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Analytical Methodologies for Arsenic Determination Exploiting Flow Injection-Based Approaches

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Abstract

Three flow injection based approaches have been developed for determination, pre-concentration and speciation analysis of arsenic by hydride generation atomic fluorescence spectrometry (HGAFS). The arsenic determination was carried out using a multisyringe burette coupled with a solenoid valve, providing precise known volumes of sample and reagents, which are dispensed into a gas-liquid separation cell. An argon flow delivers the arsine into the flame of an atomic fluorescence spectrometer. A hydrogen flow has been used to support the flame. Nitrogen has been employed as a drier gas. The second flow injection approach was constructed for arsenic pre-concentration on a solid-phase, using a column packed with an anion-exchange resin and coupled to the previous system. The speciation analysis of inorganic arsenic was carried out using a pre-reducing solution. Total inorganic arsenic was determined after on-line pre-reduction of As(V) to As(III) using potassium iodide. The concentration of As(V) was calculated by the difference of the total inorganic arsenic and As(III). Several variables such as sample and reagents volumes, flow rates and reagent concentrations were investigated in detail. The proposed techniques have been validated by means of reference solid and water materials with good agreement with the certified values. The obtained results show that the proposed methodologies offer some advantages such as compactness, high sampling frequency, optimum sensitivity, high selectivity and decreasing of reagent and sample consumption, which leads to a lower waste generation. It confirms the statement that the use of multisyringe systems considerably extends the possibilities of flow analysis.

Introduction

The toxicity of arsenic depends on its chemical forms. Inorganic arsenic species are more toxic than the organic ones. Inorganic trivalent forms are more toxic than the pentavalent forms. Therefore, it is necessary to determine the individual species in order to estimate its environmental impact and health risks. Although a number of methods have been developed for arsenic determination, the conversion of the arsenic to volatile derivatives using the hydride generation method followed by analysis with an element-selective detector has been the preferred technique [Burguera *et al.*, 1997]. Flow injection analysis (FIA) has proved to be a suitable technique for on-line analysis because of its high sampling frequency and ease of automation. Furthermore, it allows the reduction of transition metal interferences in comparison with the batch systems. It is due to a shorter period of sample-reagents interaction. In addition, the reduction of the hydride-forming elements is fast and the reaction is completed before the reduction of the transition metal ion to the interfering species [Nielsen *et al.*, 1997].

Multisyringe flow injection analysis (MSFIA) was recently developed as a practical technique for automation of serial assays. 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. The main element is a multisyringe burette with four syringes, which are connected in block to the same stepper motor, allowing the simultane-

ously movement of them. A three-way solenoid valve is coupled at the head of each syringe. The valves allow the injection of reagents only at the precise moment to perform the analytical determination or the return to the stock bottle when they are not needed, reducing the consumption of sample and reagents [Miró *et al.*, 2002]. This abstract describes the performance of new MSFIA approaches for the determination, pre-concentration and speciation analysis of arsenic using hydride generation-atomic fluorescence spectrometry. The aim of this work is to evaluate the potential advantages of the time-based injection of the MSFIA technique for inorganic arsenic determination.

Materials and Methods

The MSFIA system is constituted by a multisyringe burette with programmable rate, an auto-sampler, a glass gas-liquid separation cell and a T-piece to connect a hydrogen cylinder to the system. Each syringe has a three-way solenoid valve on each head. The multisyringe burette has also two additional independent three-way solenoid valves. Measurements were carried out with an atomic fluorescence spectrometer (Excalibur, PS Analytical). Manifold was constructed with 0.8 and 1.5mm i.d. PTFE tubes. Instrumental control and data acquisition were performed using the software Autoanalysis developed for flow techniques by our research group. A microwave oven was employed for sample digestion [Semenova *et al.*, 2002]. The column (70mm long and 4mm i.d.) for on-line pre-concentration was made from poly(methyl)-

methacrylate and packed with an anion-exchange resin (Amberlite IRA-410). A NaBH_4 solution was first loaded on to the anion-exchange column and, after washing with water, the sample was passed through the column and the arsenic is retained on the resin. In the next step, the hydrochloric acid solution is dispensed into the column, generating arsine and hydrogen [Leal *et al.*, 2002]. For speciation analysis, a pre-reducing solution (KI-ascorbic acid) and the sample are mixed in a knotted reactor, in which the on-line pre-reduction of As(V) to As(III) is carried out. After a determined pre-reduction time, sample, pre-reducing solution, hydrochloric acid and sodium tetrahydroborate solution are dispensed to the gas-liquid separator, generating arsine and achieving the acquisition of three successive peaks with only one filling of the syringe, increasing the sample frequency. In the first stage, As(III) is determined directly and immediately, whereas in the second stage, the total inorganic arsenic is carried out. As(V) is calculated by the difference between total inorganic arsenic and As(III) [Leal *et al.*, 2006]. The parameters controlling each step of the analytical process have been optimized under the criteria of providing the best sensitivity and reproducibility as well as good recoveries for the analyte measurement in samples. The proposed techniques have been validated by means of reference solid (algae and fish samples) and water materials.

Table 1. Results obtained by three MSFIA approaches, FIA and SIA systems.

| Parameters | FIA | SIA | MSFIA | MSFIA precon | MSFIA spe. |
|--|-------|--------|--------|--------------|------------|
| Detection limit ($\mu\text{g l}^{-1}$) | 0.05 | 0.67 | 0.07 | 0.03 | 0.05 |
| Linear range ($\mu\text{g l}^{-1}$) | 0.1-8 | 2.5-70 | 0.25-3 | 0.05-2 | 0.1-3 |
| % RSD | - | 1.9 | 4.9 | 4.8 | 4.4 |
| Sample throughput/h | - | 6 | 36 | 10 | 10 |
| Injection throughput/h | 45 | 33 | 113 | 30 | 47 |
| NaBH_4 conc. (%) | 1.2 | 0.12 | 0.24 | 0.05 | 0.2 |
| NaBH_4 consum. (ml/inj) | 4.7 | 0.5 | 0.3 | 3 | 0.35 |
| NaBH_4 consum. (mg/inj) | 56.4 | 0.6 | 0.7 | 1.5 | 0.7 |
| HCl consum. (ml/inj) | 11.3 | 0.5 | 0.6 | 2 | 0.7 |
| Sample volume (ml/inj) | 11.5 | 0.5 | 0.6 | 3 | 0.7 |

Results

Three different MSFIA-HG-AFS systems were developed for determination, pre-concentration and speciation analysis of arsenic, respectively. Figure 1 shows the arsenic pre-concentration system.

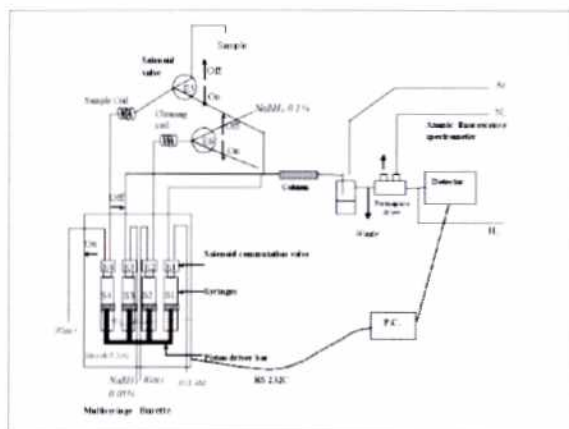


Figure 1. MSFIA-HG-AFS system used for pre-concentration and determination of As

A comparison of results obtained by the authors using the commercial flow injection analysis (FIA), sequential injection (SIA) and three developed MSFIA-HG-AFS systems (determination, pre-concentration and speciation analysis) is shown in Table 1.

Discussion

The developed MSFIA-HG-AFS systems have proved to constitute effective approaches for the determination, pre-concentration and speciation analysis of arsenic at trace levels. The multisyringe module and the constructed manifolds allow an efficient sample introduction. The MSFIA techniques offer the advantage of a higher sampling frequency than SIA and FIA techniques. Moreover, the proposed methods provide a significant reduction in reagent consumption and sample volume, which leads to a minimum waste generation. The pre-concentration of the analyte on the column improved five times the sensitivity over the MSFIA-HG-AFS technique previously developed, diminishing simultaneously the sample throughput in three times. The time-based MSFIA-HG-AFS system proposed for online speciation of inorganic arsenic allows almost simultaneous determination of As(III) and As(V). The implementation of a knotted reactor improves the on-line pre-reduction of As(V), avoiding the use of a heating unit. Other flow techniques that can be used for inorganic arsenic speciation, such as pH selective hydride generation, require controlling the reaction pH conditions and the time of hydride generation, whereas IC techniques need the implementation and maintenance of an ion chromatography system. The overall MSFIA techniques are practical, simple and robust.

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