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Multicommutation flow techniques in the hydride generation-atomic fluorescence determination of arsenic

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This review outlines automated methodologies developed for measuring arsenic in environmental samples. We report the state of the art of the most significant methods exploiting multicommutation flow techniques coupled to hydride generation-atomic fluorescence determination. We review analytical methods used and present a comparative evaluation of them. We also discuss the on-line pre-concentration procedure as being of particular interest in the development of fully automated methods.

Keywords: Arsenic; Atomic fluorescence; Automated methodology; Environmental sample; Hydride generation; Lab-on-valve; Multicommutation flow analysis; Multi-pumping flow system; Multisyringe flow-injection analysis; Pre-concentration

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1. Introduction

Since the introduction of flow-injection analysis (FIA) 35 years ago [1], different techniques have been proposed as introduction and pre-treatment systems for samples and reagents. The appearance of sequential injection analysis (SIA) in the 1990s [2] together with FIA played a key role in the development of diverse automated analytical systems for routine applications [3].

In recent years, new flow techniques {e.g., multicommutation FIA (MCFIA) [4,5], multisyringe FIA (MSFIA) [6,7], multipumping flow-injection system (MPFS) [8,9] and lab-on-valve technique (LOV) [10]} were demonstrated to be useful tools for on-line handling and pre-treatment of samples.

The concept of multicommutation in flow analysis was presented by Reis et al. in 1994 [4] and discussed by Rocha et al. [11]. They established that a multicommutation system can be considered as an analytical network that involves the actuation of *n* active devices (or *n* operations with a single device) on a single sample.

Development of versatile multicommutation flow systems allowed other flow-based approaches to be exploited. As a consequence, the original concept has undergone continual expansion [12].

Multicommutation is usually accomplished by taking advantage of valves, timing devices and other artifacts for improving system performance [13]. Catalá Icardo et al. [5] highlighted the advantages of multicommutation techniques as follows:

- miniaturization of flow approaches;
- reduced sample and reagent consumption;
- increased reproducibility;
- low cost and simplicity; and
- flexibility and expanded possibilities for flow analysis.

However, the main shortcomings are:

- periodic unloading of the liquid driver when a syringe pump is applied; and,
- limited commercial availability of electronic interfaces and software [5,14].

The degree of automation of a flow system is related to multicommutation. Multicommutation techniques are very versatile and their approaches facilitate full automation of sample handling [12].

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This feature has made multicommutation techniques excellent options for monitoring environmental parameters. They have been successfully applied to the determination of metals and metalloids [15–20], pesticides [21–23], pharmaceuticals [24–26], nutrients [27–29], among others. Environmental analysis is the main application for studies involving multicommutation [30].

It is well known that arsenic is recognized as the most serious inorganic contaminant in drinking water worldwide. Whilst some national authorities seek to reduce arsenic limits in line with the WHO guideline value (10 μg/L), many countries and indeed all affected developing countries still operate in the range of 25–50 μg/L, in part because of lack of adequate testing facilities for lower concentrations [31,32].

A great number of methodologies for arsenic determination have been developed. However, the conversion of arsenic to volatile derivatives using the hydride generation (HG) method followed by analysis with an element-selective detector has been the technique used most [33,34]. HG can separate analytes from sample matrices, thereby reducing potential chemical and spectral interferences [34,35]. A glance at the scientific literature (SciFinder database) shows that coupling HG to atomic absorption spectrometry (AAS) for arsenic determination is about twice as frequent as that to atomic fluorescence spectrometry (AFS). However, multicommutation systems with HG have been coupled most to AFS.

AFS is competitive with inductively coupled plasma-mass spectrometry (ICP-MS) in terms of sensitivity, providing a wider linear range. For example, a comparison between both techniques for arsenic speciation in environmental samples indicated limits of detection (LODs) of 0.1–0.3 μg/L in both techniques and linear ranges of 1–750 μg/L and 1–8000 μg/L for ICP-MS and AFS, respectively [36]. In addition, AFS has a lower purchase price and lower operating costs, which make it more attractive for routine analysis. However, AAS for arsenic speciation offered LODs from 0.5–5.9 μg/L with a linear range of 0–200 μg/L [37]. A critical review of the features of AFS and its application to speciation studies in hydride-forming elements was published recently [38].

In this sense, multicommutation techniques have proved to constitute an effective approach for arsenic determination at low levels. In this article, we present some multicommutation systems for determination, preconcentration and speciation analysis of arsenic. Furthermore, we discuss in detail the features of these systems and their advantages over conventional techniques.

2. Batch and flow techniques for hydride generation

Prior to 1983, HG was mainly used in manual batch systems, which were frequently difficult to manipulate [39]. Most applications of batch HG were coupled to AAS and ICP-MS.

Batch HG was first coupled to non-dispersive AFS for arsenic determination by Tsujii and Kuga [40], who used a mixed acid medium containing iodide, tin(II) and zinc powder to convert arsenic to arsine. Then, arsine was atomized in a hydrogen-argon air flame. They reported an absolute LOD of 2 ng.

Thompson [41] developed a new technique for determination of hydride-forming elements (Sb, As, Se and Te) by batch HG coupled to dispersive AFS. The reducing agent employed was sodium borohydride. Both articles reported a lower LOD and a wider linear range than those obtained by AAS.

Guo et al. [42] coupled a flow-injection (FI) system to HG-AFS and compared the results obtained with those acquired previously by batch HG for several hydride-forming elements. The FI system, comprising two peristaltic pumps and an injection valve, was controlled by computer. In the batch system, both concentration and volume of $NaBH_4$ were much higher than those required in the FI system, and, moreover, the flame was intermittent, while, in the FI system, the supplies of acid and reducing agent were continuous, maintaining the flame stable. The sampling frequency was 120 injections per hour. Reported LODs for arsenic determination by FI and batch-operated systems were 0.2 μg/L and 0.5 μg/L, respectively.

Determination of four arsenic species by batch HG coupled to cryogenic trapping with AFS detection was also carried out [43]. In this system, the sample was placed in a glass reaction vessel, which was attached to the HG system. $NaBH_4$ solution was propelled with a peristaltic pump into the reaction vessel. Volatile hydrides passed through a Nafion tube, which had a countercurrent of air flow to remove humidity. Volatile species were swept into a glass U-trap packed with a Chromosorb W 45-60 mesh. Arsines were trapped in the packing material using liquid nitrogen. A heater was employed to warm the U-trap. Argon was used as a carrier gas, while hydrogen flow was essential to support the flame while the reaction vessel was disconnected from the system. LODs of 2.3 ng/L, 0.9 ng/L, 2.4 ng/L and 3.7 ng/L were obtained for As(III), As(V), monomethylarsonate (MMA) and dimethylarsinate (DMA), respectively, in 6 min. However, the accuracy of these results depended on the timing of the HG reaction and the heating cycle, which had to be kept constant. Thus, this batch-HG technique is difficult to handle.

The disadvantages of batch-HG systems are as follows:

- laborious processes;
- intermittent production of hydrogen;
- precision depends on injection technique; and,
- time consuming.

These shortcomings were reduced or even eliminated with the introduction of the continuous-flow vapor