

SPECIATION ANALYSIS OF ARSENIC IN NATURAL WATERS AND BEVERAGES BY HG-AAS

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Abstract

Methods for speciation analysis of arsenic in natural waters and beverages by continuous flow hydride generation atomic absorption spectrometry (HG-AAS) are described. An optimization of the reaction medium for selective generation of arsine from four arsenic species in order to achieve a selective, simple, rapid, reliable direct HG-AAS determination of total arsenic, As(III), As(V), monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) is presented. Speciation analysis of arsenic in natural and sea waters without any previous derivatization and chemical or chromatographic separation is demonstrated. Methods are developed for the determination of total arsenic as well as inorganic and organic arsenic species in wines and other beverages by using HG-AAS.

Introduction

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 [1]. The differences in the toxicity, biochemical and environmental behaviour of the various arsenic compounds require the determination of these individual species. Hydride generation (HG) has become the most essential technique for As speciation and quantitation by atomic absorption spectrometry (AAS). The indirect HG-AAS methods include previous separation of the As species [2, 3]. The commonly used speciation techniques often involve a combination of chromatographic separation with HG-AAS [4, 5]. The aim of the present work is to optimize the reaction medium in order to generate hydrides of each arsenic species selectively for simple, rapid, reliable direct HG-AAS 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. Also, methods are described for the determination of inorganic and organic arsenic species in wines and other beverages by using HG-AAS.

Experimental

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 gaseous hydrides were formed after mixing and reaction of the sample with NaBH₄, they were separated by a gas-liquid separator using argon and atomized in electrically heated T-shaped quartz cell. An Ethos Touch Control pressurized microwave digestion (MW) device (Milestone, Italy) with a rotor for 12 Teflon digestion vessels was used.

Results and Discussion

Arsenic speciation in water samples

Effect of NaBH₄ concentration

The effect of 0.1–2% NaBH₄ on the absorbance signals of the arsenic species was investigated for various reaction mediums: 0.1–10 mol/l HCl, 1–6 mol/l CH₃COOH, 0.5–1 mol/l tartaric acid, 0.5–1.0 mol/l citric acid, 0.5–1 mol/l oxalic acid. It was found that the variation of the NaBH₄ concentration does not lead to any separation for selective generation of hydrides of each arsenic species. In all further experiments in the reductant channel a 0.6% NaBH₄ in 0.5% NaOH was used.

Effect of reaction medium

The effect of HCl concentration and various carboxylic acids (acetic acid, tartaric acid, oxalic acid, citric acid) reaction mediums on the hydride generation behavior of arsenic species was investigated. The obtained results give the possibility for direct selective determination of different arsenic species in waters using experimental design presented in Table 1.

Table 1. 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* | 1.0 mol/l HCl | As(III)+As(V)+MMA |
| II | 0.1 mol/l HCl | 6.0 mol/l CH ₃ COOH | As(III)+DMA |
| III | 0.1 mol/l HCl + KI* | 6.0 mol/l CH ₃ COOH | As(III)+As(V)+DMA |
| IV | 0.1 mol/l HCl + KI* | 1.0 mol/l tartaric acid | As(III)+As(V)+MMA+DMA |

* - preliminary reduction of the water samples with KI

Validation and application 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 - DMA (1 ng/ml As) and monomethylarsinate – MMA (1.0 ng/ml As). The precision of the procedure varies between 2–4 % for 3-10 ng/ml As and 7–15 % for 0.1–2 ng/ml As. The detection limit according to 3 σ criteria is 0.1 ng/ml As.

Selected sea water and mineral water from the market were analyzed using the proposed procedure indicated that major arsenic species in water is As(V).

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 red or white wine samples. It might be assumed that volatile wine matrix components interfere on the degree of atomization of the arsine in the quartz tube. The interference effect of ethanol studied confirms the suggestion, 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.

As a next step optimization of the conditions for selective determination of As(III) and As(V) in the presence of wine matrix was performed. The effect of the concentration of HCl and NaBH₄ on their absorbance signals was studied. The results obtained indicate that, the use of relatively low NaBH₄ concentration of 0.2 % (*m/V*) at 9 mol/l HCl assure selective determination of As(III) only. Both inorganic As species (As(III) + As(V)) can be determined together by using 9 mol/l HCl and 0.2 % NaBH₄ after As(V) prereduction with KI in 0.1 mol/l HCl. The limit of detection for both As species determination in wines is 0.1 µg/l and relative standard deviation (RSD) varied between 8-10 % at 0.1-30 µg/l As species level.

Determination of total As after microwave digestion

Red and white wine samples were digested in MW oven by using different amounts of HNO₃ and mixture of HNO₃ and H₂O₂. In all cases preliminary evaporation of ethanol is performed. The most serious interference for As determination by HGAAS 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 accuracy of the method proposed for total As determination in wines by HG-AAS was proved by comparative analysis using ETAAS and in all cases very good agreement between results was found. 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.

Consequently by using HG AAS it is possible to determine in wine samples: (i) inorganic As species - As(III) and As(V) after ethanol evaporation; (ii) total As content after MW digestion and (iii) organic As species content as a difference between the results obtained for total As content and inorganic As species.

Conclusion

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 arsenic, As(III), As(V), DMA and MMA in natural waters. inorganic (As(III) and As(V)) and total As determination in wines by using HGAAS. Inorganic arsenic species are determined directly in wine sample after ethanol evaporation and total As is determined after MW digestion. The amount of organic As species content in wines could be defined as a difference between the results obtained for total As content and inorganic As species measured.

References

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