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

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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

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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

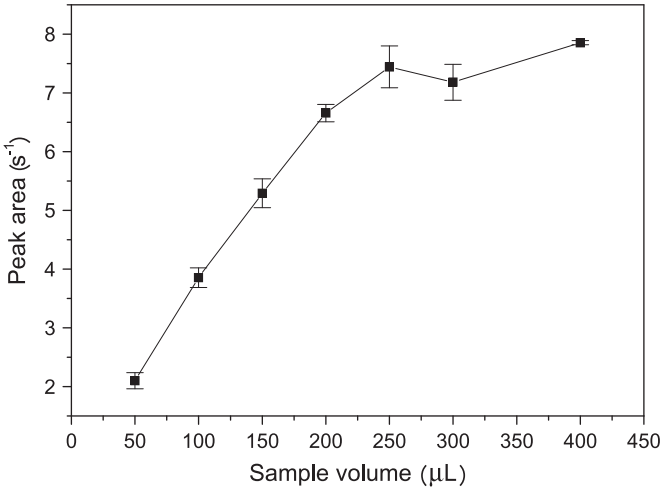

Fig. 1. Influence of the sample volume on the analytical signal. Conditions: 100 μg L^{-1} silver solution in 0.2% (v/v) HNO_3, flame: 2 L min^{-1} C_2H_2: 12 L min^{-1} air, carrier: air at 0.4 mL min^{-1}, nebulization flow rate at 6 mL min^{-1}, 99.9% (m/m) Ni tube with 60 mm^2 total hole area.

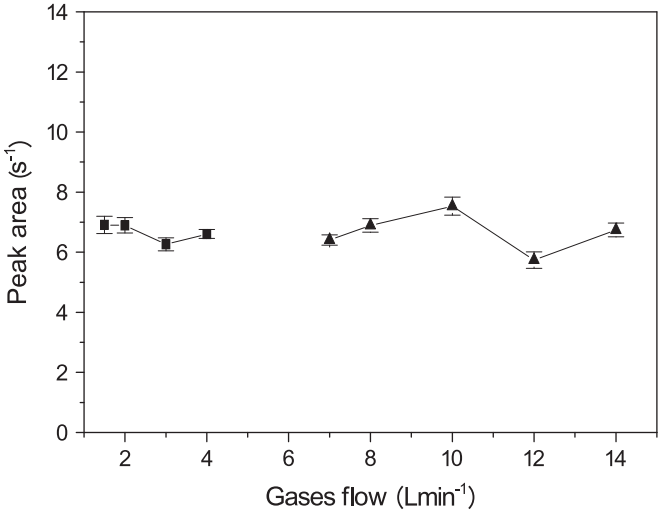

Fig. 2. Influence of the flame gases flow rates on the analytical signal. Conditions: 100 μg L^{-1} silver solution in 0.2% (v/v) HNO_3, carrier: air at 0.4 mL min^{-1}, sample volume: 100 μL, nebulization flow rate at 6 mL min^{-1}, Ni 99.9% (m/m) Ni tube with 60 mm^2 total hole area (■ C_2H_2, ▲ air).

was kept constant to evaluate the air flow rate (between 7 L min^{-1} and 14 L min^{-1}). When studying this parameter, the highest analytical signal was obtained with 10 L min^{-1} but this value also produced a higher standard deviation (ca. 25% higher) for the blank solution, compared to 12 L min^{-1}, which reflected in a poorer limit of quantification of the method. Therefore, 12 L min^{-1} was chosen as the best air flow rate, producing an excellent limit of detection. So, an oxidant acetylene–air flame is the best condition for silver atomization, since the preferential atomization is given by oxides formation [23], which corroborates with the optimized conditions (1.5 L min^{-1}:12 L min^{-1} acetylene:air, respectively).

3.1.4. Nebulizer flow rate

The nebulizer flow rate sometimes influences the analytical signal. This parameter was studied from 1 mL min^{-1} to 6 mL min^{-1} water flow rate, and 5% was the deviation between the signals. Nevertheless, 6 mL min^{-1} provided better detectability, and was chosen as the optimal condition.

3.1.5. Type and concentration of the acid

Four different acids were studied as diluent of the analyte: sulfuric, acetic, citric and nitric. Among these acids, the peak profiles were similar, except for sulfuric acid, since the signal did not return to the baseline, as shown in Fig. 3. This behavior can be explained considering that the sulfate group impairs the atomization of the analyte, which is not completely atomized during the integration time (60 s).

Considering the other acids evaluated, nitric acid provided the highest analytical signal, and then it was chosen as the best acid, and its concentration evaluated from 0.1% to 1% (v/v). The highest concentration of acid lowered the analytical signal in 10%. Then,

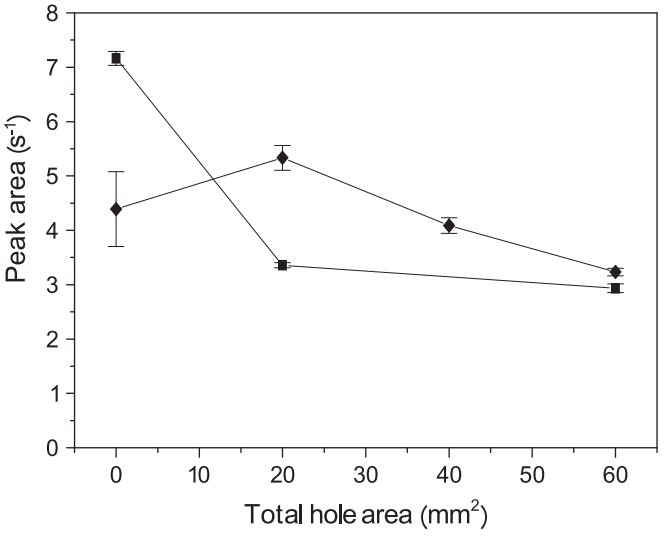

Fig. 4. Influence of the total hole area of the tube on the analytical signal. Conditions: 50 µg L^{-1} silver solution in 0.2% (v/v) HNO_3, carrier: air at 0.4 mL min^{-1}, sample volume: 200 µL, flame condition: 1.5 L min^{-1} C_2H_2: 12 L min^{-1} air, nebulization flow rate at 6 mL min^{-1} (■ Nickel tube ◆ Inconel tube).

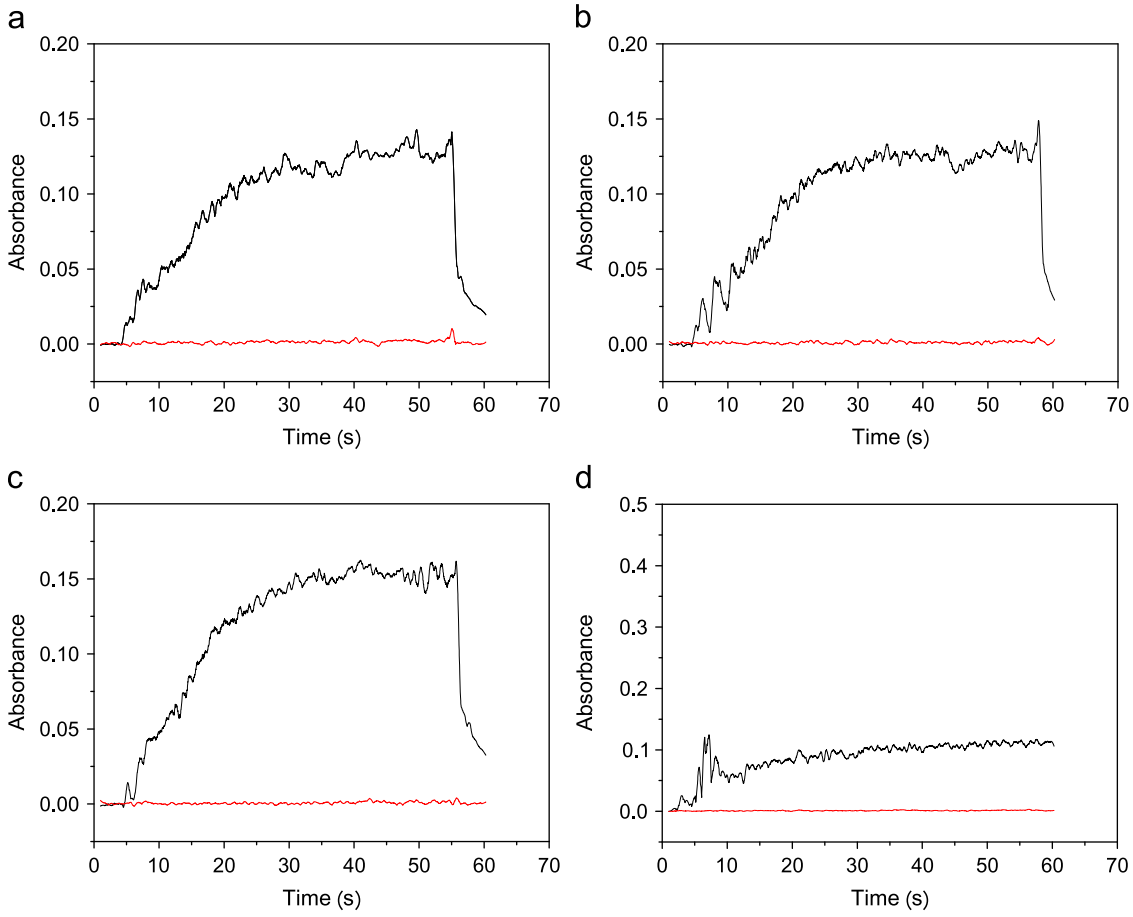

Fig. 3. Peak profiles for 100 µg L^{-1} Ag from different acids at 0.2% (v/v): (a) acetic, (b) citric, (c) nitric, (d) sulfuric. Conditions: flame 1.5 L min^{-1} C_2H_2: 12 L min^{-1} air, carrier: air at 0.4 mL min^{-1}, nebulization flow rate at 6 mL min^{-1}, sample volume: 200 µL and 99.9% (m/m) Ni tube with 60 mm^2 total hole area (dark black line AA, light black line BG).

considering the peak profile, intensity of analytical signal and the standard deviation, 0.2% (v/v) was the best concentration of nitric acid, providing a low limit of detection for the method.

3.1.6. Metallic tube

Nickel at 99.9% and Inconel alloy (Ni at 75%) were the alloys evaluated as material for composing the tubes, as well as 0 mm^2, 20 mm^2, 40 mm^2 and 60 mm^2 as hole areas. The material and holes of the tube must be evaluated because they can modify the environment to which the analyte is submitted. Holes at the bottom of the tube allow partial gas entrances. Then, the environment inside the tube changes when different total hole areas are used. So, the analytical signal decreases when the total hole area increases, and a tube without holes must be used (Fig. 4). Between the Inconel® and nickel tube without holes, the latter one provides the higher analytical signal and the lowest dispersion of the results, which can be attributed to the temperature of the tube. The temperature of the nickel tube (1053 ± 37 °C) is higher than the temperature of the Inconel tube (947 ± 64 °C), which facilitates the atomization of the analyte. It is possible to suggest that the thermal decomposition plays a more important role in the atomization of the silver species than does chemical decomposition. To obtain more reproducible results, the tube was kept in the flame for 20 min before the first injection.

Table 1
Evaluation of the concomitants in the method for silver determination by TS-FF-AAS.

Concomitant	Analyte (at 25 $\mu g\,L^{-1}$):Concomitant ratio	Recovery (%)
Be	1:1	98 ± 6
	1:10	96 ± 5
	1:100	97 ± 6
Cd	1:1	97 ± 7
	1:10	99 ± 6
	1:100	100 ± 1
Co	1:1	100 ± 6
	1:10	99 ± 8
	1:100	100 ± 8
Cr	1:1	92 ± 6
	1:10	89 ± 7
	1:100	79 ± 6
	1:1000	67 ± 3
Cu	1:1	93 ± 4
	1:10	91 ± 4
	1:100	91 ± 1
	1:500	88 ± 0.3
Li	1:1	95 ± 6
	1:10	97 ± 6
	1:100	98 ± 5
	1:500	100 ± 6
Mn	1:1	101 ± 4
	1:10	110 ± 7
	1:100	110 ± 2
	1:2000	111 ± 4
Mo	1:1	94 ± 6
	1:10	94 ± 6
	1:100	90 ± 6
Pb	1:1	97 ± 8
	1:10	97 ± 3
	1:100	95 ± 5
	1:500	93 ± 4
Sn	1:1	98 ± 6
	1:10	93 ± 8
	1:100	89 ± 6
Zn	1:1	99 ± 9
	1:10	102 ± 8
	1:100	102 ± 3
	1:1000	98 ± 5

3.2. Concomitant evaluation

An element was considered an interfering species when the recovery of the analyte was higher than 110% or lower than 90%.

To evaluate the signal in the presence of other elements, a silver solution of 25 $\mu g\,L^{-1}$ was used, and the concomitants were studied at 1:1, 1:10 and 1:100 silver:concomitant proportions. Some elements (Cu, Li and Pb) were also determined at 1:500, 1:1000 (Cr and Zn) and 1:2000 (Mn) ratios. The recovery of the analyte in the presence of other elements is shown in Table 1. Through these values, and using a *t* test, chromium (1:100 and 1:1000), copper (1:500), molybdenum and tin (1:100), and manganese (1:100 and 1:2000) may interfere in the silver determination.

3.3. Analytical performance and application

The limits of detection and quantification were calculated according to the IUPAC recommendations, and at optimal condition they were 0.15 $\mu g\,L^{-1}$ and 0.50 $\mu g\,L^{-1}$, respectively. Some methods using electrothermal atomic absorption spectrometry can reach limits of detection (Table 2) even lower, but frequently they are based on concentration steps and, then, the proposed method is less time-consuming and simpler than many methods found in the literature.

The linear range studied for this method was up to 40 $\mu g\,L^{-1}$. Higher concentrations need several injections of blank solution for cleaning the tube before another sample is injected. The analytical frequency was 20 h^{-1} and the correlation coefficient of the analytical curve was 0.995. Using a 2 $\mu g\,L^{-1}$ silver solution, the repeatability was 3.43% ($N=10$).

Two certified reference materials as well as one oyster tissue sample were analyzed by the proposed method, and the results are presented in Table 3. The oyster sample was also analyzed by ETAAS (pyrolysis and atomization temperatures were 800 and 1700 °C, respectively). A statistical analysis using Student's *t* test concluded that there is no significant difference between the values, at a 95% confidence level.

Table 2
Comparison of AAS methods found in the literature used to determine silver in different matrices.

Technique	Samples	LOD	RSD (%)	Ref.
Solid sampling and GFAAS	Bovine liver, soil, polypropylene sample containing silver	2 $ng\,g^{-1}$	6–7 (organic samples)	[24]
Preconcentration and GFAAS	Water	12 $ng\,L^{-1}$	3.5	[25]
ETAAS with slurry sampling	Soil and sediment	0.02 $mg\,kg^{-1}$	4–6	[26]
Preconcentration by reductive coprecipitation and ETAAS	High-purity metals, such as Aluminum, Cobalt, Chromium, Copper, and Iron	0.002 $\mu g\,g^{-1}$	2–4	[27]
Ultrasound-assisted extraction and ETAAS	Soil, sediment and industrial sludge	0.012 $\mu g\,g^{-1}$	2–10	[28]
Cloud point extraction and ETAAS	Water	1.2 $ng\,L^{-1}$	4.2	[29]

Table 3
Determination of silver in different samples.

Material	Found value*	Certified value	ETAAS
Fish flesh homogenate MA-A-2 ($\mu g\ g^{-1}$)	0.094 ± 0.020	0.10 ± 0.01	–
Trace elements in water SRM 1643e ($\mu g\ L^{-1}$)	1.097 ± 0.062	1.062 ± 0.075	–
Oyster tissue ($\mu g\ g^{-1}$)	0.053 ± 0.003	–	0.054 ± 0.004

* Expressed as average $\pm (ts/\sqrt{n})$ at 95% confidence level.

4. Conclusions

The initial purpose of this work was successfully attained, since a simple and sensitive method for silver determination using a metallic tube atomizer was optimized. The experimental conditions were studied and shown that air must be used as a carrier to provide sample homogeneity, and that the thermal decomposition is more important than the chemical one for silver determination by TS-FF-AAS. Under the optimal conditions the limits of detection and quantification were 0.15 e 0.50 $\mu g\ L^{-1}$, respectively. Silver was determined in water (SRM 1643e) and fish (MA-A-2) certified materials without concentration steps, and the results obtained were statistically analyzed and are in accordance with the certified values or an alternative technique at the 95% confidence level. Another advantage of the method is its easy and cheap implementation, since the tube furnace costs ca. US$ 7 and its lifetime was higher than 2000 h.

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