DMA and inorganic arsenic determination by coupling multisyringe flow injection analysis (MSFIA) to HG-AFS with on-line photo-oxidation

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Abstract
A multisyringe flow injection approach has been coupled to a hydride generation system with UV photo-oxidation for the determination of organic arsenic by atomic fluorescence spectrometry. The oxidant solution ($K_2S_2O_8$) and the sample pass through a UV irradiation, where the organic arsenic is transformed to As(V). The volatile hydride (arsine) is generated by a simultaneous injection of a reducing solution ($NaBH_4$), hydrochloric acid solution and the oxidized sample. The sample and reagents are dispensed into a gas–liquid separation cell. An argon flow delivers the arsine into the flame of the atomic fluorescence instrument. A hydrogen flow has been used to support the flame. Nitrogen has been employed as a drier gas. This technique was validated by means of a solid reference material with good agreement with the certified values. Satisfactory results for organic arsenic determination by means of the developed methodology were obtained. The proposed methodology offers several advantages, such as increasing the sampling frequency, high sensitivity and decreasing of reagents and sample consumption, which leads to a lower waste generation.

Introduction
The chemical forms and oxidation states are essentials in arsenic toxicity. At first it was believed that inorganic arsenic compounds were more toxic than the organic ones and that the methylation of inorganic arsenic was part of the detoxification process. However, numerous studies demonstrated that trivalent methylated compounds, intermediates in the methylation process of arsenic, are more toxic than inorganic arsenic (Hughes, 2002; Mandal and Suzuki, 2002). Therefore, the determination of the individual species is mandatory in order to estimate its environmental impact and health risks.
Several analytical methodologies have been developed for arsenic determination. Nevertheless, hydride generation (HG) technique coupled to atomic fluorescence has been implemented for arsenic analysis at trace levels. The oxyanions arsenite and arsenate can be reduced with $NaBH_4$ in acid medium generating volatile arsines. Other species, such as monomethyl and dimethyl arsenic (MMA and DMA), trimethyl arsenic oxide (TMAO), tetramethyl arsenic ion (TETRA), arsenobetaine (AB), arsenocholine (AC) and several arsenosugars can not form volatile species. In this case, the destruction of organic molecules is required before the HG step. It can be accomplished by means of a photo-oxidation with a strong oxidant and UV radiation, thermal oxidation with a strong oxidant and heating, or a microwave assisted digestion.
The addition of a hydrogen flow into the gas-liquid separator has been proposed in order to maintain a steady flame in the AFS atomizer and not rely on the H_2 produced during the HG step (Gomez-Ariza et al., 1999). Multisyringe flow injection analysis (MSFIA) was recently developed as a practical technique for automation of serial assays (Cerdà et al., 1999). MSFIA combines the advantages of employing the multichannel operation of peristaltic pumps with the constant pulseless and exactly known volume delivery achieved by piston pumps (Cerdà et al., 1999). This system includes a burette with four syringes, which are connected to the same stepper motor and moved simultaneously. A three-way solenoid valve is placed at the head of each syringe.
The aim of the present study was to develop an automated method for the determination of DMA and inorganic arsenic by MSFIA coupled to HG with a UV radiation source and atomic fluorescence spectrometry (AFS) as detection system.

Materials and Methods
All chemicals used were of analytical reagent grade. Stock solution 1000 mg As L^{-1} As(III) was prepared by dissolving 4 g of As_2O_3 in 1000 mL of 0.1 mol L^{-1} NaOH solution. Stock solution 1000 mg L^{-1} dimethylarsenic was prepared by dissolving $(CH_3)_2AsNaO_2.3H_2O$ (Sigma Aldrich) in water. Peroxodisulfate (3% $K_2S_2O_8$, Scharlau) was employed as a strong oxidant and prepared in 3% NaOH. 2.2% $NaBH_4$ solution (Scharlau) was prepared immediately before use in 1% NaOH solution and filtered with a membrane filter of 0.45 microns. All solutions were prepared with Millipore water. Glassware necessary for the determination of arsenic was soaked in a 10% (v/v) nitric acid bath (10%) for 24 hours and rinsed with Millipore water.
The sample introduction system consists of a programmable multisyringe burette (MicroBU 16 A Crison, Barcelona Alella) with two additional three-way solenoid valves (V1) and (V2) (Takasawo Electric, INC.) and an autosampler (Crison). Syringe S1 (10 mL) was used for sample loading (Hamilton,

Switzerland); syringe S2 (5mL) was employed for oxidant reagent $K_2S_2O_8$. The hydride generation reagents ($NaBH_4$ and HCl) were dispensed to the system through syringe S3 (2.5 mL) and syringe S4 (5 mL), respectively. The manifold tubing is made of PTFE (0.8 mm id) and three way connectors of PMMA (polymethylmethacrylate). The photo-reactor was responsible for irradiation of the sample. It is constituted by an 8 W ultraviolet lamp (Sylvania, U.S.A.) in which a PTFE tubing (200 cm, 0.08 mm i.d.) is wrapped around it (Fig. 1).

System procedure for DMA determination involves two steps. The first one involves a simultaneous injection of sample and oxidizing reagent, which are propelled to the ultraviolet lamp. In the second step, the irradiated sample and the hydride generation reagents are dispensed to the reaction coil. The generated arsine is separated from the aqueous matrix in a glass gas-liquid separator and carried with argon to the AFS detector for its analytical determination. The analysis of total inorganic arsenic is carried out without photo-irradiation.

Instrument control and data acquisition were performed using the software Autoanalysis 5.0 (Sciware, Palma de Mallorca).

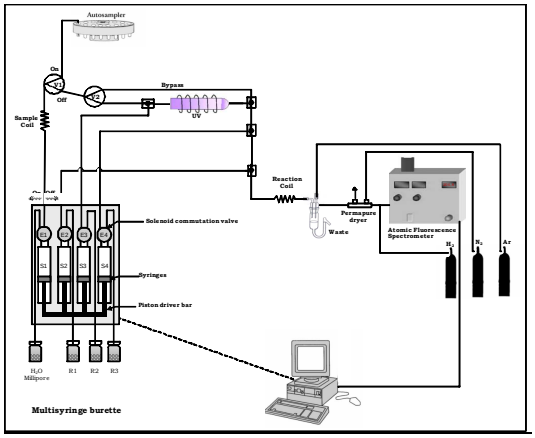

Figure 1. MSFIA-HG-UV-AFS system proposed for As determination.

Results and discussions

The preliminary tests showed that the presence of a strong oxidant is mandatory for a complete conversion of DMA to As(V). The system optimization established that an irradiation time of 20 s was enough for the decomposition of DMA to As(V). The detection limits achieved for DMA and total inorganic arsenic were 0.09 μg L^{-1} and 0.47 μg L^{-1}, respectively. The working linear ranges were 0.5-7 μg L^{-1} and 0.5-25 μg L^{-1} for DMA and total inorganic arsenic, respectively.

An injection throughput of 24 and 28 h^{-1} were obtained for DMA and total inorganic arsenic, respectively. The study of interferences indicated that Cu has interfered in the determination of 5 μg L^{-1} DMA up the value of 750 μg L^{-1}, whereas Co at 1500 μg L^{-1}. The tolerance level of Pb and Hg was higher, interfering up 3000 μg L^{-1}. The developed technique was validated by means of reference solid material (Tuna fish muscle, BCR 627) with a 98% recovery. Table 1 shows the application of the developed technique to different water samples. The recovery results were satisfactory.

Table 1. Analysis of spiked water samples.

DMA				
Sample	**Concentration Found**	**Addition of Standard**	**Value Found**	**Recovery**
Ground water	ND	5 μg L^{-1} DMA	4.86 μgL^{-1}	97 %
Tap water	ND	5 μg L^{-1} DMA	5.41 μg L^{-1}	108 %
Mineral water	ND	1 μg L^{-1} DMA	0.99 μg L^{-1}	99 %
INORGANIC ARSENIC				
Sample	**Concentration Found**	**Addition of Standard**	**Value Found**	**Recovery**
Ground water	2.27 μg L-1	3 μg L^{-1}	5.73 μg L^{-1}	91 %
Tap water	ND	1.5 μg L^{-1}	1.65 μg L^{-1}	99 %
Mineral water	ND	3 μg L^{-1}	2.99 μg L^{-1}	100 %

Conclusions

The hyphenated MSFIA-UV-HG-AFS system proposed for on-line speciation and determination of DMA and total inorganic arsenic has proved to constitute an effective approach. Other techniques that can be used for arsenic speciation, such as chromatographic techniques need the implementation and maintenance of an ion chromatography system. The proposed method offers some advantages such as high sensitivity, high sampling frequency and decreasing of reagents and sample consumption, which leads to a lower waste generation. This system has been successfully applied to the determination of dimethylarsenic in various biological and environmental matrices, such as solid reference material BCR-627 (muscle of tuna) and different samples of water.

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