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Speciation of Arsenic in Natural Waters and Beverages by Hydride Generation Atomic Absorption Spectrometry

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Abstract: Methods for speciation analysis of arsenic in natural waters and beverages by hydride generation atomic absorption spectrometry (HG-AAS) are described. An optimization of the reaction medium for direct HG-AAS determination of total As, As(III), As(V), monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) is presented. Selected water and wines samples from Macedonia from various parts of Macedonia were analyzed using the proposed procedure.

Key words: Arsenic, speciation, water, beverages, HG-AAS

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 (U.S. EPA, 1998). Arsenic may exist in the environment and in biological systems in different chemical forms. The differences in the toxicity, biochemical and environmental behaviour of the various As compounds require the determination of these individual species. There is considerable information regarding the speciation of As in water (CULLEN AND REIMER, 1989; GONG ET AL., 2002). Hydride generation atomic absorption spectrometry (HG-AAS) has become the most essential technique in As speciation and quantitation although the commonly used speciation techniques often involve a combination of chromatographic separation with HG-AAS (CULLEN AND REIMER, 1989; GONG ET AL., 2002).

The concentration of As in wines depends on aerosol deposits on the grape, grape variety and climatic conditions, soil composition and use of pesticides and also on the wine making process and storage conditions. The method proposed by *Office International de la Vigne and du Vin* (2003) for total As determination in wines is based on wine digestion and measurement by HG-AAS. Total As in uncontaminated wine ranges 0.5–30 μg l^{-1} which is covered by ICP-MS method (BAXTER ET AL., 1997; Castineira et al., 2001). Some papers concerning direct ETAAS (CVETKOVIC ET AL., 2004) or HG-AFS (SEGURA ET AL., 1994) determination of As in wine reported for strong matrix interference and preliminary wine sample preparation is recommended.

The aim of the present work is to optimize the reaction medium in order to generate hydrides of each As species selectively for direct HG-AAS determination of total As, As(III), As(V), monomethylarsenic acid (MMA) and dimethylarsonic acid (DMA) in waters and beverages without derivatization and chemical or chromatographic separation.

Results and discussion

Arsenic speciation in water samples

The effect of 0.1–2% $NaBH_4$ on the absorbance signals of the As species was investigated for various reaction mediums: 0.1–10 mol l^{-1} HCl, 1–6 mol l^{-1} CH_3COOH, 0.5–1 mol l^{-1} tartaric, 0.5–1.0 mol l^{-1} citric and 0.5–1 mol l^{-1} oxalic acid. It was found that the variation of the $NaBH_4$ concentration does not lead to any separation for selective generation of hydrides of each As species. In all further experiments 0.6% $NaBH_4$ in 0.5 % NaOH was used. The effect of HCl concentration and the investigated carboxylic acids reaction mediums on the HG behavior of As species was investigated. The obtained results give the possibility for direct selective determination of different As species in waters using experimental design presented in Table 1. The acidified (0.1 mol l^{-1} HCl) water sample is passed through the sample channel of the HG system and the response for As is recorded using 6.0 mol l^{-1} acetic acid in the acid channel (response II). Than an aliquot of the sample is pretreated with KI (1 %, *m/V*) and new 3 responses for As are recorded changing the reaction medium in the acid channel (Table 1). The concentration of the various As species is calculated from the equations (I) – (IV): As(V) = III – II; DMA = IV – I; As(III) = III – [As(V)+DMA]; MMA = I – [As(III)+As(V)].

Table 1. Direct hydride analysis of As species in natural waters

Procedure	Sample medium (sample channel)	Reaction medium (acid channel)	Determined arsenic species
I	0.1 mol l^{-1} HCl + KI*	1.0 mol l^{-1} HCl	As(III)+As(V)+MMA
II	0.1 mol l^{-1} HCl	6.0 mol l^{-1} CH_3COOH	As(III)+DMA
III	0.1 mol l^{-1} HCl + KI*	6.0 mol l^{-1} CH_3COOH	As(III)+As(V)+DMA
IV	0.1 mol l^{-1} HCl + KI*	1.0 mol l^{-1} tartaric acid	As(III)+As(V)+MMA+DMA

* - preliminary reduction of the water samples with KI

The ability of the proposed procedure to distinguish between the various As forms when they are present together was carried out using drinking water spiked with different concentrations of arsenite, arsenate, DMA and MMA. A continuous flow vapour generation accessory (VGA-77, Varian) connected to an atomic absorption spectrometer (SpecterAA 55B, Varian) was used for HG-AAS measurements. The precision of the procedure varies between 2–4 % for 3-10 μg l^{-1} As and 7–15 % for 0.1–2 μg l^{-1} As. The detection limit is 0.1 μg l^{-1} As.

Selected water samples and mineral waters from the market were analyzed using the proposed procedure indicated that major As species in water is As(V), Table 2.

Table 2. Arsenic species in water samples from the market in Macedonia (in μg l^{-1})

Sample	As(III)	As(V)	MMA	DMA	Total As
Underground, Rimjanka	3.2 ± 0.2	19.8 ± 0.4	1.2 ± 0.2	2.8 ± 0.2	27.0
Underground, Kožuvčanka	2.3 ± 0.2	18.4 ± 0.4	0.8 ± 0.1	1.4 ± 0.2	22.1
Mineral water (Momina Čuka)	4.7 ± 0.2	8.5 ± 0.3	-*	-*	13.2
Mineral water (Planinska)	2.1 ± 0.1	7.0 ± 0.3	-	-	9.1
Table water (Aqua Heba)	4.0 ± 0.2	10.2 ± 0.3	-	-	14.2
Mineral water (Pelisterka)	1.6 ± 0.1	< 0.1	-	-	1.6
Mineral water (Dobra voda)	1.7 ± 0.1	3.9 ± 0.2	-	-	5.6
Mineral water (Kumanovo izvor)	1.8 ± 0.1	4.8 ± 0.4	-	-	6.6
Mineral water (Korpi)	0.9 ± 0.1	0.4 ± 0.1	-	-	1.3
Mineral water (Studenac)	3.0 ± 0.2	4.1 ± 0.2	-	-	7.1
Mineral water (Glina)	1.7 ± 0.2	0.5 ± 0.1	-	-	2.2
Spring water (Rašče)	0.3 ± 0.1	0.4 ± 0.1	-	-	0.4
Table water (Miloš-limon)	< 0.1	0.4 ± 0.1	-	-	0.4
Mineral water (Menada)	< 0.1	0.5 ± 0.1	-	-	0.5
Mineral water (Lukarka)	< 0.1	1.8 ± 0.1	-	-	1.8
Mineral water (Ilina)	< 0.1	0.9 ± 0.1	-	-	0.9
Table water (Aqua nega)	0.6±0.09	1.2 ± 0.1	-	-	1.8

* - bellow the detection limit

Arsenic determination in wine samples

Determination of inorganic As(III) and As(V) in wine samples. Very strong signal depression for direct HG-AAS determination of As was observed even for 20 times diluted wine samples. It was found that ethanol vapors as fine aerosol formed in the gas liquid separator is responsible for the remarkably decreased degree of arsine atomization. Therefore it was chosen mild evaporation of the ethanol from the wine sample before the analysis. The effect of the concentration of HCl and $NaBH_4$ on As(III) and As(V) absorbance signals indicates that, the use of relatively low $NaBH_4$ concentration of 0.2 % (*m/V*) at 9 mol l^{-1} HCl assure selective determination of As(III) only. Both inorganic As species can be determined together by using 9 mol l^{-1} HCl and 0.2 % $NaBH_4$ after As(V) prereduction with KI. The limit of detection for both As species determination in wines is 0.1 μg l^{-1} and RSD varied between 8-10 % at 0.1-30 μg l^{-1} As species level.

Determination of total As after microwave digestion. Red and white wine samples were digested in MW oven by using HNO_3 and H_2O_2. In all cases preliminary evaporation of ethanol is performed. The most serious interference for As determination by HG-AAS after MW digestion of the sample is caused by the dissolved nitrogen oxides remaining in the solution. It was found that hydrazine hydrochloride is very effective as reducing reagent, but nevertheless KI should be also used for final reduction of As(V) to As(III). The experiments performed showed that proposed MW digestion program insure successful measurement of both MMA and DMA. The limit of detection for total As determination in wines is 0.1 μg l^{-1} and RSD of 9-14 % at 0.1-30 μg l^{-1} arsenic level.

Several red and white wine samples from the market in Macedonia were analyzed according to the above described conditions (Table 3). The results obtained showed that

almost all inorganic As in wine sample is presented as As(III). Taking into account reducing conditions during the whole wine making process the conclusion, that As(III) is the major inorganic species of As in wines, seems very reasonable and confirm the conclusions of WANGKARN AND PERGANTIS (2000).

Table 3. Results for inorganic arsenic total As obtained by direct HG-AAS

Sample	As(III), [mean ± s] μg l^{-1}	Total arsenic, [mean ± s] μg l^{-1}
Cabernet Sauvignon	6.7 ± 0.2	6.9 ± 0.2
Burgundec	12.5 ± 0.1	12.4 ± 0.2
Makedonsko Crveno	15.5 ± 0.1	15.6 ± 0.2
Rosenatller-Kadarka	5.7 ± 0.1	5.9 ± 0.1
Merlot	9.8 ± 0.2	10.0 ± 0.2
Aleksandria red	21.3 ± 0.1	21.4 ± 0.1
Kratošija	18.3 ± 0.2	18.5 ± 0.2
T'ga za Jug	19.5 ± 0.1	19.4 ± 0.2
Rajnski Rizling	5.7 ± 0.2	5.5 ± 0.2
Sauvignon Blanc	6.9 ± 0.2	7.1 ± 0.2
Aleksandria white	20.3 ± 0.2	20.4 ± 0.2
Smederevka	29.9 ± 0.1	30.2 ± 0.1

Conclusions

Simple and fast procedures are described for selective determination of As species in mineral waters and beverages by using HG-AAS without any previous chromatographic separation. Selective reaction mediums based on HCl and tartaric and acetic acids are used for total As, As(III), As(V), DMA and MMA in natural waters. Inorganic As species are determined directly in wine sample after ethanol evaporation and total As is determined after MW digestion.

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