Speciation of inorganic and organic arsenic forms using HPLC-ICP-MS technique in aqueous matrices

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Abstract. The aim of the study was to develop, optimize and validate an analytical method for the simultaneous detection and quantification of As species (As (III), dimethylarsinate (DMA), monomethylarsonate (MMA) and As (V)) from various water matrices (drinking water, surface water and groundwater) using the technique of high performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (HPLC-ICP-MS). The separation of the species was achieved using an Agilent G3154-65002 precolumn, 4.6 mm x 10 mm, and an Agilent G3154-65001 column, 4.6 mm x 150 mm, at ambient temperature. The mobile phase used was 1M NaH_2PO_4 and 0.1 mM EDTA-2Na solution at a flow rate of 1 mL/min. Linear regression lines were drawn in the range 10-50 µg/L, the coefficients of determination (R^2) obtained for each species were higher than 0.99. The quantification limits (LOQ) varied in the range 1.8 µg/L As(V) to 2.0 µg/L As(III), and in the range 3.9 µg/L DMA to 4.1 µg /L MMA for all studied matrices. These limits allow the quantification of As species in drinking water samples, surface water and groundwater at the trace level.

Keywords: As species, HPLC-ICP-MS, detection, organic and inorganic forms

1. Introduction

Arsenic is a ubiquitous metalloid, having a wide distribution in the aquatic environment, as a result of natural processes and anthropogenic activities (Hong et al, 2016). Arsenic is found naturally in water, mainly in the form of arsenite and arsenate, but methylated forms may be present as a result of biological activity. In natural waters, arsenic occurs most often in inorganic forms, to a lesser extent in organic forms, such as monomethylarsonic acid – MMAA and dimethylarsinic acid – DMAA (Leermakers et al, 2006; Smedley and Kinniburgh. 2002). Among the inorganic forms, it is mainly found in the form of oxyanions, such as: as trivalent arsenate (H_3AsO_3) in the reducing environment and as pentavalent arsenite ($H_2AsO_4^-$) under oxidizing conditions.

The toxic effects of arsenic are related to its oxidation state, changes in oxidation state have an important role on the degree of bioavailability and toxicity. The toxicity of different arsenic species varies in the order: arsenite > arsenate > monomethylarsonate (MMA) > dimethylarsinate (DMA).

Anthropogenic human activities lead to increased levels of arsenic in soil and groundwater (Chen et al, 2016; Rahman et al, 2021) which eventually seep into the diet and cause disturbances in the biochemical balance of living systems. In this regard, a multitude of reports have appeared on arsenic-affected regions around the world (Meduni at al, 2020; Podgorski and Berg, 2020; Shaji et al, 2021). Currently, the major source of arsenic exposure of the human population is through contaminated food, that is, through drinking water and food, which mainly includes rice and seafood (WHO, 2018). Worldwide, 107 countries are affected by arsenic contamination through groundwater, which include Asia (32 countries), Europe (31 countries), Africa (20 countries), North America (11 countries), South America (9 countries) and Oceania (4 countries) (Singh and Stern, 2017).

In Romania, groundwater from different sources were affected by pollution (some sources from Timis, Bihor, Arad, Covasna Counties), earlier studies reported As concentration in the range 11 µg/L to 1505 µg/L (Tudorache et al, 2011), values higher than maximum admissible value according to European Drinking Water Directive (Directive (EU) 2020/2184) and Commission Directive 2003/40/EC regarding mineral water quality (Commission Directive 2003/40/EC), which is 10 µg/L.

The usual analytical methods for controlling As concentrations in water are Grafite Furnance Atomic Absorption Spectrometry (GF-AAS), Inductively Coupled Plasma Optical Emission Spectrometry with ultrasonic nebuliser (USN-ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), due to their high sensitivity, selectivity and wide range of linearity. In addition, electrochemical methods are considered easy to use due to the low cost, short analysis time, minimal pretreatment of the sample (Badescu et al, 2016). For the analysis of arsenic species, chromatographic techniques such as: high-performance liquid chromatography (HPLC), gas chromatography (GC) and capillary electrophoresis (CE), are generally coupled with AAS and ICP-MS detectors to

simultaneously obtain a good separation and excellent sensitivity (Huimin et al, 2020).

The aim of the study was to develop a HPLC-ICP-MS method for simultaneous detection and quantification of As species (As (III), DMA, MMA and As (V)) from water samples.

2. Materials and methods

2.1. Materials

The standards use for the calibration curves were two inorganic salts (sodium (meta)arsenite $NaAsO_2$ for As(III) species, sodium arsenate dibasic heptahydrate $Na_2HAsO_4 \cdot 7H_2O$ for As(V) species) and two organic compounds (monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA)). For the experimental part were purchase $NaAsO_2$ (≥90%, Sigma-Aldrich, Merck), $Na_2HAsO_4 \cdot 7H_2O$ (≥98%, Sigma-Aldrich, Merck), Dimethylarsinic Acid Standard Solution (Standard Reference Material 3031 NIST, 20.47 mg/kg ± 0.18 mg/kg As), Monomethylarsonic Acid Standard Solution (Standard Reference Material 3030 NIST, 17.64 mg/kg ± 0.15 mg/kg As).

The mobile phase were prepared with using NaH_2PO_4, EDTA-2Na and NaOH. Ultrapure water was used for all standards and mobile phase solutions. 2 mL of 1M NaH_2PO_4 and 2 mL of 0.1 mM EDTA-2Na was mixed in 1L ultrapure water, pH of the solution was corrected at 6 pH units using 1M NaOH solution. After pH correction, the final solution was degassed using the ultrasound-assisted technique and filtered through a 0.45 μm filter.

2.1. Methods

In order to prepare standard solutions, for each species was obtained a stock solution (10 mg/L for As(III) and As(V), 0.8188 mg/kg for DMA, 0.7056 mg/kg for MMA). The calibration curves were ploted in the range 10 μg/L to 50 μg/L, each standard being a mixture of all compounds.

For the validation tests, were prepared 10 different solution of 10 μg/L in order to evaluate precision. For quantification limits, 5 independent solutions of 1 μg/L were analysed for As(III) and As(V) and 5 independent solutions of 3 μg/L were analysed for DMA and MMA. The experimental part was applied on an Agilent 1260 Infinity II HPLC system coupled to an Agilent 7850 ICP-MS. The optimal parameters for detection of As species (As (III), DMA, MMA and As (V)) for both HPLC and ICP-MS are presented in table 1.

The chromatographic data were collected using the acquisition and control software Mass Hunter version D.01.01 (SI 637), manufacturer Agilent Technologies, which was also used for data processing and quantification of As species.

Table 1. The optimal parameters of HPLC-ICP-MS for the detection of As species

| HPLC Parameters	ICP-MS Parameters
Pre-column: Agilent G3154-65002, 4.6mm x 10 mm	RF Power: 1400 W
Column: Agilent G3154-65001, 4.6mm x 150 mm	Nebuliser pump: 0.4 rps
Column temperature: ambiental temperature	Presure gas in Nebuliser: 1.10 L/min
Mobile phase: mixture of NaH_2PO_4 1M and EDTA-2Na 0.1 mM at pH=6	Internal temperature in sistem: 35.1˚C
Volume injected: 50 μL	Flow gas plasma: 15 L/min
Flow mobile phase: 1.0 mL/min	Flow auxiliar: gas 0.9 L/min
Elution: in gradient	Flow He: 4.3 mL/min
Time/sample: 14 min	

3. Results and discussions

The performance parameters evaluated for the method developed and in-house validation were linearity, detection limit (LOD), quantification limit (LOQ) and precision (repeatability). In figure 1 is presented the obtained cromatogram at 10 μg/L for all As species.

In table 2 are presented determination coeficients for liniar regresion curves (R^2), quantification limits and precison data. The quantification limits varied around 2 μg/L for As(III) and As(V) and around 4.0 μg/L for DMA and MMA. These limits allow the quantification of As species (As(III), As(V), DMA, MMA) in drinking water samples, surface water and groundwater at trace level. All determination coeficients for liniar regresion curves were equal or higher than 0.995. The precision data shows values of 15% for As(III) and As(V) and around 9% for DMA and MMA species.

Table 2. Performance parameters obtained experimental for HPLC-ICP-MS method

| As species	R^2	LOQ, μg/L	Repeatability, %
As (III)	0.997	2.0	15.21
As (V)	0.995	1.8	15.63
DMA	0.998	3.9	8.69
MMA	0.996	4.1	9.01
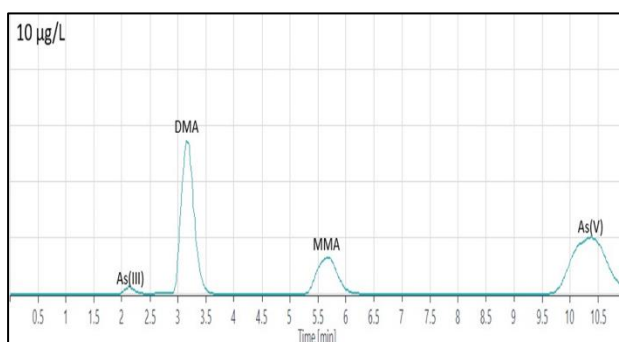
Figure 1. Cromatogram of As species

In figure 2 are presented linear regression curves for all As species in the range 10 μg/L to 50 μg/L.

4. Conclusions

The paper present a method for simultaneous detection of As species (As(III), As(V), DMA, MMA) in drinking water samples, surface water and groundwater at trace level using HPLC-ICP-MS technique. The proposed method was in-house validated and liniarity range, quantification limits and precision were evaluated for all As species. The paper present the optimized parameters for the equipment used (HPLC and ICP-MS).

(a) (b) (c) (d)
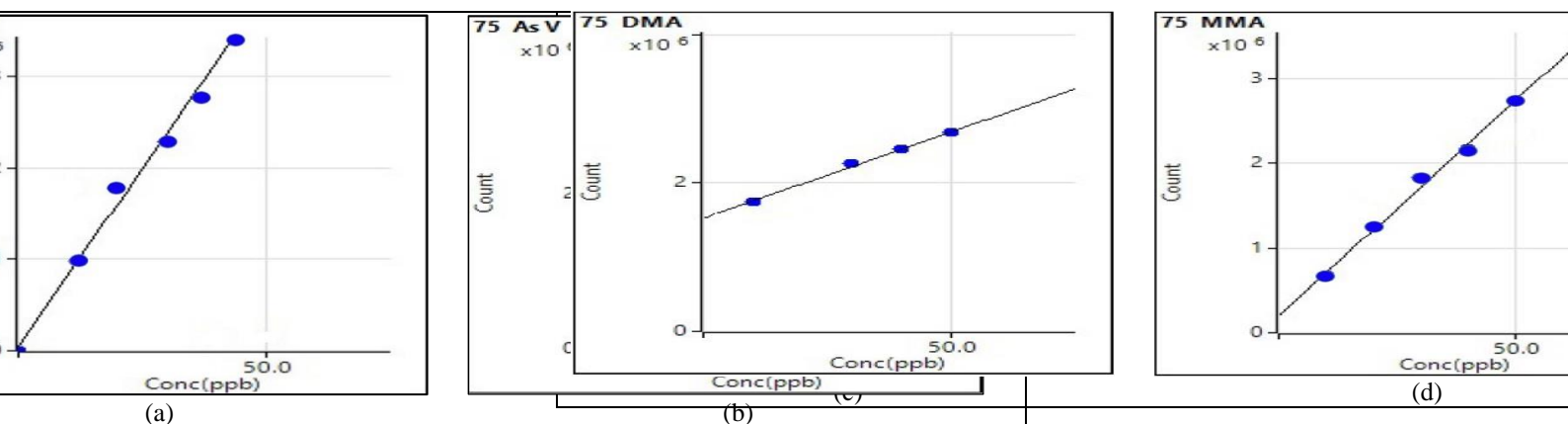
Figure 2. Linear regression curves for (a): As(III), (b) As(V), (c) DMA, (d) MMA in the range 10 µg/L to 50 µg/L

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