

# Determination of total inorganic arsenic in water using on-line pre-concentration and hydride-generation atomic absorption spectrometry

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## Abstract

A rapid and sensitive method for the on-line separation and pre-concentration of inorganic arsenic in water samples is described. The analyte in the pentavalent oxidation state is reduced to its trivalent form with L-cysteine and the total inorganic arsenic is sorbed onto activated alumina in the acid form in a mini-column coupled to a FI-HG AAS system. Afterwards, it is eluted with  $3 \text{ mol l}^{-1}$  HCl. An enrichment factor of 7 was obtained, allowing an analytical flow rate of about 28 determinations per hour. The limits of detection ( $3\sigma$ ) and of quantification ( $10\sigma$ ) were calculated as  $\text{LOD} = 0.15 \mu\text{g l}^{-1}$  of As and  $\text{LOQ} = 0.5 \mu\text{g l}^{-1}$  of As, respectively. Relative standard deviations ( $n = 10$ ) less than 8% were obtained for different arsenic concentrations and the accuracy was verified by analysing certified reference materials. Different kinds of samples, such as mineral water, drinking water, river water and natural spring water were analyzed and good agreement was obtained with the values from spiked experiments.

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## 1. Introduction

Arsenic is a ubiquitous specie in the environment and it is a seriously toxic element for man, who is mainly exposed via drinking water and seafood. While organic species like dimethylarsenic acid (DMA) show a median lethal dose in animals of  $\text{LD}_{50}(\text{DMA}) = 1200 \text{ mg kg}^{-1}$ , and are considered as non-toxic compounds, the inorganic forms arsenite and arsenate show  $\text{LD}_{50} = 4.5 \text{ mg kg}^{-1}$  and  $\text{LD}_{50} = 14 \text{ mg kg}^{-1}$ , respectively, and should be considered to be rather toxic. Most of the international agencies established acceptable values for arsenic in drinking water in the range of  $0.005\text{--}0.050 \text{ mg l}^{-1}$  [1]. Consequently, there is an increasing interest in the development of methodologies characterised by simplicity, speed and economy of reagents and materials aiming at the determination of arsenic in water.

Atomic absorption spectrometry (AAS) is a well-established and well-known technique that has been used for the determination of many elements using flame or electrothermal atomization [2,3]. In 1969, Holak [4] used the concept of hydride generation to determine arsenic by AAS. When the acidified sample containing arsenic was put in contact with a reducing reagent, the volatile hydride  $\text{AsH}_3$  was generated, providing an excellent tool to detect and quantify this element.

Considering the benefits obtained with this technique, the development of a new analytical method employing FI-HG AAS is of significant interest. Sometimes, however, the concentration of the analyte is very low, considering other species present in the sample, so a pre-concentration step is necessary.

Pre-concentration techniques of trace metals, like sorption of the analyte on solid materials, modified or not with organic reagents have frequently been used. The metal or the metal-complex is eluted from the solid material by a suit-

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able solvent and afterwards the determination of the metal is performed.

The usual reactions for As pre-concentration make use of organic reagents which are able to separate As(III) from As(V), such as dithiocarbamate [5–7] and dithiophosphate [8–11] compounds sorbed on solid materials.

Some inorganic materials, such as ion-exchange resins [12], zeolites [1], and alumina [13,14] have also been used as sorbent materials for ions from aqueous solutions. Sperling et al. [13] in 1992 determined Cr(III) and Cr(VI) in water using FI-FAAS, after pre-concentration on activated alumina. In 1994, Ebdon et al. [14] used activated alumina in the acid form to pre-concentrate As, Cr, Se, and V before their determination by ICP-MS, with good pre-concentration factors. Recently, Lin and Wu [15] evaluated the use of activated alumina as a sorbent for arsenite and arsenate ions in a procedure for the decontamination of water.

In the present work, an on-line pre-concentration method employing activated alumina as sorbent for total inorganic arsenic, followed by its determination by HG AAS was developed. The method was applied to the determination of inorganic arsenic in rivers, mines and natural spring waters from Quadrilátero Ferrífero, a mining region in Minas Gerais, Brazil.

## 2. Experimental

### 2.1. Apparatus

The FI pre-concentration system coupled to HG AAS is shown in Fig. 1. In the FI-HG system, an eight-channel peri-

static pump (Ismatec®, ICP High Precision Multichannel Dispenser) introduced the sample and the reducing reagent into carrier flows using a merging-zones manifold. Samples and reagents were aspirated through Tygon tubes (Technicon) with appropriate flow rates for each solution. Sample loop, reaction coil and transmission lines were prepared using Teflon tubing (CPL, 0.8 mm i.d.). For the pre-concentration, the total inorganic arsenic present in the sample is reduced to As(III) with 0.1% (w/v) L-cysteine, which is then retained in a glass column ( $\phi_i = 3$  mm;  $L = 35$  mm) containing 70 mg of activated alumina (150 mesh) in the acid form by the passage of a solution flowing at  $3.2$  ml  $\text{min}^{-1}$ . After 2 min, the pre-concentrated species are eluted with  $3$  mol  $\text{l}^{-1}$  HCl ( $3.2$  ml  $\text{min}^{-1}$ ) loading a  $150$   $\mu\text{l}$  loop, while a  $1.0\%$  (m/v) sodium tetrahydroborate solution loads the other loop ( $150$   $\mu\text{l}$ ) of the system. The time of the elution step is 8 s and at the same time, the alumina is regenerated for the next pre-concentration cycle. The arsine generated is carried with  $\text{N}_2$  (flow rate =  $90$  ml  $\text{min}^{-1}$ ) to a quartz cell wound with Ni–Cr wire where the atomization process occurs. The temperature of the quartz cell needed for  $\text{AsH}_3$  atomization was obtained and controlled with a Varivolt regulator, connected to the Ni–Cr coil of the cell. The As was measured with an atomic absorption spectrometer (Varian, Model Gemini AA 12/1475) equipped with a hollow cathode lamp for arsenic as well a deuterium lamp for background correction under the following conditions: wavelength,  $193.7$  nm; slit width,  $0.5$  nm; lamp current,  $10$  mA. For the adjustment of the solution pH, a Hanna Instruments pH meter equipped with a combined electrode was utilized.

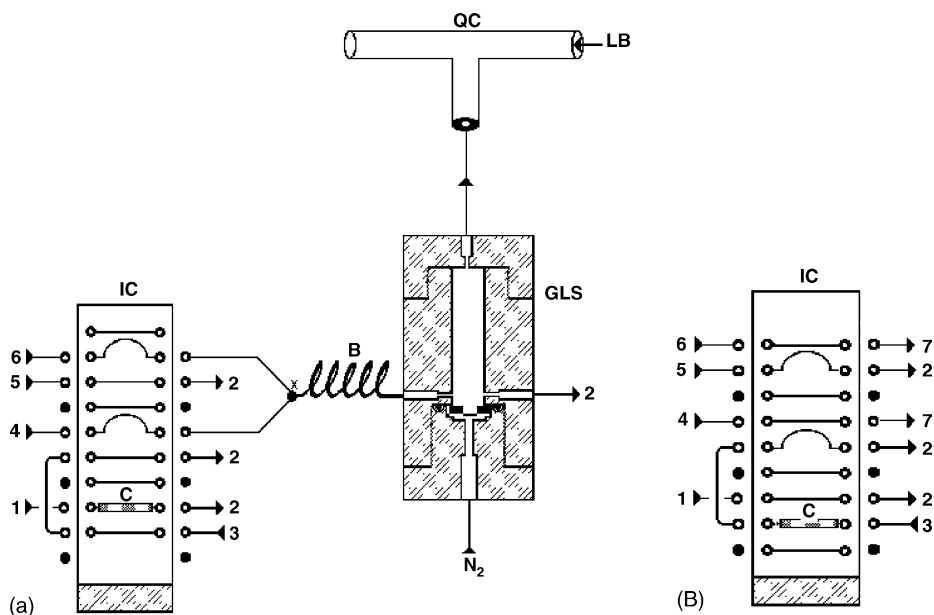


Fig. 1. (a) FI-HG AAS pre-concentration system in the sorption position for the determination of As: (1) sample ( $3.2$  ml  $\text{min}^{-1}$ ); (2) waste; (3) eluent ( $3.2$  ml  $\text{min}^{-1}$ ); (4)  $1$  mol  $\text{l}^{-1}$  HCl ( $2.8$  ml  $\text{min}^{-1}$ ); (5)  $1\%$  (w/v)  $\text{NaBH}_4$  ( $2.8$  ml  $\text{min}^{-1}$ ); (6)  $\text{H}_2\text{O}$  ( $2.8$  ml  $\text{min}^{-1}$ ); (7) HG AAS system; (IC) injector; (B) reaction coil (30 cm); (X) confluence point; (GLS) gas-liquid separator; (QC) atomizer; (LB) optical path; (C) glass mini-column with sorbent material. (b) Injector-commutator in the elution position.

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