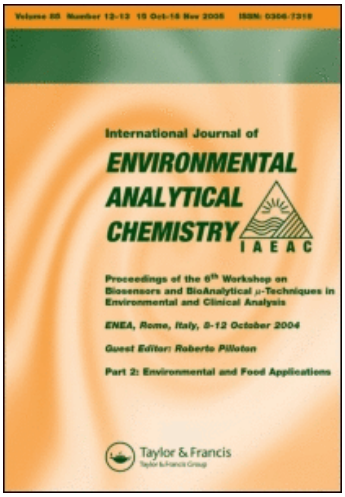

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Direct analysis of natural waters for arsenic species by hydride generation atomic absorption spectrometry

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Direct analysis of natural waters for arsenic species by hydride generation atomic absorption spectrometry

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Selective reaction media were applied to generate hydrides of total arsenic, As(III), As(V), dimethylarsonic acid (DMA) and monomethylarsonic acid (MMA) from natural waters acidified with HCl (0.1 mol/L HCl in the sample) using reduction with 0.6% $NaBH_4$ in a continuous flow hydride generation system:

1. 1.0 mol/L HCl in the acid channel, water samples pretreated with KI: determination of As(III) + As(V) + MMA
2. 6.0 mol/L CH_3COOH in the acid channel: determination of As(III) + DMA
3. 6.0 mol/L CH_3COOH in the acid channel, water samples pretreated with KI: determination of As(III) + As(V) + DMA
4. 1.0 M tartaric acid in the acid channel, water samples pretreated with KI: determination of total arsenic As(III) + As(V) + DMA + MMA

With the selected medium reactions (1–4) the same response can be obtained for all arsenic species. Calibration with arsenic(III) standard solutions was applicable to the four reactions for arsenic speciation in mineral water, underground water and sea water.

Keywords: Arsenic speciation; Hydride generation AAS; Reaction medium

1. Introduction

Arsenic has been recognized as a Class A human carcinogen and is a public concern due to its widespread usage in both agriculture and industry [1]. Arsenic may exist in the environment and in biological systems in different chemical forms. Natural waters are reported to contain appreciable quantities (16–54% of total As) of methylated arsenic compounds [2–4]. The differences in the toxicity, biochemical

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and environmental behaviour of the various arsenic compounds require the determination of these individual species. There is considerable information regarding the speciation of arsenic in water. Hydride generation (HG) has become the most essential technique in arsenic speciation and quantitation by atomic absorption spectrometry (AAS) [5–7]. The indirect HG-AAS methods include previous separation of the arsenic species by selective extraction, precipitation, flotation, and sorption [8–13]. The commonly used speciation techniques often involve a combination of chromatographic separation with HG-AAS [14–16]. Cryogenic trapping of the arsenic hydrides and consequent gas chromatographic separation of the various hydrides have also been widely applied for determination of different arsenic compounds [2–4, 8–13, 17]. The indirect methods present several disadvantages, namely the laborious procedures required, complicated analytical procedures and time consumed. The direct methods reported are based on selective medium reactions to generate selectively hydrides of different arsenic species. Several relevant 'non-chromatographic' methods based on reduction with $NaBH_4$ and selective hydride generation in different reaction mediums are summarized in table 1. The major problem of the direct procedures is the difficulty in finding a compromise acid concentration under which the same response can be obtained for all arsenic species. The type and concentration of the acid used have a critical effect on the HG response for arsenite, arsenate and organic arsenic species [18–20]. In order to minimize this drawback, previous derivatization with thiol group containing ligands is applied [21–25]. In our experience with L-cysteine, we obtained an unacceptably high blank value; this was the reason to investigate, search and find selective medium reactions for arsenic speciation with equal sensitivity for the different arsenic compounds investigated without pre-derivatization.

The aim of the present work is to optimize the reaction medium to generate hydrides selectively for each arsenic species for a selective, simple, rapid, reliable direct HG-AAS

Table 1. Direct methods for arsenic speciation using HG-AAS[a].

Water	Reaction medium	Determined species	Measurement	Ref.
Geyser, river	pH 4.55 (acetate buffer)	As(III)	Batch HG-AAS	[26]
	5 mol/L HCl	As(III + V)		
River	Acetate buffer	As(III)	CF-HG-AAS	[27]
	KI + ascorbic acid	As(III + V)		
River	0.4 mol/L Na-citrate (pH 6.0)	As(III)	CF-HG-AAS	[19, 28]
	0.16 mol/L CH_3COOH	As(III) + DMA		
	0.1 mol/L CH_3CSOH-0.02 mol/L EDTA–0.04 M thiourea–0.005 M 1,10 phenantroline	As(III + V + DMA + MMA)		
Sea, hot spring	4 mol/L HCl, 2% $NaBH_4$	As(III + V)	HG-ETAAS (Zr-coated graphite tube)	[29]
	citrate buffer (pH 5) + 0.2% $NaBH_4$	As(III)		
	0.14 mol/L CH_3COOH + 0.2% $NaBH_4$	As(III + DMA)		
	0.02 mol/L thioglycolic acid + 1% $NaBH_4$	As(III + V + MMA + DMA)		

[a]CF: continuous flow; ETAAS: electrothermal AAS.

Table 2. Instrumental parameters for HG-AAS.

Parameter	Setting
Source lamp	Varian hollow cathode lamp
Wavelength	193.7 nm
Bandpass	0.5 nm
Integration time	3 s
Delay time	40 s
Replicates	3
Quartz cell temperature	925°C
Reaction medium	Variable
Pre-reductant	KI
Sample flow rate	7 mL/min
Acid flow rate	1 mL/min
$NaBH_4$ flow rate	1 mL/min

determination of total arsenic, As(III), As(V), monomethylarsenic acid (MMA) and dimethylarsonic acid (DMA) in natural waters without any derivatization and chemical or chromatographic separation.

2. Experimental

2.1 *Apparatus*

A continuous-flow vapour generation accessory (VGA-77, Varian) connected to an atomic absorption spectrometer (SpectrAA 55B, Varian) was employed for HG-AAS measurements. The peristaltic pump maintains a constant flow of analytical solutions. The sample and acid are allowed to merge first before the sodium tetrahydridoborate(III) ($NaBH_4$) enters the stream. Argon is then introduced into the liquid stream, and the reaction proceeds while the mixture is flowing through the reaction coil. Vigorous evolution of hydrogen during the reaction assists the stripping of the hydride from the liquid into the argon. The gas stream passes from a gas–liquid separator into an electrically heated T-shaped quartz cell (ETC-60). The instrumental parameters are given in table 2.

2.2 *Reagents*

All chemicals used were of analytical reagent grade. Double distilled water was used throughout the experiment. The arsenic reagents used were as follows: arsenic(III) chloride stock standard solution, 1.000 g/L (BDH, Poole, UK) 1000 µg/mL As(V), Titrisol standard, Merck, 9989; disodium salt of monomethylarsonic acid (MMA), $CH_3AsO(ONa)_2 \cdot 6H_2O$, g/mL (Carlo Erba, Italy); sodium salt of dimethylarsinic acid (DMA), $C_2H_6O_2AsNa \cdot 3H_2O$ (Carlo Erba, Italy). The stock solutions were prepared monthly and kept refrigerated at 4°C. Working standard solutions were prepared daily. Sodium tetrahydridoborate(III) solution (0.1–2% m/V) in 0.5% sodium hydroxide was prepared just prior to use.

All vessels used were pre-cleaned by leaching for 24 h each in 15% HNO_3 and 15% HCl, followed by rinsing with doubly distilled water.

2.3 *Sample preservation*

Sea water, river water and underground water samples were stored acidified with HCl (0.1 mol/L HCl end concentration) at 4°C in polyethylene bottles. The mineral water samples from the Macedonian market were acidified with HCl (0.1 mol/L HCl) immediately after opening the polyethylene bottles and then stored at 4°C.

2.4 *Analytical procedure*

The water sample acidified with hydrochloric acid (0.1 mol/L HCl) was passed through the sample channel of the hydride generation system, and the response for arsenic was recorded using 6.0 mol/L acetic acid in the acid channel (response II). Then, an aliquot of the sample was pretreated with KI (1% m/V, final concentration), and three new responses for As were recorded, changing the reaction medium in the acid channel (according to table 4): (1) 1.0 mol/L HCl (response I); (2) 6.0 mol/L CH_3COOH (response III); (3) 1.0 mol/L tartaric acid (response IV). The concentration of the various arsenic species was calculated from equations (1)–(4): $As(V) = III - II$; $DMA = IV - I$; $As(III) = III - [As(V) + DMA]$; $MMA = I - [As(III) + As(V)]$. For all four experiments, the calibration was against aqueous As(III) standard solutions acidified with 1.0 mol/L HCl and 9.0 mol/L HCl in the acid channel. The concentration of sodium tetrahydridoborate(III) was always 0.6% $NaBH_4$ in 0.5% NaOH. The reagent blank contributions were corrected for each measurement.

3. Results and discussion

3.1 *Effect of $NaBH_4$ concentration*

The effect of 0.1–2% $NaBH_4$ on the absorbance signals of the arsenic species was investigated for various reaction mediums: 0.1–10 mol/L HCl, 1–6 mol/L CH_3COOH, 0.5–1 mol/L tartaric acid, 0.5–1.0 mol/L citric acid, 0.5–1 mol/L oxalic acid. In all cases, an increase in the arsenic signal up to a $NaBH_4$ concentration of 0.4% and a very broad plateau afterwards were observed. As an example, the effect of $NaBH_4$ concentration on the absorption signals of the arsenic species when the aqueous standards were prepared in 1.0 mol/L HCl and 1.0 mol/L tartaric acid was pumped through the acid channel is shown in figure 1. This means that the variation of the $NaBH_4$ concentration does not lead to any separation by selective generation of hydrides of each arsenic species. In all further experiments in the reductant channel, a 0.6% $NaBH_4$ in 0.5% NaOH was used.

3.2 *Effect of different reaction media*

The relative hydride-forming behaviour of the arsenic compounds was investigated for hydrochloric acid and for various carboxylic acids (acetic acid, tartaric acid, oxalic acid, citric acid) reaction mediums. Table 3 shows the observed atomic absorption responses for hydrides from four arsenic species obtained for aqueous standards, aqueous standards acidified with hydrochloric acid with final concentration 0.1 mol/L HCl and 1.0 mol/L HCl.

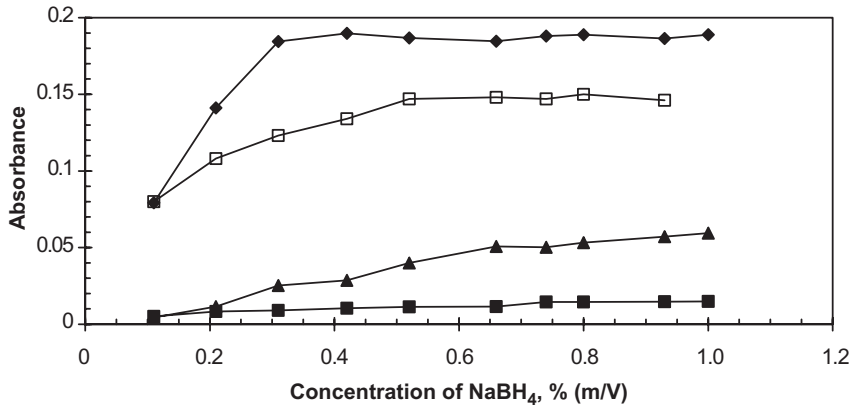

Figure 1. Dependence of the absorbance signal for arsenic on the concentration of $NaBH_4$ (◆: As(III); ▲: As(V); ■: DMA; □: MMA). Acid channel: 1 mol/L tartaric acid. Sample channel: sample in 1 mol/L HCl.

The results obtained and presented in table 3 can be summarized as follows:

- In the case of hydrochloric acid in the acid channel (1.0–10.0 mol/L HCl), the hydride response from non-acidified and acidified with hydrochloric acid (0.1 mol/L and 1.0 M HCl) aqueous standard solutions for DMA was found to be 4% or less of the response for an equal amount of arsenic in the form of inorganic arsenic(III). For MMA, the response is around 100% for 1.0–5.0 mol/L HCl in the acid channel. At the same time, the hydride response for inorganic As(V) is always reproducible around 22% for all the investigated acid area. This means that operating with 1.0–5.0 mol/L HCl in the acid channel, we could attribute the response to inorganic As(III), MMA and partly (20–25%) to As(V). After pre-reduction of As(V) to As(III) with KI, it is possible to determine the sum of the three species As(III) + As(V) + MMA.
- Inorganic arsenic (III) and DMA quantitatively generate hydrides from water solutions in 0.1 mol/L HCl and 1.0–6.0 mol/L acetic acid in the acid channel. The use of 6.0 mol/L acetic acid in the acid channel provides a means of minimizing the hydride contribution from As(V) and MMA. This allows the concentration of As(III) + DMA (calibration with As(III)) to be estimated in the water sample.
- Using 1.0 mol/L tartaric acid in the acid channel and 0.1 mol/L HCl in the water samples, a quantitative generation of the hydrides of As(III), MMA and DMA is achieved. Arsenic(V) does not form hydride under these conditions. This means that using 1.0 mol/L tartaric acid in the acid channel and 0.1 mol/L HCl in the sample channel, it is possible to determine the sum from As(III), MMA and DMA.
- Without a prereduction step, it is impossible to generate hydride from As(V) with a response equal to that from As(III). After prereduction with KI and generation of hydrides with 1.0 mol/L tartaric acid in the acid channel and 0.1 mol/L HCl in the sample channel, it is possible to determine the total inorganic and organic arsenic.

The results obtained enable a direct hydride analysis of arsenic species in waters using equation systems I–IV in table 4, representing the procedures described

Table 3. Atomic absorption responses for hydrides from arsenic species[a].

Reaction medium (acid channel)	Response relative to inorganic arsenic(III) in 1.0–10.0 mol/L HCl = 100%							
	As(III)	As(V)		DMA		MMA		
	SC: 0; 0.1 and 1 mol/L HCl	0.0 and 0.1 mol/L HCl	1 mol/L HCl	0.0 and 0.1 mol/L HCl	1 mol/L HCl	0.0 mol/L HCl	0.1 mol/L HCl	1 mol/L HCl
1.0 mol/L HCl	100 ± 2	22 ± 1		4		100 ± 2		
3.0 mol/L HCl	100	22 ± 1		3		98 ± 3		
5.0 mol/L HCl	100	22 ± 1		3		98 ± 3		
6.0 mol/L HCl	100 ± 5	22 ± 1		3		64 ± 6		
10.0 mol/L HCl	100 ± 2	24 ± 2		2		50 ± 7		
1.0 mol/L acetic acid	100 ± 3	14 ± 1	95 ± 4			10	57	66 ± 4
3.0 mol/L acetic acid	100 ± 2	3	48 ± 5	100 ± 2	32 ± 6	8	8	73 ± 3
6.0 mol/L acetic acid	100 ± 2	3	46 ± 4	100 ± 4	29 ± 6	2	2	78 ± 3
0.5 mol/L oxalic acid[b]	84 ± 4	2	–	82 ± 3	–	2	2	–
1.0 mol/L oxalic acid[b]	100 ± 3	3	–	69 ± 3	–	–	–	–
0.5 mol/L tartaric acid	77 ± 3 93 ± 3[c]	11 ± 1	23 ± 1	95 ± 5	2	29 ± 2	80 ± 4	84 ± 3
1.0 mol/L tartaric acid	100 ± 2	14 ± 1	34 ± 2	95 ± 5	2	26 ± 3	92 ± 3	78 ± 4
0.5 mol/L citric acid	82 ± 4	2	12 ± 1	80 ± 3	1	24 ± 2	84 ± 3	86 ± 3
1.0 mol/L citric acid	88 ± 3	3	13 ± 1	79 ± 4	1	22 ± 3	84 ± 2	87 ± 4

[a]Sample channel (SC): aqueous standards (3–12 μg/L As) with different concentration of HCl (0, 0.1 and 1 mol/L); reductant channel: 0.6% $NaBH_4$ in 0.5% NaOH.
[b]No data for As species in 1.0 mol/L HCl in the sample channel.
[c]Data obtained for As(III) in 1.0 mol/L HCl in the sample channel.

Table 4. Direct hydride analysis of arsenic species in natural waters: calibration with As(III) standard solutions.

Procedure	Sample medium (sample channel)	Reaction medium (acid channel)	Determined arsenic species
I	0.1 mol/L HCl + KI[a]	1.0 mol/L HCl	As(III) + As(V) + MMA
II	0.1 mol/L HCl	6.0 mol/L CH_3COOH	As(III) + DMA
III	0.1 mol/L HCl + KI[a]	6.0 mol/L CH_3COOH	As(III) + As(V) + DMA
IV	0.1 mol/L HCl + KI[a]	1.0 mol/L tartaric acid	As(III) + As(V) + MMA + DMA

[a]Preliminary reduction of the water samples with KI.

Table 5. Arsenic speciation in drinking water spiked with various arsenic species (2 ng/mL of each species expressed as arsenic)[a].

Spiked species	Procedure	Recovery, expected (%)	Recovery, obtained (%)
As(III) + MMA	I	100	102 ± 3
	II	50	47 ± 5
	III	50	53 ± 3
	IV	100	96 ± 5
As(III) + DMA	I	50	52 ± 1
	II	100	106 ± 4
	III	100	103 ± 2
	IV	100	98 ± 1
As(III) + MMA + DMA	I	67	68 ± 2
	II	67	64 ± 3
	III	67	69 ± 1
	IV	100	101 ± 2
As(V) + MMA	I	100	98 ± 3
	II	< 5	< 5
	III	50	46 ± 2
	IV	100	95 ± 3
As(V) + DMA	I	50	53 ± 2
	II	50	48 ± 3
	III	100	105 ± 2
	IV	100	101 ± 2
As(III) + As(V) + MMA	I	100	98 ± 2
	II	25	26 ± 1
	III	65	66 ± 2
	IV	100	95 ± 3
As(III) + As(V) + DMA	I	67	64 ± 2
	II	67	66 ± 1
	III	100	104 ± 3
	IV	100	98 ± 3
As(III) + As(V) + MMA + DMA	I	75	77 ± 3
	II	50	52 ± 2
	III	75	74 ± 2
	IV	100	97 ± 2

above, e.g.:

$$\mathrm{As(V)} = \mathrm{III} - \mathrm{II} \quad (1)$$

$$\mathrm{DMA} = \mathrm{IV} - \mathrm{I} \quad (2)$$

Table 6. Arsenic species in natural waters, corresponding to four replicate analysis.

Sample	As(III)	As(V)	MMA	DMA
Sea water, Harem (TR)	1.8 ± 0.2	< 0.1	0.15 ± 0.02	< 0.1
Sea water, Platamona (GR)	2.2 ± 0.2	< 0.1	0.19 ± 0.02	< 0.1
Underground, Rimjanka	3.2 ± 0.2	19.8 ± 0.4	1.2 ± 0.2	2.8 ± 0.2
Underground, Kožuvčanka	2.3 ± 0.2	18.4 ± 0.4	0.8 ± 0.1	1.4 ± 0.2
Mineral water (Pelisterka)	1.6 ± 0.1	< 0.1	–[a]	–[a]
Mineral water (Dobra voda)	1.7 ± 0.1	3.9 ± 0.2	–	–
Mineral water (Kumanovo izvor)	1.8 ± 0.1	4.8 ± 0.4	–	–
Table water (Aqua Heba)	4.0 ± 0.2	10.2 ± 0.3	–	–
Mineral water (Korpi)	0.9 ± 0.1	0.4 ± 0.1	–	–
Mineral water (Studenac)	3.0 ± 0.2	4.1 ± 0.2	–	–
Mineral water (Glina)	1.7 ± 0.2	0.5 ± 0.1	–	–
Spring water (Rašče)	0.3 ± 0.1	0.4 ± 0.1	–	–
Table water (Miloš-limon)	< 0.1	0.4 ± 0.1	–	–
Mineral water (Menada)	< 0.1	0.5 ± 0.1	–	–
Mineral water (Lukarka)	< 0.1	1.8 ± 0.1	–	–
Mineral water (Ilina)	< 0.1	0.9 ± 0.1	–	–
Table water (Aqua nega)	0.63 ± 0.09	1.2 ± 0.1	–	–
Mineral water (Momina čuka)	4.7 ± 0.2	8.5 ± 0.3	–	–
Mineral water (Planinska)	2.1 ± 0.1	7.0 ± 0.3	–	–

[a]Below the detection limit.

$$\text{As(III)} = \text{III} - [\text{As(V)} + \text{DMA}] \quad (3)$$

$$\text{MMA} = \text{I} - [\text{As(III)} + \text{As(V)}] \quad (4)$$

3.3 *Validation of the method*

The ability of the proposed procedure to distinguish between the various arsenic forms when they are present together was carried out using drinking water spiked with different concentrations of arsenite (6 ng/mL As), arsenate (6 ng/mL As), dimethylarsinate (1 ng/mL As) and monomethylarsinate (1.0 ng/mL As). The results are presented in table 5. The experimentally obtained recoveries from three parallel determinations of arsenic species in each procedure are in good agreement with the expected recovery values according to the proposed procedure (table 5).

The precision of the procedure varies between 2 and 4% for 3–10 ng/mL As and between 7 and 15% for 0.1–2 ng/mL As. The detection limit according to 3σ criteria is 0.1 ng/mL As.

3.4 *Application*

Selected water samples from various parts of the Republic of Macedonia, sea water and mineral water bottles from the market were analysed using the proposed procedure. The sample preservation was performed as indicated in Section 2.3, according to Cheam and Agemian [30]. The results are shown in table 6. It can be seen that in mineral and spring waters, no organic forms of arsenic are detectable. However, the results obtained for underground waters (old factory for arsenic production in the region) indicate that a substantial portion of the total As in these particular samples exists in organic forms. In the sea waters from Greece (GR) and Turkey (TR), only about 8% of MMA was detected.

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