



Development of an on line miniaturized non-chromatographic arsenic speciation system[☆]



Ariel Maratta, Luis Dante Martinez, Pablo Pacheco^{*}

Instituto de Química de San Luis, INQUISAL, Centro Científico-Tecnológico de San Luis (CCT-San Luis), Consejo Nacional de Investigaciones Científicas y Universidad Nacional de San Luis, Chacabuco y Pedernera, Ciudad de San Luis 5700, Argentina

ARTICLE INFO

Article history:

Received 24 February 2016

Accepted 19 March 2016

Available online 21 March 2016

Keywords:

Arsenic speciation

Miniaturization

Hydride trapping

Carbon nanotubes

ETAAS

ABSTRACT

An arsenic speciation method is proposed introducing selective hydride generation, UV photooxidation and hydride trapping on oxidized multiwall carbon nanotubes (CNTs) with electrothermal atomic absorption spectrometry (ETAAS) for detection. To this end a flow injection system was designed to focus on miniaturization with minimal reagent consumption. As a result reagent consumption was kept in μL level with no need of carrier gas for hydride transport. This study obtained an enhancement factor of 60 when 2 mL of sample were loaded in the gas–liquid separator, arsine adsorbed on CNTs, and eluted with 30 μL of 5% HNO_3 (v/v^{-1}). A limit of detection (LoD) of 0.78 ng L^{-1} was obtained. The precision was evaluated by relative standard deviation (RSD%) corresponding to 8.3% ($n = 10$). The method determined organic and inorganic arsenic fractions; and As^{3+} and As^{5+} concentrations in well and cistern water samples from arsenic endemic regions of Argentina.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Arsenic is recognized as a ubiquitous element in the environment, from both natural and anthropogenic sources. As occurs in various oxidation states (-3 , 0 , $+3$ and $+5$) and undergoes complex biotic and abiotic transformations to organic and inorganic compounds in the environment. In natural water, As is found mainly as inorganic oxyanions such as trivalent arsenite (As^{3+}) or pentavalent arsenate (As^{5+}), while organic arsenic compounds, as monomethylarsonate (MMA), can be found in low concentrations in surface water, product of the biological activity [1,2]. Arsenic toxicity varies depending mainly on the oxidation state, being inorganic species the most toxic [3,4]. According to this, research in the development of analytical methods for As speciation in environmental samples has a remarkable importance.

In literature, several researches have been reported on arsenic speciation [5]. Most of these researches involve the introduction of separation techniques like liquid chromatography (LC) coupled to atomic spectrometries like atomic fluorescence spectrometry (AFS) [6] or inductively coupled plasma mass spectrometry (ICP MS) [7]. Despite of their efficiency for analyte separation, LC is a relatively expensive technique that consumes ultrapure water and solvents. For these reasons, many of the best speciation procedures remain at the laboratory scale and cannot be used in routine analysis [8].

Non-chromatographic methods for arsenic speciation can involve two strategies: UV photooxidation and selective hydride generation

[9,10]. UV irradiation treatment has been probed to efficiently transform methylated arsenic species (non-forming hydride species) to inorganic As species (hydride forming). In addition it has been previously shown that As^{3+} could be determined alone in a mixture of As^{3+} and As^{5+} by selective hydride generation through strict pH control [11].

Research involving UV photooxidation, selective hydride generation and hydride trapping with graphite furnace atomic absorption spectrometry (GFAAS) for detection has been already described in literature [12,13]. However research reporting As speciation by these strategies sometimes involves hydride trapping and selective release of trapped hydrides by means of temperature control [11]. These methodologies that employ different temperatures to trap and release hydrides, like cryogenic trapping, require complex instrumentation and sophisticated control mechanisms. Recently a novel methodology, exploits carbon nanotubes' (CNTs) properties of gas adsorption on their surface [14, 15], to trap arsenic hydrides for analytical purposes [16].

A preference for online extraction systems involving solid phase extraction has been reported, due to advantages obtained in automation such as speed, sensitivity, reproducibility, simplicity and economy in the use of reagents. These systems consist in metal species retention or its derivatives on an appropriate solid sorbent contained in a column or micro column with subsequent recovery by elution with an adequate solvent [17–19]. Flow injection system design minimizes the amount and the toxicity of solvents and reagents employed in the measurement step, especially by automation and miniaturization, to be framed into Green Chemistry principles [20].

Despite the fact that there is an elevated number of researches involving As speciation in literature, most of it involves LC coupling to atomic spectrometries, mainly ICP MS, sophisticated instrumentation banned for many laboratories. The objective of this work is to

[☆] Selected research paper presented at the biannual Argentine Analytical Chemistry meeting held in Argentina, AAQA-2015.

^{*} Corresponding author.

E-mail address: ppacheco@unsl.edu.ar (P. Pacheco).

encompass UV photooxidation and selective hydride generation with a simple hydride trapping strategy on CNTs to reach As speciation employing ETAAS for determination. To this end an FI design is proposed, focused on miniaturization and minimizing reagent consumption and waste generation. Different variables were optimized regard FI manifold and As speciation. The proposed methodology was applied to analysis of water samples from Arsenic endemic regions of Argentina.

2. Experimental

2.1. Reagents

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. Standard As^{3+} solution ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 0.3300 g of As_2O_3 (Sigma, St. Louis, USA) in 10 mL of 1 M NaOH and diluting to a final volume of 250 mL with 2 M HCl. Standard As^{5+} solution ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving 0.4526 g of $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (Sigma, St. Louis, USA) in 10 mL of NaOH diluted to a final volume of 250 mL with 2 M HCl. Standard monomethylarsonate solution ($1000 \mu\text{g mL}^{-1}$) containing $543.21 \mu\text{g mL}^{-1}$ of As was prepared from analytical grade $\text{CH}_3\text{AsO}(\text{ONa})_2 \cdot 6\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) [21]. Thiourea and L-cysteine, used as reductants agents, were obtained from Sigma-Aldrich. Titanium dioxide, employed as photocatalyzer was obtained from (Sigma, St. Louis, USA) A 0.5% (w/v) sodium borohydride solution (Aldrich Chemical Co. 98%) was prepared in 0.5% (w/v) sodium hydroxide solution and was filtered through Whatman N° 42 filter paper to remove undissolved solids. This solution was prepared daily.

Commercial multiwalled CNTs were obtained from Sunnano (Jiangxi, China). CNTs were treated with concentrated nitric acid to clean them and eliminate possible residues present in CNTs due to the generation process. This procedure also allowed the generation of —COOH and —OH groups on the CNTs' surface, improving their solubility. After this, CNTs were centrifuged, filtrated, and dried [22].

Chemical modifier solutions (100 mL of a concentration of $10,000 \text{ mg L}^{-1}$) were prepared by dissolution of the proper solid salt into deionized water as follows: for Ni chemical modifier, 4.9545 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were weighed and diluted [23].

2.2. Sample preparation

Well and cistern water samples were collected in As endemic regions of Argentina, specifically from south of Córdoba province. Samples were collected directly from the tap of the pumping system. Then they

were filtered through 0.45 mm pore size membrane. Samples were transported refrigerated at 5°C to avoid any As species interconversion. Once in the lab they were analyzed immediately.

2.3. Apparatus

Determination of As concentration was carried out on a Shimadzu Model AA-7000 atomic absorption spectrometer (Tokyo, Japan) equipped with a background correction system employing a continuum source, a GFA-EX7 electrothermal atomizer, and an ASC-7000 auto sampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. An arsenic hollow-cathode lamp (Hamamatsu, Photonics K. K., Japan) was employed as radiation source operated at 10 mA, the analytical wavelength of 193.7 nm was employed for all measurements. Gilson Minipuls 3 peristaltic pumps (Villiers, Le-Bell, France) and Tygon-type pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel sample, eluent and reagents. The employed gas-liquid separator (GLS) was homemade (1 cm internal diameter, 8 cm high, 6 mL volume) and it can be observed in Fig. 1. Reagents were deposited directly in the bottom of the GLS to improve homogenization and hydride generation. All unions were sealed to avoid gas losses. A conical minicolumn (40 mm length, 4.5 mm internal upper diameter, and 1.5 mm internal lower diameter) was used as sorbent holder. It was prepared by placing 10 mg of oxidized CNTs into an empty conical tip by the dry packing method. To avoid CNTs losses when the simple solution passed through the conical minicolumn, small amounts of quartz wool were placed at both ends. The photoreaction system consists of a PTFE tube (I.D. 0.55 mm) from Cole Parmer (Vernon Hills, IL, USA) surrounding a high-pressure Hg vapor lamp Phillips (Hanau, Germany).

2.4. Preconcentration procedure and determination

To develop As speciation methodology, different variables like pH, UV exposure time, type of reducing reagent, addition of catalyst and flow rates were optimized. The system shown in Fig. 1 was used for this purpose.

Previous to all analysis, the gas-liquid separator (GSL) was filled with NaBH_4 solution (Pump P₁; valve V₁, NaBH_4) and valve V₄ was closed. For determination of hydride and non-hydride forming arsenic species sample was previously added with TiO_2 prior photooxidation. After this sample is loaded (pump P₁; valve V₁, position S) and introduced into photoreactor (UV PR) to oxidize arsenic organic species or non-hydride forming species. Then it is merged with HCl (Pump P₂;

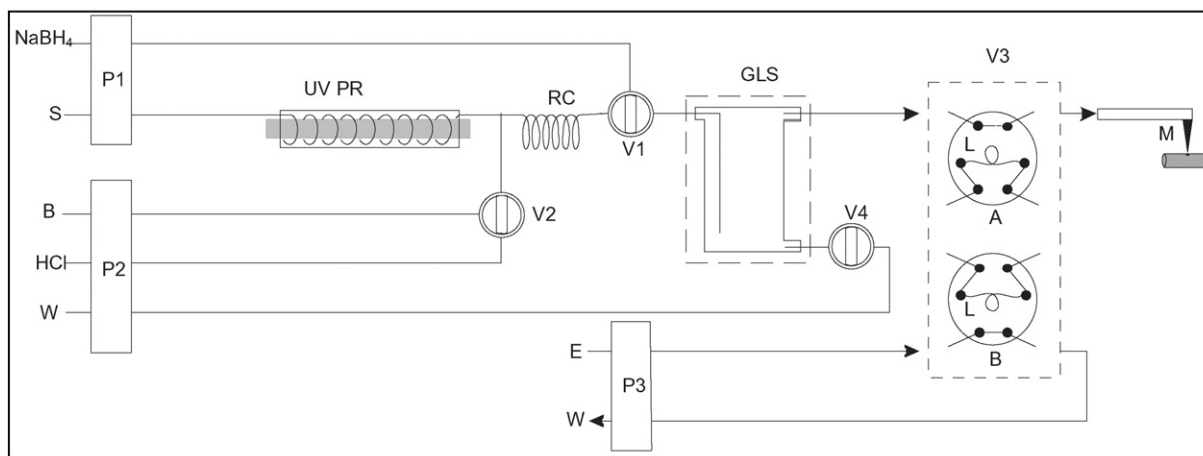


Fig. 1. Schematic diagram of the configuration of the instrumental. S, sample; B, buffer; E, eluent; V₁, V₂ and V₃, injection valves, valve positions: (A) sample loading; (B) injection; L, loop (30 μL volume); P₁, P₂ and P₃, peristaltic pumps; GLS, gas-liquid separator; RC, reaction coil; W, waste; M, mini-column filled with oxidized multi-walled carbon nanotubes mounted on the arm of ETAAS autosampler.

Download English Version:

<https://daneshyari.com/en/article/1227519>

Download Persian Version:

<https://daneshyari.com/article/1227519>

[Daneshyari.com](https://daneshyari.com)