



Multiple microflame quartz tube atomizer: Study and minimization of interferences in quartz tube atomizers in hydride generation atomic absorption spectrometry

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ABSTRACT

A systematic study was performed to evaluate the performance of a multiple microflame (MM) quartz tube atomizer (QTA) for minimizing interferences and to improve the extent of the calibration range using a batch system for hydride generation atomic absorption spectrometry (HG AAS). A comparison of the results with conventional QTA on the determination of antimony, arsenic, bismuth and selenium was performed. The interference of As, Bi, Se, Pb, Sn and Sb was investigated using QTA and MMQTA atomizers. Better performance was found for MMQTA, and no loss of linearity was observed up to 160 ng for Se and Sb and 80 ng for As, corresponding to an enhancement of two times for both analytes when compared to QTA (analyte mass refers to a volume of 200 μ l). For Bi, the linear range was the same for QTA and MMQTA (140 ng). With the exception of Bi, the tolerance limits for hydride-forming elements were improved more than 50% in comparison to the conventional QTA system, especially for the interferences of As, Sb and Se. However, for Sn as an interferent, no difference was observed in the determination of Se and Sb using the MMQTA system. The use of MMQTA-HG AAS complied with the relatively high sensitivity of conventional QTA and also provided better performance for interferences and the linear range of calibration.

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1. Introduction

Elements forming volatile hydrides, such as antimony, arsenic, bismuth and selenium, are currently determined by hydride generation atomic absorption spectrometry (HG AAS). In general, this technique presents suitable limits of detection (LOD) for these elements in many kinds of matrices, including environmental and biological samples among others [1]. An important advantage is related to the analyte separation from the matrix components, offering considerable suppression of matrix effects [1]. However, this technique is prone to some drawbacks that could occur in the process of generation and release of the hydride, during the transport up to the atomization cell, and in the gas phase during the atomization step [1–4].

The most common device used for atomization is the conventional quartz tube atomizer (QTA). Despite the advantages of this kind of atomizer, curved calibration graphs and low tolerance to the interferences during the atomization step have been reported [4–6]. Following the original explanation of the unsatisfactory linear range as a result of molecule dimer formation [7], more recent opinions tend to attribute the curvature to either the enhanced recombination rate of hydrogen radicals (which are required for hydride atomization), the enhanced free atom decay rate in the presence of higher analyte concentrations, or the

particles present in the atomizer [3,8,9]. Similarly, the predominant mechanism for the mutual interferences of hydride forming elements in QTA has been explained by the competitions for hydrogen radicals between the analyte and interferent and/or by changes in the free atom decay caused by reactions with the interferent [1].

Some authors [10–12] studied the atomization step and the effect of oxygen on the sensitivity of hydride-forming elements and found that the atomization in the quartz tube was caused by collisions with hydrogen radicals. Although the mechanism of formation of these radicals is not completely understood, oxygen traces seem to play an important role in the radical generation step.

Trying to minimize the deficiencies observed for conventional QTA, Dědina and Matoušek [5] proposed a quartz atomizer that allows for multiatomization steps inside the tube. This device, named the multiple microflame quartz tube atomizer (MMQTA), includes two externally heated horizontal concentric quartz tubes. A controlled flow of air or an argon-oxygen mixture is introduced to the cavity between the tubes (outer gas). The inner tube has several small holes along its length, each one about 0.5 mm in diameter that allow the entrance of the outer gas [5]. The oxygen that enters the inner tube reacts with hydrogen from the hydride generation step, producing small and localized microflames. The microflames produce hydrogen radicals that are dispersed, causing a suitable atomization environment in the optical path along the quartz tube. Therefore, the problems related to narrow calibration range and interferences caused by competition of hydride forming elements are

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substantially minimized [5]. This device was further improved by changing the oxygen inlet; this new design resulted in an improved tolerance to gas-phase interferences [6]. The performance was evaluated and compared to a conventional QTA and to the previous MMQTA model for the determination of As, Se and Sb using a continuous flow hydride generation system. The linearity of calibration range was extended for all analytes, and better tolerance limits (interferent concentration that causes a decrease in the absorbance signal of 10%) were obtained that related to the interferences of As and Sb on Se, and Se on As and Sb determinations [6]. However, these results were reported only for a continuous flow hydride generation system, and no information was given for Bi as an analyte or as interferent for As and Sb determination, despite their importance for some samples [13]. Moreover, information about the effect of other elements (e.g., Pb and Sn) on the determination of As, Bi, Se and Sb was not given.

In the present work, a systematic study was performed in order to evaluate the linear range and the mutual interferences of As, Bi, Se and Sb using the MMQTA and a batch hydride generation system. A comparison with the performance of conventional QTA using the same basic conditions was also carried out. A systematic study was also performed for other analytes (Bi) and interferents (Pb and Sb) that were not studied in previous works.

2. Experimental

2.1. Apparatus and instrumental parameters

A Model AAS Vario 6 atomic absorption spectrometer (Analytik Jena, Jena, Germany) with deuterium background correction coupled to a Model MHS-10 batch hydride generation system (Perkin-Elmer, Norwalk, CT, USA) was used for the determination of As, Bi, Sb and Se by HG AAS. Argon (99.996%, White Martins, Brazil) was used as the purge gas at a flow rate of 1000 ml min⁻¹. The details of the MHS-10 system are described by Walcerz et al. [14]. The operating parameters and instrumental settings were adjusted according to the manufacturer recommendations (Table 1). All measurements were evaluated as integrated absorbance, and all results given in this work are the mean of four determinations.

2.2. Atomizers

In this work, the performance of two atomizers was compared. Both atomizers were of the T-tube design with their horizontal arms (160 mm length, 12 mm) aligned in the optical path of the spectrometer (inlet arms were 80 mm length). For conventional QTA, the internal diameters were 12 and 6 mm for the horizontal arm and inlet arm, respectively. For the MMQTA, the outer tube was also 12 mm internal diameter, the inner tube was 7 mm internal diameter (14 mm length), and the inlet arm of the inner tube (serving for the introduction of gases from hydride generator) was 2 mm internal diameter. The inner tube had 10 orifices of 1-mm each distributed along the tube length. For both atomizers, the thickness of the quartz tube walls was 1 mm. For the MMQTA system, air was introduced to the outer tube (20 ml min⁻¹), similarly to that

Table 1
Analytical parameters for As, Bi, Sb and Se determination by HG AAS

Parameter	As	Bi	Sb	Se
Wavelength, nm	193.7	223.1	217.6	196.0
Lamp current, mA	8	8	10	10
Band pass, nm	0.8	0.5	0.2	1.2
HCl, mol l ⁻¹	1.00	1.00	1.00	1.00
NaBH ₄ *, % m/v	1.00	1.00	1.00	1.00
Volume of NaBH ₄ , ml	4.0	4.0	4.0	4.0
Ar flow rate, ml min ⁻¹	1000	1000	1000	1000
Purge time, s	10	10	10	10
Integration time, s	30	30	30	30

*Solution prepared in 0.1% (m/v) NaOH.

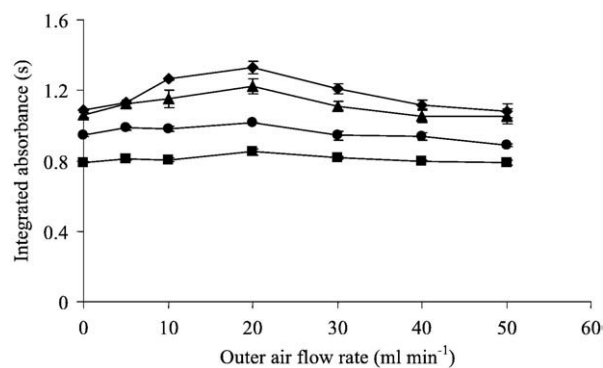


Fig. 1. Study of the influence of the outer air flow rate using the MMQTA atomizer on the sensitivity of 20 ng of ■ antimony, ▲ arsenic, ● bismuth and ◆ selenium (reaction medium: 6 ml of 1.00 mol l⁻¹ HCl).

described in reference [6]. Both atomizers were electrically heated to 950 °C. The quartz cells were periodically cleaned by immersion into a 2.8 mol l⁻¹ HNO₃ + 0.3 mol l⁻¹ HF solution for 10 min and further rinsed with distilled water.

2.3. Reagents

All chemicals used were of analytical reagent grade obtained from Merck (Darmstadt, Germany). The water was distilled, deionized and further treated in a Milli-Q system (Millipore, Bedford, USA). Concentrated HNO₃ and HCl were distilled in a sub-boiling system (Milestone, Model Duopur, Bergamo, Italy). All glass apparatuses were soaked in 2.8 mol l⁻¹ nitric acid for 12 h and thoroughly washed with water before use. Working reference solutions of As(III), Bi(III), Pb(II), Sb(III), Se(IV) and Sn(IV) were prepared daily by serial dilution of a stock solution containing 1000 mg l⁻¹ in 1.00 mol l⁻¹ HCl from a Titrisol solution (Merck, Darmstadt, Germany). Solutions of 1.00% m/v sodium tetrahydroborate were prepared daily by dissolving the solid reagent in 0.1% m/v NaOH and filtering before use.

2.4. Procedure

To investigate the mutual interferences, As, Bi, Sb and Se were studied as analytes and As, Bi, Pb, Sb, Se and Sn as interferents using the QTA and MMQTA with the same hydride generation system. Initially, an evaluation of the linear range and interference magnitude in QTA was performed, and the experimental conditions were set for each analyte. The following parameters were evaluated: purge time, NaBH₄ concentration and HCl concentration. The chosen operating conditions are summarized in Table 1. For the evaluation of the linear range and study of interferences for both atomizers, 6 ml of 1.00 mol l⁻¹ HCl was placed into the reaction vessel, and 200 µl of the analytical solutions were added. In the case of the interference study, the analyte mass was always 20 ng. A small volume of solution (100 µl) corresponding to 0.01 to 100 µg of each interferent was added. For the addition of analytical or interferent solutions, the volume was constant (200 or 100 µl, respectively), and the concentration of the stock solutions was changed. For this study, the relative standard deviation was lower than 13% (n=3). The linear range was evaluated up to 200 ng for all analytes using the software GraphPad InStat (version 3, 1998, San Diego, USA) with scatter among replicates set at 95% confidence interval.

3. Results and discussion

3.1. Preliminary studies

The operational conditions for the hydride generation using QTA were optimized with respect to the maximum signal (Table 1). The purge time

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