Talanta 97 (2012) 395–399

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Thermospray flame furnace atomic absorption spectrometry for determination of silver in biological materials

Fabiana Gerondi [a,b], Marco Aurélio Zezzi Arruda [a,b,*]

[a] Department of Analytical Chemistry, Group of Spectrometry, Sample Preparation and Mechanization—GEPAM, Institute of Chemistry, P.O. Box 6154, University of Campinas—UNICAMP, 13083 – 970 Campinas, SP, Brazil

[b] National Institute of Science and Technology for Bioanalytics, Institute of Chemistry, University of Campinas—Unicamp, PO Box 6154, 13083–970 Campinas, SP, Brazil

ARTICLE INFO

Article history:
Received 30 March 2012
Received in revised form
20 April 2012
Accepted 24 April 2012
Available online 4 May 2012

Keywords:
TS-FF-AAS
Biological materials
Flow system
Silver

ABSTRACT

A method for silver determination without concentration steps is described using thermospray flame furnace atomic absorption spectrometry. Carrier type and flow rate, sample volume, flame conditions (acetylene and air flow rate), water flow rate in the nebulizer, metallic tube and type and concentration of the acid diluent of the analyte are the parameters evaluated in the optimization of the method. Using the optimized conditions, eleven elements are evaluated as concomitants. The limits of detection and quantification are 0.15 $\mu g\,L^{-1}$ and 0.50 $\mu g\,L^{-1}$, respectively. The linear range is from 0.50 $\mu g\,L^{-1}$ to 40 $\mu g\,L^{-1}$ and the accuracy of the method is obtained through two certified reference materials: MA-A-2 (fish flesh homogenate) and SRM 1643e (trace elements in water).

1. Introduction

Although recently proposed [1], thermospray flame furnace atomic absorption spectrometry—TS-FF-AAS presents a diversity of applications, as pointed out in the literature [2–12], being considered a powerful technique in terms of detectability, besides its inherent easy implementation. It consists in a metallic tube used as an atomizer, which is positioned above the burner head of FAAS equipment, the sample being introduced through spray formation [13]. This mechanism was recently described, with the spray generated by the heating of the sample inside a ceramic capillary coupled to a peristaltic pump, acting as a fluid propeller. As the sample is efficiently introduced into the atomizer, good detectability is frequently attained with this technique. In view of these good analytical characteristics, the TS-FF-AAS technique is very useful for determining those elements present at low concentrations in samples.

Silver is generally found between 0.45 and 4.5 $ng\,g^{-1}$ in oysters and mussels, and it has never been determined using TS-FF-AAS. Thus, this may be an important technique for silver quantification, since it presents enough detectability for this task. Additionally, for most of the proposed methods aiming at silver determination, and based on atomic spectrometry, a concentration step is almost imperative for attaining the necessary detectability [14–17].

The importance in determining silver is related to its toxicity, even at low concentrations, because it can impair the growth of algae, oysters and trout [18]. In humans and animals, silver is absorbed by the gastrointestinal tract, skin, mucous and membranes, and its accumulation in humans produces the argyria, giving a grayish color to the person [19]. Then, the main purpose of this work is to determine silver without any concentration step, taking into account the good characteristics of TS-FF-AAS.

2. Experimental

2.1. Instruments, materials and solutions

A PerkinElmer (AAnalyst 300) flame atomic absorption spectrometer equipped with deuterium lamp background correction, and a hollow cathode lamp (current 10 mA, 328.1 nm wavelength, slit 0.7 nm) was used. The signals were recorded as peak area mode and an optical pyrometer (Ircon Ultimax™ 20 Infrared Thermometer) was used for measuring the tube temperature.

Silver reference solutions were prepared using sub-boiled nitric acid at 0.2% (v/v), and from the stock solution of 1000 $mg\,L^{-1}$ silver (Qhemis).

2.2. TS-FF-AAS arrangement

The TS-FF-AAS arrangement consists of a metallic tube positioned above the burner of the spectrometer. In this work, a 99.9% nickel tube with 10 cm length, 1 cm inner diameter and only one hole (3 mm diameter), positioned in the front of the tube for the

* Corresponding author at: Department of Analytical Chemistry, Group of Spectrometry, Sample Preparation and Mechanization—GEPAM, Institute of Chemistry, P.O. Box 6154, University of Campinas—UNICAMP, 13083 – 970 Campinas, SP, Brazil. Tel.: +55 19 3521 3089; fax: +55 19 3521 3023.
E-mail address: zezzi@iqm.unicamp.br (M.A.Z. Arruda).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.04.051

introduction of a ceramic capillary (10 cm length, 0.5 mm inner diameter) was used. A homemade injector-commutator, frequently used in applications involved TS-FF-AAS [20,21], and a peristaltic pump (Ismatec IPC) for propelling the sample volume (200 μL) at 0.4 mL min^{-1} into the tube were also used.

2.3. Evaluation of concomitants

The signal of silver in the presence of eleven elements was evaluated. The concomitants were studied in the (Ag:concomitant) ratios of 1:1, 1:10, 1:100, 1:500, 1:1000 and 1:2000. The concentration of the analyte was kept constant at 25 μg L^{-1}.

2.4. Sample preparation

Two certified reference materials were used for accuracy evaluation of the method: *Fish flesh homogenate* (MA-A-2) and *Trace elements in water* (SRM 1643e). A microwave assisted decomposition of 200 mg of the MA-A-2 material was carried out with 4 mL of concentrated nitric acid (sub-boiled) and 0.3 mL of 30% (v/v) H_2O_2. The program used in the microwave oven was (1) 6 min at 330 W, (2) 3 min at 530 W, (3) 3 min at 660 W and (4) 3 min at 0 W. Then, the acid mixture was evaporated to near dryness, and the volume completed to 10 mL with 0.2% (v/v) HNO_3. A similar procedure was done for 200 mg of oyster sample, and a volume of 1 mL of 30% (v/v) H_2O_2 was used for this sample. For SRM 1643e, this material was directly introduced into the TS-FF-AAS arrangement, but for its analysis the reference solutions of the analyte were prepared in 0.8 mol L^{-1} HNO_3 because of the acidity of the material. The sample volume injected in the TS-FF-AAS system was 220 μL.

3. Results and discussions

3.1. Optimization of the method

In the development of the method, the parameters studied were carrier type and flow rate, sample volume, flame conditions, materials and holes of the tube, water flow in the nebulizer and nature and concentration of the acid diluent of the analyte. Each parameter was studied in a univariated way.

3.1.1. Carrier type and flow rate

The carrier transports the sample towards the tube atomizer. Six different carrier solutions were evaluated: nitric acid at 0.2% (v/v) and 5% (v/v), air, water, mixture of ethanol:water at 60:40 (v/v) ratio, and 0.1 mol L^{-1} acetate buffer (pH 4). The one that presented the most acceptable peak profile was air. Air involves the sample solution producing a turbulent flow, improving the sample homogeneity [22]. Therefore, the peak presents a good profile compared to the others carriers. Water, the mixture of ethanol:water at 60:40 (v/v) ratio, acid and buffer solutions dilute the analyte, did not provide acceptable peak profiles. Thus, the air was chosen as the sample carrier and, the carrier flow rate was studied between 0.2 and 1.5 mL min^{-1}. At this range, an increase in the carrier flow rate causes a decrease of 24% in the analytical signal. This is because the thermal component does not have enough energy to transform all the solution into spray [13], being the atomization of the analyte not complete. Then, lower carrier flow rates must be used. The carrier flow rate that provides the highest analytical signal and good analytical frequency was 0.4 mL min^{-1}, being chosen as the optimal condition.

3.1.2. Injected sample volume

The injected sample volumes evaluated for method optimization were 50, 150, 200, 250, 300 and 400 μL. As expected, their increases also improve the analytical signal (374%) when considering the 50–400 μL range (Fig. 1). However as the volume became higher, the peak profile became worse. The best peak profile and peak area was at 200 μL, this value being chosen as the optimal sample volume. However, when using solutions at acid concentrations higher than 0.2% (v/v), the sample volume must be 220 μL, because at higher acid concentration, the analytical signal decreases, affecting the detectability.

3.1.3. Flame conditions

To study the influence of the acetylene flow rate (from 1.5 L min^{-1} to 4.0 L min^{-1}), the air flow rate was kept at 12 L min^{-1}. An increase in this parameter decreases the analytical signal about 9% (for 3 L min^{-1}), as can be seen in Fig. 2. Considering the best analytical signal and the lowest limit of detection, 1.5 L min^{-1} was chosen as acetylene flow rate. This value

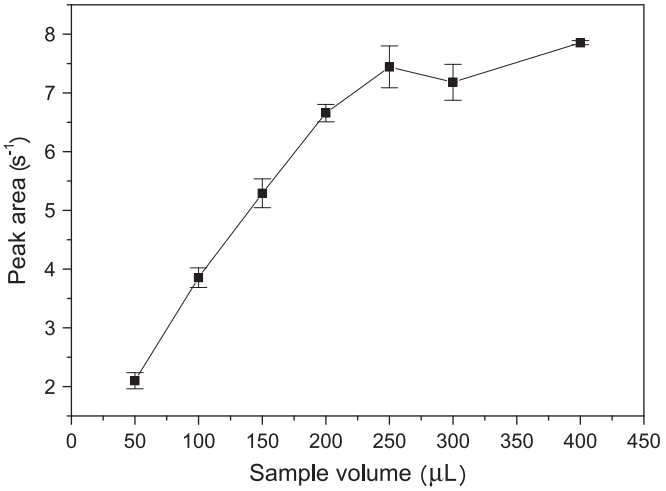

Fig. 1. Influence of the sample volume on the analytical signal. Conditions: 100 μg L^{-1} silver solution in 0.2% (v/v) HNO_3, flame: 2 L min^{-1} C_2H_2: 12 L min^{-1} air, carrier: air at 0.4 mL min^{-1}, nebulization flow rate at 6 mL min^{-1}, 99.9% (m/m) Ni tube with 60 mm^2 total hole area.

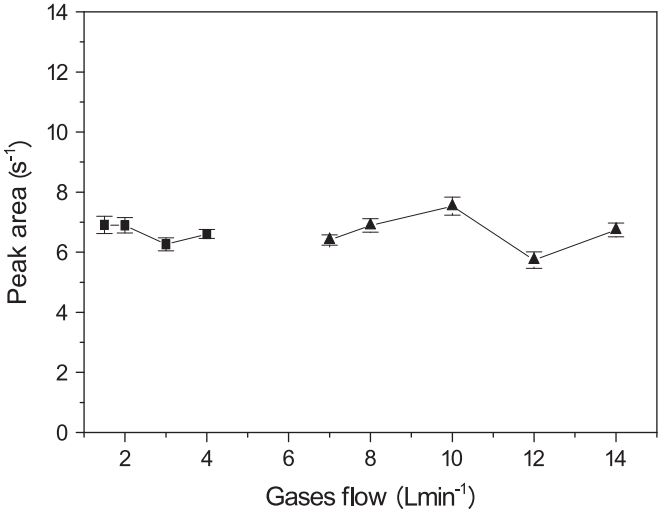

Fig. 2. Influence of the flame gases flow rates on the analytical signal. Conditions: 100 μg L^{-1} silver solution in 0.2% (v/v) HNO_3, carrier: air at 0.4 mL min^{-1}, sample volume: 100 μL, nebulization flow rate at 6 mL min^{-1}, Ni 99.9% (m/m) Ni tube with 60 mm^2 total hole area (■ C_2H_2, ▲ air).