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RESEARCH ARTICLE

Quantitative Determination of Arsenic in Bottled Drinking Water Using Atomic Absorption Spectroscopy

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Background: Many studies have been performed in the past few years, to determine arsenic speciation in drinking water, food chain and environment, arsenic being a well-recognized carcinogenic and toxic agent mainly in its inorganic species. 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 provide a great sensitivity only on the total amount.
Objective: The aim of this study was to develop a simple and rapid method and to analyze the concentration of total inorganic arsenic in bottled drinking water.
Methods: Total arsenic was determined in samples from six different types of commercially available bottled drinking water using atomic absorption spectrometry with electrothermal or hydride generation vaporisation. All drinking water samples were acidified with 0.1M nitric acid to match the acidity of the standards.
Results: The method was linear within the studied range (1–5 µg/L, R = 0.9943). The quantification limits for arsenic determination were 0.48 µg/L (HGAAS) and 0.03 µg/L (GFAAS). The evaluated arsenic content in drinking water was within the accepted limits provided by law.
Conclusions: A simple and sensitive method for the quantification of arsenic in drinking water using atomic absorbtion spectroscopy was described, which can be further used in toxicological studies. As an additional advantage, the system is very fast, efficient and environmental friendly.

Keywords: inorganic arsenic, atomic absorption spectrometry, bottled drinking water

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Introduction

Arsenic (As) is among the top 20 most toxic known substances which can lead to a wide range of health problems in humans. As is described as a metalloid and a ubiquitous element in the environment. As in the environment originates from weathering of arsenic-containing minerals and less from human activities. Exposure to As, even at very low amounts, can cause a variety of health problems, As being considered as highly toxic and carcinogenic, therefore raising concerns when present in the environment [1,2]. On the other hand, As toxicity depends on its chemical form, inorganic species being more toxic than their organic counterparts, and the inorganic trivalent form [As(III)] being more toxic than the pentavalent one [As(V)].

Inorganic forms of As appear in the environment mainly in water samples and fallings. The toxicity of As is determined by its oxidation state, thus the toxic answer to different As species will change depending on the biotic and abiotic conditions in water [3,4]. In groundwater, arsenic is predominantly present as As (III) and As (V), with a minor amount of methyl and dimethylarsenic compounds [1]. The concentration of arsenic in most groundwater is <10 µg/L and often below the detection limit of routine analytical methods.

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The instrumental techniques generally 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 provide results only on the total amount of As and not on its chemical forms [5]. 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 hyphenation of these techniques to element specific detectors have attracted great interest in elemental speciation analysis [6,7].

The atomic absorption spectrometry (AAS) has been widely used for arsenic determination at trace levels, in techniques such as electrothermal atomic absorption spectrometry (ETAAS) and hydride generation atomic absorption spectrometry [8]. In the recent years the interference problems which appear in electrothermal atomic absorption have been reduced by improving the background correction techniques. However, there are still interferences in the determination of arsenic by electrothermal atomic absorption spectrometry [9].

The aim of the present study was to develop a simple and rapid method (with minimal preliminary treatment of the sample) for the determination of total inorganic arsenic in bottled drinking water. This method should be further applicable to routine analyses and monitoring studies.

Materials and methods

Standards and reagents

All solutions were prepared with high-purity deionized water obtained with a Millipore Deioniser system. All glassware and polyethylene bottles were cleaned by soaking in 10% nitric acid (high purity concentrated nitric acid 65%, Merck, Suprapur) and rinsed three times with deionized water. [10,11].

High purity master standard solution containing 1000 mg/L As in 0.5 M nitric acid was bought from Merck. This was appropriately diluted with 1% v/v (approximately 0.1 M) nitric acid in water to provide the working standards within the range 1-5µg/L.

The calibration blank solution used throughout was a 0.1M solution of nitric acid.

For the Hydride Generation method, 5 M hydrochloric acid solution was prepared by diluting the appropriate amount of concentrated high purity HCl (Merck) with water. The reducing agent used, was 1% (m/v) sodium tetrahydroborate (Merck) in 0.5% NaOH (Sigma), freshly prepared and filtered before use. For each sample and standard 5g of potassium iodide (Sigma) was used as pre-reductant of arsenic.

For the Graphite Furnace technique we used 2% nickel nitrate (Fluka, purity >99%) solution in water as a chemical matrix modifier.

Samples

The samples were commercial bottled drinking water denoted as: W1, W2, W3, W4, W5, W6. These samples were acidified to approx. 0.1 M nitric acid (Merck, Suprapur, As < 0.0000001%) to match the standards acidity.

To determine the detection limit, analytical blanks were prepared in a similar manner to samples and standards.

Instrumentation

A Thermo Scientific SOLAAR 5M atomic absorption spectrometer equipped with a deuterium lamp background corrector, GF95Z Zeeman Graphite Furnace, FS95 Graphite Furnace Autosampler and VP 100 Hydride Vapour Generation System was used for the analysis.

The recommended spectrometer parameters provided by the spectrometer provider were used; working wavelength 193.7 nm and 0.5 nm slit-width were selected from previous optimization steps.

In HGAAS technique, the sample and standard solutions were pumped into a manifold where they reacted with the hydrochloric acid and sodium tetrahydroborate solutions, generating arsine. Using argon (purity of 99.9%), the generated arsines were swept to a T-shaped quartz tube atomizer cell and heated in an air-acetylene flame (plasma) containing the As atoms.

For the GFAAS technique, two types of graphite cuvettes were used: a Normal Electrographite Cuvette (NEC) and Extendet Lifetime Cuvette (ELC); sample injection volume and standards injection volume were of 20 µL, whilst the volume injected of chemical matrix modifier was of 20 µL. The height of the FS95 capillary tip in the cuvette was adjusted while observing the injection using the Graphite Furnace TeleVision (GFTV) accessory fitted to the spectrometer. All measurements were carried out with at least two replicates per sample and based on integrated absorbance. Zeeman correction was applied to all measured signals. The injection temperature was set at 70°C. Argon was used as protective gas throughout [12].

Table I. Instrumental parameters (GF–HG AAS) used for the determination of arsenic

Hydride Generation Atomic Absorption Spectrometry					
Oxidant (air) L/min	17				
Fuel (acetylene) L/min	1.0				
Lamp curent (%)	75				
Slid width	0.5				
Carrier gas (Argon) mL/min	200				
Graphite Furnace Atomic Absorption Spectrometry					
Step	Temp (°C)	Time (s)	Ramp (°C/s)	Gas type	Gas flow
Dry	125	30	100	2 Inert	0.2 L/min
Pyrolysis	1500	30	1000	2 Inert	0.2 L/min
Atomization	2250	6	0	2 Inert	Off
Cleaning	2600	5	0	2 Inert	0.2 L/min

The instrumental parameters selected for both techniques based on our investigation are systematically given in Table I.

The concentration of arsenic in each sample was calculated from the corresponding regression line absorbance vs. concentration.

The performance of the GFAAS and the HGAAS methods used for arsenic determination was established in our laboratory using standard samples. The detection (LOD) and quantification (LOQ) limits were computed as LOD = 3.3 x s/m and LOQ = 10 x s/m, respectively, where s is the standard deviation of the response and m is the slope of the calibration curve [13].

Results

In order to study the linearity of each method, the calibration curves were plotted for the concentration range 1–5 µg/L. The methods were linear in the range investigated, with a correlation coefficient greater than 0.99. The quantification limits for arsenic using Hydride Generation and Graphite Furnace techniques evaluated using our method were 0.48 µg/L and 0.03 µg/L, respectively.

Six different drinking water samples from different suppliers, with a declared content of dissolved inorganics were analyzed. Table II presents the values for the major elements in the water samples declared by the water provider.

All the declared elements analyzed are within the admissibility limits set by Directive 98/83/CE. At the same time, the providers declare that arsenic is below the quantifica-

Table II. Drinking water samples declared composition

Drinking water	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	As (µg/L)
W1	17.60	3.80	1.60	0.60	n.a.*
W2	66.68	2.88	0.98	0.45	n.a.*
W3	44.90	14.30	0.78	–	n.a.*
W4	57.70	30.60	2.53	–	n.a.*
W5	61.53	3.06	0.62	0.74	n.a.*
W6	124.1	8.42	13.52	0.81	n.a.*

* not available: the level of arsenic in drinking water samples was declared below the quantification limit

tion limit of the method, but do not clearly mention the method of analysis used in the evaluation.

All the samples were analyzed using the Hydridre Vapor Generation technique, but the results obtained were below the detection limit of the method.

All six drinking water samples were further analyzed using the Graphite Furnace method, with both NEC and ELC. The results are presented in table III.

The values obtained using NEC are in the range 0.14–0.87 µg/L, whilst for ELC the values were between 0.13 and 0.61 µg/L. The LOD and LOQ determined for the two types of cuvettes were 0.047 µg/L and 0.143 µg/L (for NEC), and 0.130 µg/L, 0.396 µg/L (for ELC), respectively.

The evaluated arsenic content in drinking water was within the accepted limits provided by Directive 98/83/CE.

Discussions

HGAAS method

In the Hydride Vapour Generation technique, argon was used as the carrier gas for arsine, a quartz T-tube cell with a pathlength of 165 mm and a diameter of 12 mm was heated to approximately 900 °C in an air–acetylene flame, with gas flow rates of 17.0 L min^{-1} (air) and 1.0 L min^{-1} (acetylene). All the samples were analyzed according to the method described, taking into account that this method is considered highly reliable for the determination of arsenic in biological matrices. However, even if we could obtain a low absorbance signal for the lowest standard solution used (1 µg/L), the samples showed absorbance levels below that value. We tried to further lower the concentration of the standards, but the results lacked precision, as the absorbance obtained was around 0.001 AU, therefore we concluded that the technique lacks precision below 1 µg/L.

GFAAS method

Determination of arsenic in environmental matrices using GFAAS encounters some difficulties. Many arsenic species are highly volatile, and possibility of losses during the ashing step is very high. Spectral interferences which appear in the presence of some anions and cations such as phosphate, iron, and aluminum are associated with the atomization step [14].

Table III. Results obtained for As in drinking water samples using GF-AAS

	Normal Electrographite Cuvettes			Extended Lifetime Cuvettes		
Samples	Mean (µg/L)	SD* (µg/L)	RSD%**	Mean (µg/L)	SD (µg/L)	RSD%
W1	0.155	0.013	8.3	0.467	0.198	42.4
W2	0.236	0.007	3.1	0.251	0.031	12.4
W3	0.142	0.022	15.2	0.419	0.093	22.2
W4	0.873	0.150	17.2	0.611	0.095	15.5
W5	0.351	0.062	17.8	0.138	0.013	9.8
W6	0.426	0.014	3.3	0.445	0.158	35.5

* Standard deviation
** Relative standard deviation

To overcome these difficulties, matrix modifiers are used to both stabilize the analytes during the graphite furnace cycle and permit increases in the charring and atomization temperatures. Better separation of the element from interferences can be achieved by using proper matrix modifiers [15]. In order to stabilize arsenic at higher temperature of the ashing stage we used nickel nitrate as matrix modifier.

The method seems to be more sensitive when using NEC, compared with ELC. Even more, the values obtained for arsenic using NEC are more precise than those obtained with ELC, as the current used in for heating the cuvette is higher in the first case. Besides, the cook-book of the spectrometer recommends the use of these cuvettes for arsenic assay.

We tried also to perform the deuterium lamp background correction (instead of Zeeman correction), but the results were even more imprecise. Therefore we consider the Zeeman background correction to be more fitted to the assay.

Among other limitations of the study, we can point out that we tested only one matrix modifier (nickel nitrate); other recommended modifiers (magnesium and palladium nitrate) are going to be tested, too. The pyrolysis temperature is rather high compared to other published methods [16], thus leading to possible analyte looses. The investigated concentration range is also limited compared to other recently published studies [17,18].

Further studies will try to eliminate the matrix effect (the relative high Ca, Mg and Na content of the drinking water) by using the standard addition method.

Conclusions

A simple and sensitive (LOD = 0.047 µg/L and LOQ = 0.143 µg/L) method for the quantification of As in drinking water using AAS was described, using the graphite furnace technique.

The results are more precise when using Normal Electrographite Cuvettes and Zeeman background correction. The method can be further used in toxicological studies.

As an additional advantage, the system is very fast, efficient and environmental friendly.

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