) 1033–1036.
- [33] H. Minami, M. Yada, T. Yoshida, Q. Zhang, S. Inoue, I. Atsuya, Anal. Sci. 20 (2004) 455-459.
- [34] D.C. Montgomery, Design and Analysis of Experiments, 4th ed., Wiley, New York. 1997.
- [35] S.N. Deming, S.L. Morgan, Experimental Design: a Chemometrics Approach, Elsevier, Amsterdam, 1987.
- [36] S.L.C. Ferreira, W.N.L. dos Santos, M.A. Bezerra, V.A. Lemos, J.M. Bosque-Sendra, Anal. Bioanal. Chem. 375 (2003) 443–449. [37] D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, F. Kaufman, Chemo-
- metrics: a Textbook, Elsevier, Amsterdam, 1988.
- [38] N. Jalbani, T.G. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, S.T. Sheerazi, R. Ansari, J. AOAC Int. 90 (2007) 1682-1688.
- [39] B. O'Shea, J. Jankowski, J. Sammut, Sci. Total Environ. 379 (2007) 151-166.
- [40] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I. Afridi, R.A. Sarfraz, A.Q. Shah, Spectrosc. Lett. 40 (2007) 861-878.
- [41] B. Izgi, U.C. Demir, S. Gucer, Spectrochim. Acta Part B 55 (2000) 971-977.
- [42] Z. Gong, X. Lu, M. Mingsheng, W. Corinn, X.C. Le, Talanta 58 (2002) 77-96.
- [43] M.B. Arain, T.G. Kazi, J.A. Baig, M.K. Jamali, H.I. Afridi, A.Q. Shah, N. Jalbani, R.A. Sarfraz, Food Chem. Toxicol. 47 (2009) 242-248.
- [44] AOAC, Association of Official Analytical Chemists, Official Methods of Analysis, 16th ed., AOAC International, Gaithersburg, MD, 1995 (March 1998 revision).
- [45] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. de Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics Part A, Elsevier, Amsterdam, 2003.
- [46] M. Soylaka, I. Narina, M.A. Bezerrac, S.L.C. Ferreira, Talanta 65 (2005) 895-899.
- Y.C. Sun, J.Y. Yang, Anal. Chim. Acta 395 (1999) 293-300. [48] M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N. Jalbani, A.R. Memon, A. Shah,
- Environ. Chem. Lett. 5 (2007) 209-218. [49] E.A. Crecelius, The geochemistry of arsenic and antimony in Puget Sound and
- Lake Washington, Washington Ph.D. Thesis, University of Washington, Seattle, WA. 1974.
- [50] O.S. Thirunavukkarasu, T. Viraraghavan, K.S. Subramanian, S. Tanjore, Urban Water 4 (2002) 415-421
- [51] P.L. Smedley, H.B. Nicolli, D.M.J. Macdonald, A.J. Barros, J.O. Tullio, Appl. Geochem, 17 (2002) 259-284.