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Arsenic speciation in water and snow samples by adsorption onto PHEMA in a micro-pipette-tip and GFAAS detection applying large-volume injection

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ABSTRACT

A miniaturized solid phase extraction procedure has been developed for ultra-trace determination of inorganic arsenic species. Arsenic(III) as pyrrolidinedithiocarbamate complex was selectively adsorbed on 30 mg poly(hydroxyethyl methacrylate) (PHEMA) micro beads, which is simply packed into a micro-pipette-tip. The adsorbed arsenic was quantitatively eluted by 700 μL 0.25 M NH_3 and determined by graphite furnace atomic absorption spectrometry (GFAAS). Injection of larger volume (i.e., 50 μL v.s. conventional 10–20 μL) eluent into graphite furnace and the use of $Mg(NO_3)_2$ as chemical modifier have improved atomic absorption signal intensity (sensitivity as characteristic mass of 25 pg) and precision (RSD of 2.6%, $c=10\ \mu g\ L^{-1}$, $n=11$). Total arsenic amount was determined after reduction of arsenic(V) to arsenic(III) by thiourea-HCl system. As(V) concentration was calculated by the difference between As(III) and total arsenic. The detection limit (3 s) of the method was found as $10\ ng\ L^{-1}$ As(III) with an enrichment factor of 86. The relative standard deviation and relative error for six replicate determinations of $0.5\ \mu g\ L^{-1}$ As(III) were found to be 4.0% and −0.7%, respectively. The method was successfully applied to drinking water, snow and reference water (SEM-2011) samples. When the samples were spiked with 0.5 and $1.0\ \mu g\ L^{-1}$ As(III) and As(V), the recoveries varied between 96 and 100%.

1. Introduction

Arsenic is described as a metalloid and a ubiquitous element in the environment. Arsenic levels in the environment originate from weathering of arsenic-containing minerals and human activities. Exposure to arsenic, even at very low amounts, can cause a variety of health problems, thus highly concerned as a toxin and carcinogen [1]. On the other hand, toxicity of arsenic depends on its chemical form; inorganic arsenic species are more toxic than their organic counterparts and inorganic trivalent form [As(III)] is more toxic than the pentavalent one [As(V)]. Inorganic forms of arsenic in the environment mainly appear in water samples and fallings. Therefore, precise determination of minute amounts of different arsenic species in real samples is absolutely necessary to estimate the environmental impact and potential health risks.

The instrumental techniques used for arsenic determination, such as hydride generation atomic absorption spectrometry (HGAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS), can yield only total amount rather than its chemical forms. The techniques for preliminary separation of species by chromatographic or electrophoretic techniques such as liquid chromatography (LC), gas chromatography (GC) and capillary electrophoresis (CE) and coupling/hyphenation of these techniques to element specific detectors [2–4] have attracted great interest in elemental speciation analysis. Although hyphenated techniques [5] serve many advantages in terms of analytical figures of merit, operating costs and instrument prizes and are quite high for many laboratories. The techniques necessitate special interfaces and experienced operators as well. On the other hand, chemical speciation based on non-chromatographic methodologies, such as solid phase extraction (SPE), liquid–liquid extraction (LLE), supercritical fluid extraction (SFE), cloud point extraction (CPE), co-precipitation and hydride generation (HG), are continuously growing, because they offer simple, inexpensive and efficient possibilities for trace elemental speciation [6,7]. SPE allows not only selective enrichment of inorganic ions but also elimination of matrix in real-world samples prior to determination step by GFAAS [8]. SPE, especially in the miniaturized form, provides some important advantages such as simplicity, effectiveness, rapidity and cheapness. Besides, the method is environment- and user-friendly due to the low solvent usage/exposure and the adsorbent reusing.

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Many different materials such as palladium nanoparticles [9], titanium dioxide [10], carbon nano tubes [11], biomass-coated resin [12], modified silica [13–15], carbon nanofibers [16], C-18 sorbent [17], titania immobilized hollow fiber [2], manganese dioxide [3], have been used as solid phase support for preconcentration of arsenic species in water samples. Poly(hydroxyethyl methacrylate), PHEMA, is a methacrylate based polymer with relatively hydrophobic character [18]. It has previously been used as solid phase material for the adsorption of inorganic ions in diverse applications, such as selective Cu(II) adsorption after imidazole attachment [19], extraction of Pb(II) [20] and Cd(II) [21] after ion imprinting. However, PHEMA has not yet been used for selective adsorption of ions after complexation. Since aliphatic carbon chains make PHEMA partly hydrophobic, it is expected to adsorp metal or metalloids after complexation by hydrophobic chelates such as ammonium pyrrolidinedithiocarbamate (APDC). In this study, PHEMA was simply packed into a micro-pipette-tip to apply a miniaturized SPE procedure for preconcentration of very low amount of arsenic species in snow and water samples prior to determination by GFAAS. In the detection part, injection of large-volume sample to graphite tube and use of $Mg(NO_3)_2$ as chemical modifier have been evaluated to increase sensitivity and precision.

2. Experimental

2.1. Apparatus

A Perkin Elmer AAnalyst 100 atomic absorption spectrometer (Norwalk, CT, USA) equipped with deuterium lamp background corrector and a HGA-800 graphite furnace atomizer was used for arsenic determination. Graphite tubes (Perkin Elmer Part No. B010-9322) were pyrolytically coated. Argon, 99.996% purity, as sheat gas was purchased from Mitan (Ankara, Turkey). All the absorbance measurements were performed by integrating peak areas. Operating parameters and graphite furnace temperature program for arsenic determination were given in Table 1. Ultrapure water was produced in a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed-bed system.

2.2. Reagents and solutions

The stock aqueous solutions (1000 mg L^{-1}) of As(III) and As(V) were prepared by dissolving appropriate amounts of Na_3AsO_3 and As_2O_5 salts (Fluka, Switzerland), respectively. The nitrate salt solutions of Mg and Ni were employed as chemical modifier. Thiourea was prepared as 10% (w/v) solution in 0.001 M HCl. A 1% (w/v) solution of ammonium pyrrolidinedithiocarbamate, APDC, (Aldrich, USA) was used as chelating agent to form hydrophobic As(III) complexes. The pH of the solutions was adjusted by adding HCl or NH_3. A reference water sample (SEM-2011), analyzed by 29 different laboratories, (arsenic concentration of 8.20 ± 1.17 μg L^{-1}, mean ± standard deviation) was obtained from SEM (Istanbul, Turkey). Plastic and glassware were kept in 10% (v/v) HNO_3 for three days or at least overnight and rinsed gently with ultra-pure water. All other reagents used were obtained ultra-pure or at least analytical grade from Merck (Darmstadt, Germany).

Table 1
Temperature programming for the determination of As by GFAAS.

Stage	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (mL min^{-1})
Drying I	90	8	15	250
Drying II	120	15	10	250
Pyrolysis	1000	10	10	250
Atomization	2000	0	3	0
Clean-up	2400	1	5	250

Wavelength: 193.7 nm; lamp current: 10.0 mA; slit width: 0.7 nm; volume: 50+10 μL (standard+modifier).

2.3. Preparation of solid phase

An adsorbent-in-a-pipette-tip system was very easily constructed by packing 30 mg PHEMA microbeads into 100 μL-volume micro-pipette-tip and plugging both side of tip with a small portion of glass wool to avoid the loss of adsorbent. The size range of microbeads, which had been synthesized according to reference [18] as non-magnetic polymer, was 71–100 μm (o.d) that arranged by a mechanical sieve. After the packing, microbeads were successively washed with 0.1 M HNO_3, water and 0.25 M NH_3 solutions, maintaining a flow by the aid of peristaltic pump.

2.4. Solid phase extraction of As(III) in model solutions

The pH of a 10 mL portion of aqueous solution containing 10 ng of As(III) was adjusted to the desired value. A 1 mL solution of 1.0% (w/v) APDC was added and the sample solution passed through the column at a certain flow rate. Following the adsorption of As(III)-PDC complex on PHEMA, the micro column was rinsed with a 2 mL of water. The analyte trapped in the column was eluted by diverse test solutions at a desired flow rate. The eluent was injected into the graphite furnace to determine arsenic concentration. The procedure was applied for determining optimum conditions (pH, sample volume, flow rate, eluent type, etc.). Two parallel experiments were carried out for the optimization studies and GFAAS measurements were triplicated.

2.5. Reduction of As(V) to As(III) and total arsenic determination

In order to quantitatively convert As(V) to As(III), three different reducing agent, i.e., thiourea, thiosulphate and potassium iodide, were tested and the analytical strategy given in Section 2.4 was applied to determine total arsenic.

2.6. Arsenic determination by GFAAS

For a reliable quantitation of arsenic by GFAAS, some parameters such as the injection volume of sample, type of chemical modifiers (Mg and Ni), amount of chemical modifiers, graphite furnace temperature program, (i.e., drying, pyrolysis and atomization temperatures and regarding ramp and hold times) were carefully optimized.

2.7. Application in real world samples

The optimized speciation procedure was applied to bottled drinking water samples, snow and reference water sample (SEM-2011). The water samples were acidified with HCl to pH: 3.0, filtered through 0.22 μm membrane filter and speciation procedure was applied. The fresh snow samples were collected from Beytepe Campus, Ankara. The snow was directly sampled into polyethylene sampling flasks with air-tight caps during downfall. After melting at room temperature, it was immediately passed through the 0.22 μm filter and analyzed within the same day.

3. Results and discussion

3.1. Effect of sample acidity on recovery of arsenic species

Because the sample pH determines the charge and the complexation ability of arsenic species with APDC, the effect of pH is an important parameter on the adsorption behaviour of species. Adsorption of As(III) and As(V) ions onto PHEMA micro beads was investigated at different pHs in presence of APDC. As shown in Fig. 1, in the pH range of 1.0–4.0 the recovery of As(III) was always higher than 95%, while As(V) did not retained on PHEMA and passed through the micro-pipette-tip. Adsorption of As(III)-PDC complex allows to efficient separation of As(III) from As(V). Accordingly, sample pH was adjusted to be 3.0 thereafter.

3.2. Effect of the APDC amount

Since separation of As(III) from As(V) depends on the formation of As(III)-PDC complex, the effect of APDC amount on the recovery was examined. As can be shown in Fig. 2, when a 0.5–2.5 mL portion of %1 APDC (w/v) was added to the model solution, As(III) recovery was quantitative ($\geq$95%). Therefore, a 1.5 mL solution was added during procedure.

3.3. Effect of sample flow rate

The flow rate affects not only the adsorption kinetics of As(III)-PDC complex onto adsorbent but also the analysis time. For this reason, a 10 mL portion of As(III) model solution at pH 3.0 was passed through the column at flow rates of 0.5–4.0 mL min^{-1}. As can be shown in Fig. 2, quantitative As(III) recovery was possible up to 2.0 mL min^{-1}. Thus, a flow rate of 1.5 mL min^{-1} was employed subsequently.

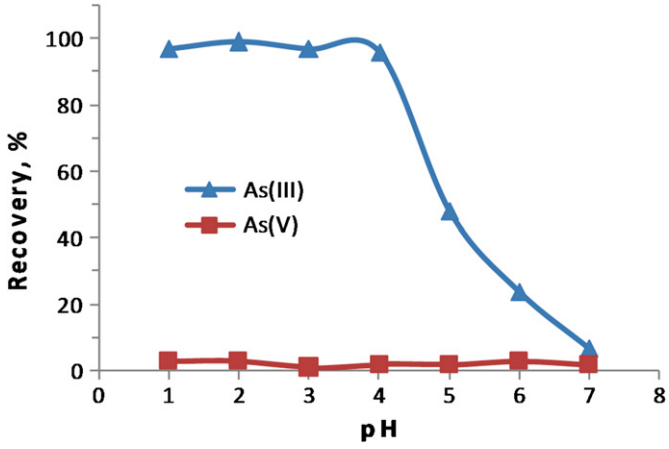

Fig. 1. The effect of pH on the recoveries of As(III) and As(V).

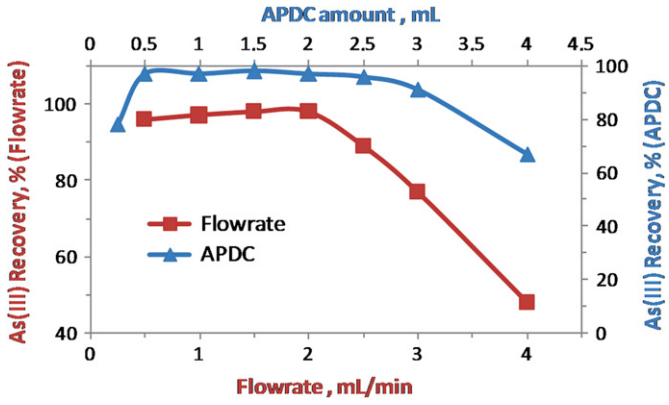

Fig. 2. The effect of APDC amount and sample flowrate on the recoveries of As(III).

3.4. Determination of As(V)

In the present speciation scheme, the concentration of As(V) was calculated by subtracting the concentration of As(III) from the concentration of total inorganic arsenic. The experiments showed that in presence of 0.5 M HCl, a thiourea concentration of 0.5–1.0% was sufficient for quantitative reduction of As(V) to As(III). Complete reduction occurred after 20 min at room temperature, so a 30 min period has been found appropriate (data not shown). The use of thiosulphate and potassium iodide were not chosen due to formation of elemental sulphur and precipitation problems, respectively.

3.5. Examining desorption conditions

For desorption of arsenic from solid phase, a series of desorbing agent was employed. The best result was obtained when 700 μL 0.25 M NH_3 solution was passed through the micro column at a flow rate of 0.2 mL min^{-1} (Table 2). On the other side, quantitative recovery could also be achieved by 2 M HNO_3 but the volume of the solution should be at least 5 mL. With a 2 mL of 2 M HNO_3 analyte recovery was obtained as 86.6% even if a very low-flow rate of 0.2 mL min^{-1} was employed. Preparing HNO_3 in acetone or flashback mode-desorption (desorption through reverse direction) slightly improved recovery, up to 89.1%. Desorption of inorganic species from different solid phase materials has been achieved by concentrated acidic solutions [9,12–14,17] that potentially harmful to adsorbent material and/or graphite furnace. In desorption step, the use of 0.25 M NH_3 does not harmful to adsorbent material or graphite furnace.

3.6. Effect of sample volume

One of the challenges in elemental speciation analysis is that the total amount of an element which already in minute levels is further distributed between different species during separation. Therefore, in order to achieve high enrichment factors initial sample volume must be kept as high as possible. For this purpose, 5.0–80.0 mL of sample solutions containing 10 ng As(III) were applied to the enrichment procedure in the pre-determined conditions. The quantitative recoveries were obtained when the sample volume was kept less than 60 mL. Because of a quantitative recovery has been performed by 700 μL of 0.25 M NH_3, an enrichment factor of 86 were achieved by using 60 mL sample.

Table 2
Influence of eluent volume and flow rate on recovery [a].

Eluent	Volume	Flow rate (mL min^{-1})	Recovery (%)
2 M HNO_3	5 mL	2	98.2
2 M HNO_3	2 mL	2	65.4
2 M HNO_3	2 mL	0.2	86.6
2 M HNO_3 (flashback)	2 mL	0.2	89.1
2 M HNO_3 (in acetone)	5 mL	0.2	88.1
2 M HCl	2 mL	0.2	79.3
1 M NH_3	2 mL	0.2	98.4
0.5 M NH_3	1 mL	0.2	100.0
0.25 M NH_3	1 mL	0.2	99.5
0.25 M NH_3	500 μL	0.2	92.2
0.25 M NH_3	700 μL	0.2	98.3

[a] Means of two parallel experiments.

3.7. Adsorption capacity and amount of the adsorbent

In order to determine how much adsorbent is required to quantitatively concentrate As(III) in a sample, the adsorption capacity of the adsorbent was investigated according to literature using a batch procedure [22]. As(III) adsorption capacity of PHEMA microbeads was found to be 4.1 mg g^{-1}. Accordingly, a 30 mg of adsorbent was used for all practical purposes. The prepared SPE system was very robust that there was no considerable loss in adsorbent performance or analyte recoveries after at least 35 adsorption/desorption cycles.

3.8. Optimization of GFAAS conditions

GFAAS is a very suitable and selective technique for determination of metals and metalloids, however, the technique has some drawbacks for arsenic determination. The first is analyte loss in pyrolysis step due to volatile nature of arsenic and the second is background interferences resulting from nonspecific absorption of light by matrix components. Although the applied SPE procedure was quite effective for the removal of many of matrix, chemical modifiers should ideally be used for stabilizing arsenic until high pyrolysis temperatures and completely eliminating sample matrix. As could be seen in Fig. 3a, when chemical modifier was not used, atomic absorbance signal intensity of arsenic was really low due to volatilization of arsenic, even at very low pyrolysis temperatures (300 °C). Therefore, the use of chemical modifier is essential in arsenic determination.

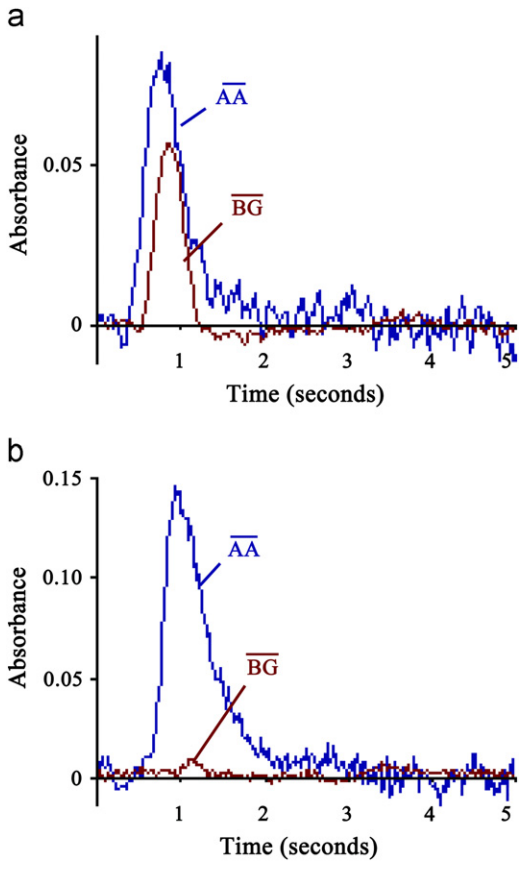

Fig. 3. Influence of Mg (2 μg) on the background (BG) and atomic absorption (AA) signals. Atomization profiles of arsenic in the presence of APDC: 20 μg L^{-1} arsenic standard without modifier (pyrolysis temperature of 300 °C) (a); 10 μg L^{-1} arsenic standard with modifier (pyrolysis temperature of 1000 °C) (b). Injection volumes: 50 μL sample+10 μL modifier.

It should be noticed that injection of large-volume aliquots (50 μL) does not only increase the amount of the analyte loaded into graphite tube, but also increases the amount of matrix components such as APDC and thiourea (ligand and reducing agent, respectively). For this reason, sample matrix loaded into graphite tube should be effectively decomposed. Accordingly, magnesium and nickel were tested as chemical modifier. Magnesium gave the best result; extension of pyrolysis temperature up to 1300 °C (Fig. 4) and alleviation of background signal without loss in arsenic signal (Fig. 3). As can be seen in Fig. 4, the range of 1800–2300 °C was found convenient to effectively atomize arsenic. However, for the sake of furnace life, 2000 and 1000 °C were selected as atomization and pyrolysis temperatures, respectively. Thus, that was any considerable loss in graphite furnace performance with more than at least 1000 injections. In case of Ni as modifier, atomization temperatures should be higher than 2200 °C to obtain complete atomization and well-shaped peaks. This is probably due to higher stability of Ni–As compounds.

Increment in modifier amount (Mg) from 0.0 to 2.0 μg considerably increased arsenic signal intensity. However, further increment up to 8.0 μg did not increase the signal. Thus, 2.0 μg of Mg (10 μL of 200 mg L^{-1} Mg) was applied thereafter to avoid contamination of graphite tube.

A good linearity (R^2=0.999) between the sample injection volume and the integrated absorbance allowed large-volume sample injection to graphite tube for higher atomic absorption signal. Indeed, by injecting 50 μL sample into graphite tube, a LOD value of 0.5 μg L^{-1} was obtained. The limit of quantitation (LOQ), generally defined as three times the limit of detection (LOD), was found to be 1.5 μg L^{-1}. The calibration curve is linear in the range of 1.5–25.0 μg L^{-1} with $R^2 \geq 0.999$. A typical regression equation could be expressed as $A=0.013c-0.002$ where A is absorbance and c is concentration (μg L^{-1}). The large-volume injection (50 μL) improved not only the sensitivity but also the precision. Relative standard deviation (RSD) of 10 μg L^{-1} As(V) standard was found to be 2.6% (n=11) which is quite good precision for a GFAAS method.

It is worth noting, the use of As(III) or As(V) aqueous standards practically gave the same calibration characteristics. In order to avoid scattering during thermal pre-treatment of the injected solution, a two-level drying step was established by observing the volatilization in graphite tube. Optimization of the ramp and hold times for all steps were finalized as in Table 1. Graphite furnace program was very effective in terms of sensitivity, precision and matrix removal; therefore an external calibration method was applied using aqueous standards.

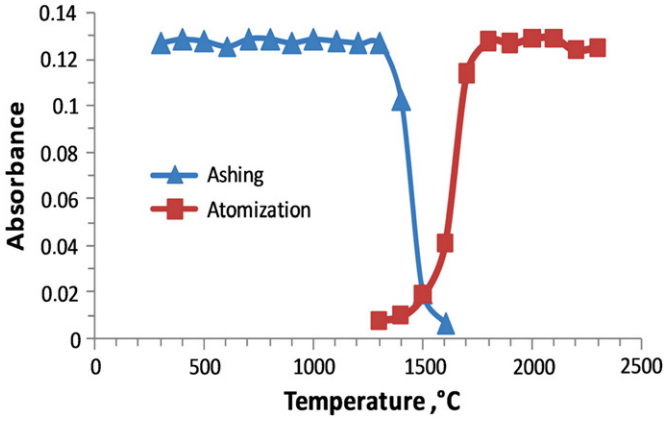

Fig. 4. The ashing and atomization curves for 10 μg L^{-1} As standard (50 μL). Modifier amount: 2 μg.

3.9. Analytical performance

The LOD of the presented SPE method for As(III) was found as 10 ng L^{-1} with an enrichment factor of 86 (sample volume 60 mL and eluent volume 0.7 mL) under optimum conditions. LOD was calculated as the concentration corresponding to three times the standard deviation (3 s) of nine runs of blank.

When the model solutions were spiked with 0.5 and 5 μg L^{-1} As(III), RSD values were found to be 4.0 and 2.1%, respectively ($n=6$); and relative errors of determinations were −0.7 and −2.6%, respectively. Recovery values of arsenic species were between 97% and 102% (Table 3). The results show that the proposed SPE method could be applied for the determination of total arsenic and arsenic species, even if their concentrations were very different to each other.

Comparing the analytical features of the method with other studies, the results are superior in terms of sensitivity and precision (Table 4). The procedure is easily applicable with low-amount samples. Moreover, it is low-cost compared to the other methods using state-of-the-art instrumental techniques [2–4] (Table 4).

3.10. Interference study

Influence of co-existing ions on the analyte recovery was investigated. The potentially interfering ions were individually added to the model solutions and the procedure was applied. It should be noticed that a pre-washing step before the elution is essential for effective removal of the non-specifically adsorbed concomitants. As shown in Table 5, ions at the specified levels did not interfere to the determination of As(III). Due to high sensitivity of the described procedure, samples can be simply diluted to overcome matrix effect. The results showed that the proposed method is highly selective towards As(III).

3.11. Applications to real samples

The proposed speciation method was applied to the determination of As(III), As(V) and total arsenic in bottled drinking water and snow samples. Before applying speciation procedure, the samples were directly measured by GFAAS to check the total arsenic levels. Drinking water samples DW-A, DW-C and snow gave almost any absorbance. The analytical signals for drinking waters DW-B and DW-D were quite low that correspond to the concentrations on the low-edge of calibration range (~1.5 μg L^{-1}). Thus, the obtained results were quite poor in precision (~25%). However, arsenic concentrations were precisely determined by applying the established method (Table 6). The results showed that none of the

Table 5
Tolerance limit of some co-existing ions [a].

Co-existing ion	Ratio[b]
Na^+, K^+	100,000
Ca^{2+}, Mg^{2+}	100,000
Al^{3+}, Fe^{3+}, Co^{2+}, Cr^{6+}, Ni^{2+}	400
Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Se^{4+}, Cd^{2+}	250

[a] Concentration making recovery of As(III) less than 90%.
[b] Concentration of ions to analyte.

Table 3
Arsenic speciation in spiked model solutions [a].

Added [b]		Found [b c]			Recovery (%)			RSD (Relative error) [d] (%)		
As(III)	As(V)	As(III)	As(V)	tAs [e]	As(III)	As(V)	tAs	As(III)	As(V)	tAs
0.50	5.0	0.50 ± 0.02	5.03 ± 0.08	5.52 ± 0.07	99 ± 4	101 ± 2	100 ± 1	4.0 (−0.7)	1.5 (0.5)	1.3 (0.4)
5.0	0.50	4.87 ± 0.10	0.51 ± 0.01	5.38 ± 0.11	97 ± 2	102 ± 4	98 ± 2	2.1 (−2.6)	2.1 (2.0)	2.0 (−2.2)

[a] Initial volume: 60 mL, final volume: 0.7 mL.
[b] (μg L^{-1}).
[c] Mean ± standard deviation, ($n=6$).
[d] Figures in parentheses show relative error.
[e] Total inorganic arsenic.

Table 4
Comparision of performance characteristics of the proposed method with some recent studies.

Adsorbent	Detection	PF [a]	LOD [b]	RSD ([c])	Reference
Pd nanoparticles	GFAAS	50	0.029	4.2 (5)	[9] Sounderajan (2009)
Titanium dioxide	GFAAS	20	0.1	2.4 (2.5)	[10] Zhang (2007)
Carbon nano tubes	GFAAS	250	0.020	3.5 (0.6)	[11] Lopez-Garcia (2009)
Biomass-coated resin	HGAAS	35	0.011	<7	[12] Tüzen (2010)
Octadecyl immobilized silica	HGAFS	7	0.020	2.8 (1)	[13] Chen (2009a)
CTAB modified alkyl silica	ICPAES	26.7	0.15	4.0 (5.0)	[14] Xiong (2008)
Carbon nano-fibers	ICPMS	33	0.0045	2.6 (1)	[16] Chen (2009)
C-18 sorbent	ICPMS	50	0.0012	–	[17] Mulugeta (2010)
$-NH_2$ and –SH modified silica	ICPMS	Non	0.041	–	[15] Boyacı (2011)
Titania immobilized hollow fiber	HPLC–ICPMS	15.3 [d]	0.065	6.7	[2] Mao (2011)
Manganese dioxide	HPLC–HGAAS	19.2	0.019	2.7(2)	[3] Tian (2011)
–	IC–(HR)ICPMS[e]	–	0.005	0.7	[4] Ammann (2010)
PHEMA	GFAAS	86	0.010	4.0 (0.5)	Present work

[a] Preconcentration factor.
[b] μg L^{-1}.
[c] The concentration at which the RSD(%) was evaluated.
[d] Enhancement factor.
[e] Ion chromatography coupled to high resolution (sector field) ICPMS.

Table 6
Concentrations [a] [μg L^{-1}] of inorganic arsenic species in drinking water samples and snow [b].

Sample	As(III)	As(V)	tAs[c]
DW-A	0.19 ± 0.01	0.40 ± 0.02	0.59 ± 0.02
DW-B	0.11 ± 0.02	1.18 ± 0.02	1.29 ± 0.03
DW-C	0.12 ± 0.01	0.21 ± 0.03	0.33 ± 0.04
DW-D	0.19 ± 0.02	1.22 ± 0.06	1.40 ± 0.04
Snow (water)	ND	0.16 ± 0.02	0.16 ± 0.02

[a] Mean ± standard deviation, (n=4).
[b] Initial volume: 50 mL, final volume: 1.0 mL.
[c] Total inorganic arsenic.

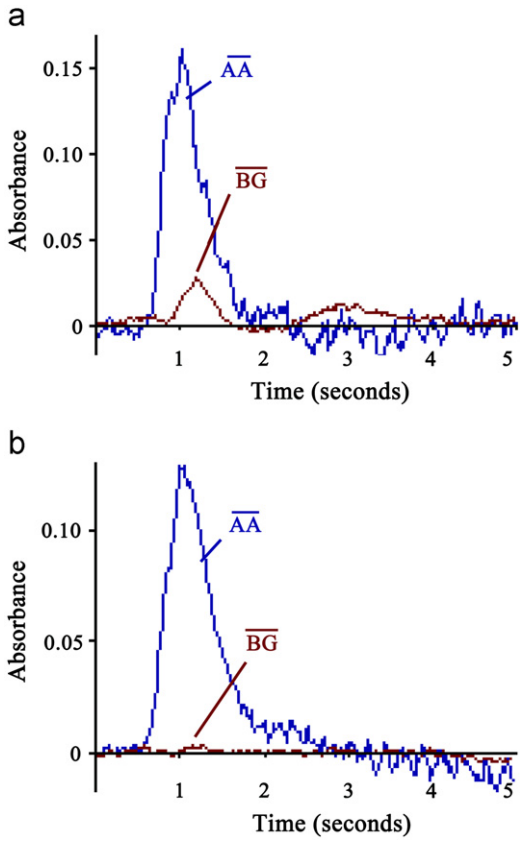

Fig. 5. Atomization profile of As in snow water: after filtering and spiking 10 μg L^{-1} As standard without applying the procedure (a); and atomization of total arsenic after applying the preconcentration/speciation procedure without spike (initial volume: 50 mL, final volume: 1.0 mL).

analyzed samples exceeded the drinking water limit of 10 μg L^{-1} [23,24].

Regarding snow sample it obviously consist of As(V) at a level of 0.16 ± 0.02 μg L^{-1}, n=4. Determination of arsenic in snow has attracted great interest, especially in the environmental monitoring studies [25,26], during last decade. However, to the best of our knowledge, this is the first report on the concentration of total arsenic or inorganic arsenic species in snow in Turkey.

The direct measurement of As in snow by GFAAS did not give any absorbance. However, when the sample was spiked with 10 μg L^{-1} arsenic standard, the obtained atomic absorbance (AA) peak was appreciably well-shaped (Fig. 5a). As the atomization profile shows, the use of Mg as chemical modifier was very effective for the atomization of arsenic in natural aquatic media. A low-level background signal (BG) apparent in Fig. 5a can be easily corrected by the deuterium background correction system. On the other hand, atomization profiles of arsenic in Fig. 5b reveals that AA signal intensity, which was too low for a reliable quantitation in snow sample, has become readable for quantification by applying SPE method. Moreover, background interferences which are the main difficulty in GFAAS in the analysis of real world samples can be effectively eliminated by SPE [8]. Comparison of atomization profiles in snow sample when SPE method was applied and not applied (Fig. 5a and b), two points are readily distinctive. First, the background signal in Fig. 5a was completely disappeared in Fig. 5b and second, atomic absorption signal was more symmetrical and well-shaped in Fig. 5b.

Spike recovery experiments were also carried out to see the feasibility of speciation procedure for determination of As(III), As(V) and total inorganic arsenic in snow and water samples. The obtained recovery values were quite high which were found between 97–100% (Table 7). The validity of the method was verified also by the analysis of a reference water sample (SEM-2011). The determined value of the sample, (8.01 ± 0.16 μg L^{-1}, mean ± standard deviation, n=5), was in good agreement with the reference value (8.20 ± 1.17 μg L^{-1}, mean ± standard deviation, n=29). When the t-test was applied, calculated t value (2.62) is less than critical value ($t_{0.05,\ 4}$=2.78) at 95% confidence level, validating there is no distinctive difference between reference value and determined value.

4. Conclusion

In this study, a miniaturized SPE approach and a large-volume sampling approach in GFAAS have been integrated for selective preconcentration of arsenic species. By combining the advantages of the two approaches, the developed procedure was successfully applied for trace/ultra-trace arsenic speciation in aqueous samples. The procedure is simple, low-cost and environment-friendly.

Table 7
Recovery study in spiked samples.[a]

Samples	Added [b]		Found [b c]			Recovery [%]		
	As(III)	As(V)	As(III)	As(V)	tAs [d]	As(III)	As(V)	tAs
DW-A	–	–	0.19 ± 0.01	0.40 ± 0.02	0.59 ± 0.02	–	–	–
	0.5	0.5	0.69 ± 0.02	0.88 ± 0.03	1.57 ± 0.03	100 ± 2	96 ± 2	98 ± 2
	1.0	1.0	1.17 ± 0.02	1.37 ± 0.03	2.53 ± 0.04	98 ± 3	97 ± 1	97 ± 2
Snow (water)	–	–	ND	0.16 ± 0.02	0.16 ± 0.02	–	–	–
	0.5	0.5	0.49 ± 0.02	0.65 ± 0.01	1.14 ± 0.02	97 ± 4	99 ± 3	98 ± 3
	1.0	1.0	0.97 ± 0.03	1.14 ± 0.03	2.11 ± 0.02	97 ± 3	98 ± 3	98 ± 1

[a] Initial volume: 50 mL, final volume: 1.0 mL.
[b] [μg L^{-1}].
[c] Mean ± standard deviation, (n=4).
[d] Total inorganic arsenic.

PHEMA has shown excellent performance as a solid phase material and the analytical features of the proposed method have been found superior.

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