



Determination of silver in airborne particulate matter collected on glass fiber filters using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sampling

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ABSTRACT

The present work aims at the determination of silver in airborne particulate matter (APM) collected on glass fiber filters using direct solid sampling and high-resolution continuum source graphite furnace atomic absorption spectrometry. The secondary line at 338.289 nm was used for all measurements. A manual solid sampling accessory and solid sampling platforms were used for sample introduction. A mass of 400 µg of ruthenium was thermally deposited on the platform surface as permanent modifier. The optimum pyrolysis and atomization temperature was 1,000 and 2,000 °C, respectively. Aqueous standard solutions were used for calibration exclusively. The analytical parameters obtained for the proposed method were as follows: characteristic mass, 4.4 pg Ag; detection limit (3σ , $n = 10$), 17 ng g⁻¹; and quantification limit (10σ , $n = 10$), 58 ng g⁻¹. These limits are equivalent to 0.05 and 0.16 ng m⁻³, respectively, for 0.36 mg of sample mass (filter + APM) and an average volume of 1,440 m³ air that had passed through the filter. The certified reference material urban particulate matter, NIST 1648, was used for checking the accuracy. Four filter samples with APM collected in Buenos Aires, Argentina, were analyzed. According to our study, the concentration of silver (average ± confidence interval at 95% level, $n = 5$) varied between 0.64 ± 0.06 and 1.18 ± 0.07 µg g⁻¹, corresponding to 1.99 ± 0.11 and 4.54 ± 0.26 ng m⁻³. The precision, expressed as relative standard deviation, varied between 1.6 and 7.1% ($n = 5$). The analytical method proved to be simple, fast and reliable.

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1. Introduction

Silver is an element found naturally in the environment and also combined with other elements such as sulfur, chlorine, nitrogen and oxygen. It is a lustrous noble metal with the highest electrical and thermal conductivity of all elements. Silver and its alloys possess attractive electrical and mechanical properties. As a consequence of these characteristics, silver has a wide variety of applications in electronics, batteries, conductive pastes, dental alloys, silverware, jewelry etc. It is also used in photography, brazing alloys and solders, to

disinfect drinking water and as an antibacterial agent. Silver has also been used in lozenges and chewing gum to help people stop smoking [1,2].

The possible toxic effects for humans associated to the presence of silver still generate controversy and are not very well established, although it is well known that silver has a significant adverse effect on aquatic plants and animals, being frequently considered as one of the main environmental pollutants [3]. In Tokyo, suspected sources of Ag in APM were some recycling plants, operating for computer, building materials, and metallic materials including non-ferrous and noble metals [4].

The Agency for Toxic Substances and Disease Registry (ATSDR) of the USA set a limit concentration for exposure to silver and its compounds in air. In turn, the Occupational Safety and Health Administration (OSHA) fixed a limit of silver in the workplace air of 0.01 mg m⁻³ for an 8-h workday, 40-h workweek. The National Institute of Occupational

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Safety and Health (NIOSH) also recommend that workplace air contains no more than 0.01 mg m^{-3} of silver. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended that workplace air contains no more than 0.1 mg m^{-3} silver metal and 0.01 mg m^{-3} of soluble silver compounds [2,5].

Several studies have reported the chemical composition of airborne particulate matter (APM) collected in different cities in order to assess their impact and trace their sources of emission. However, the determination of trace and ultra-trace elements becomes a challenge because of their low concentrations in the air. In this context, very sensitive and selective analytical techniques are required for their quantification [6–10].

High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) is a valuable tool due to its special features, which include visibility of the spectral environment at high resolution, automatic and simultaneous correction for continuous background and the possibility to correct for fine structured background by subtracting a reference spectrum. The HR-CS AAS using a graphite tube atomizer (GF) is one of the most commonly used techniques for the determination of trace elements in complex and concentrated matrices [11]. This technique makes possible the direct analysis of solid samples (SS) and offers several interesting advantages, such as a greatly reduced risk of contamination and analyte loss as well as a relatively moderate cost. All these features make HR-CS SS-GF AAS very attractive for routine application, as accurate results can be obtained very rapidly; sub-milligram masses of sample can be analyzed without previous preparation and dilution, enabling higher detection power for low concentrations of the analyte [12–14].

In this context, the present work considers the optimization of an analytical method for the determination of silver in airborne particulate matter collected on glass fiber filters using HR-CS SS-GF AAS. The goal of the work was to develop a faster, simpler, more reliable and more sensitive routine procedure for the determination of silver in environmental samples avoiding dissolution, which is kind of a prerequisite for most of the other techniques.

2. Experimental

2.1. Instrumentation

All experiments have been carried out using a prototype high-resolution continuum source atomic absorption spectrometer, developed at ISAS (Berlin, Germany), based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany), which has been described in detail elsewhere [11–15]. The instrument is equipped with a xenon short-arc lamp, a high-resolution double monochromator and a linear charge coupled device (CCD) array detector with 512 pixels, 200 of which are used for analytical purposes; the other pixels are used for internal control purposes, such as the adjustment of the prism position. The conventional transversely heated graphite tube atomizer supplied with the model AAS 6 Vario has been used for all determinations. The secondary silver line at 338.289 nm was used for all measurements, as the silver content in the investigated samples was relatively high, and the use of the secondary line made possible to introduce a higher sample mass, which improved the precision of the determination.

All experiments were carried out using pyrolytically coated SS graphite tubes without dosing hole (Analytik Jena, Part No. 407-A81.303). Samples were weighed onto SS platforms (Analytik Jena, Part No. 407–152.023), using an M2P micro-balance (Sartorius, Göttingen, Germany), and inserted into the graphite tubes using a pre-adjusted pair of tweezers, which is part of the SSA 5 manual solid sampling accessory (Analytik Jena). Argon 99.996% (White Martins, São Paulo, Brazil) was used as purge and protective gas. Ruthenium was thermally deposited as the permanent modifier onto the platform surface by 10 repetitive injections of $40 \mu\text{L}$ of a $1,000 \text{ mg L}^{-1}$ stock solution [16]. After each injection, the temperature program shown in Table 1 was applied. The

temperature program adopted for aqueous standards (calibration) and for solid samples is shown in Table 2. Peak volume selected absorbance (PVSA) [17], i.e., the integrated absorbance summed over three pixels ($A_{\Sigma 3, \text{int}}$) was used exclusively for signal evaluation, as this resulted in the best signal-to-noise ratio. In all figures in which time-resolved absorbance is shown, recording starts with the 'auto-zero' stage, i.e., 1 s prior to the atomization stage.

2.2. Reagents and samples

Analytical grade reagents were used throughout. The nitric acid 65% v/v (Merck, Germany), used to prepare aqueous calibration standards, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). Water was de-ionized to a resistivity of $18.2 \text{ M}\Omega$ in a Milli-Q apparatus (Millipore, Bedford, MA, USA). All containers and glassware were soaked in 3 mol L^{-1} nitric acid for at least 24 h and rinsed three times with de-ionized water before use. A stock standard solution containing $1,010 \text{ mg L}^{-1}$ Ag in 0.5% v/v HNO_3 (Sigma-Aldrich, Milwaukee, USA) was used. Calibration solutions have been prepared by appropriate dilution in 0.07 mol L^{-1} HNO_3 . The certified reference material (CRM) NIST SRM 1648 Urban Particulate Matter (National Institute for Standards and Technology, Gaithersburg, MD, USA) was used for method validation. Four glass fiber filters with APM collected in Buenos Aires, Argentina, were analyzed in this study. Airborne particulate matter was collected on ash-free glass fiber filters using a high-volume air sampler (SIBATA, HV 1000F, Japan) with a PM_{10} sampling head. The sampling flow rate was $1,000 \text{ L min}^{-1}$ and the average total sampling time was 24 h; the average air volume collected was $1,440 \text{ m}^3$. Details of the sampling procedure and the treatment of the filters loaded with APM have been described previously [18]. Sample masses between about 0.06 and 0.36 mg were weighed directly onto the SS platforms and inserted into the graphite tube with the SSA 5 accessory for the determination of Ag in filter samples.

3. Results and discussion

3.1. Optimization of HR-CS SS-GF AAS conditions

All method development and optimization have been carried out using filter LDC-6 with 0.0932 g of APM deposited on its surface. All calculations have taken into consideration the total mass of the filter + APM and the mass of APM, respectively.

Pyrolysis curves for Ag were established using filter LDC-6 and an aqueous standard solution in 0.07 mol L^{-1} HNO_3 without a modifier and with the use of $400 \mu\text{g}$ of ruthenium as permanent modifier. As can be seen in Fig. 1, a pyrolysis temperature of up to $900 \text{ }^\circ\text{C}$ could be used for Ag in an aqueous solution, while up to $1,200 \text{ }^\circ\text{C}$ could be employed for Ag on the filter sample without a modifier. Using Ru as permanent modifier, silver both in the aqueous solution and in the filter sample was thermally stable at least up to $1,000 \text{ }^\circ\text{C}$.

The atomization temperature has been optimized in a similar manner as described for the pyrolysis stage, as is also shown in Fig. 1. Although the highest sensitivity was obtained at an atomization temperature of $1,700 \text{ }^\circ\text{C}$ under all conditions, higher atomization temperatures were preferred because much more symmetric peaks

Table 1
Temperature program for deposition of ruthenium on the SS graphite platform.

Step	Temperature/ $^\circ\text{C}$	Ramp/ $^\circ\text{C}$	Hold/s	Ar flow rate/ L min^{-1}
1	130	10	40	2
2	160	10	50	2
3	1000	20	25	0
4	1400	100	5	2
5	2000	100	5	0

Table 2

Graphite furnace temperature program for the determination of silver in filter samples by solid sampling HR-CS GF AAS using 400 μg Ru as permanent modifier.

Stage	Temperature/ $^{\circ}\text{C}$	Ramp/ $^{\circ}\text{C}$	Hold/s
Drying 1	90	10	10
Drying 2	130	5	5
Pyrolysis	1000	50	15
Atomization*	2000	3000	7
Cleaning	2300	1000	5

*Purge gas (argon) flow rate 2 L min^{-1} in all steps, except during atomization, where the gas flow was interrupted for reading.

were obtained. As a compromise a pyrolysis temperature of 1,000 $^{\circ}\text{C}$ and an atomization temperature of 2,000 $^{\circ}\text{C}$ have been chosen for the determination of Ag in all further experiments, using 400 μg of ruthenium as permanent modifier.

During the optimization of the atomization temperature it has been observed that rather similar profiles of the transient signals were obtained for Ag in an aqueous solution and in the filter sample under the same conditions, whereas the CRM Urban Particulate matter was behaving differently. Fig. 2 shows the superimposed transient signals for Ag in the filter + APM sample (mass: 116 μg Ag), an aqueous standard solution (mass: 101 μg Ag) and the CRM urban particulate matter (mass: 107 μg Ag) using an atomization temperature of 2,000 $^{\circ}\text{C}$. The absorbance profile for Ag in an aqueous solution is quite similar to that obtained for the filter material, although the appearance time and the peak maximum for the aqueous solution are slightly earlier. This can easily be explained with the absence of any matrix in case of the aqueous solution, compared to the filter sample. However, the appearance time and particularly the peak maximum for Ag in the CRM are clearly shifted late, indicating that the atomization of this analyte from that matrix is slower than from the filter material, probably due to the much denser property of the CRM compared to the cotton-like structure of the ground filters [18]. Nevertheless, working under stabilized temperature platform furnace (STPF) conditions, this shift in appearance time and peak maximum do not have an influence on the accuracy of the measurement.

3.2. Correction for continuous background absorption

In HR-CS AAS, all “continuous spectral events” that affect all pixels to the same extent are corrected automatically by the software. As all pixels are read out simultaneously, the system functions like a truly simultaneous double beam system, in which lamp flicker noise, continuous

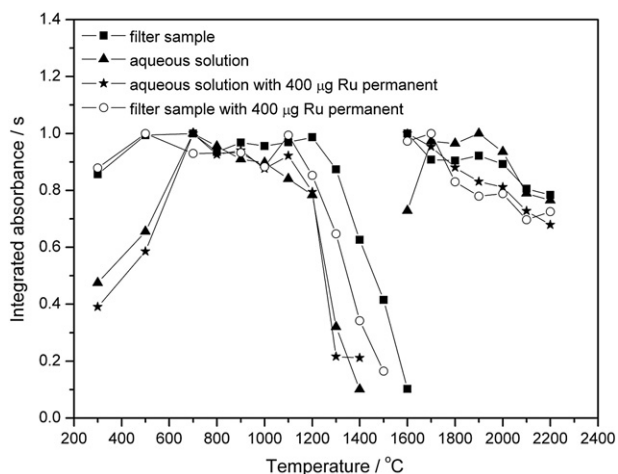


Fig. 1. Pyrolysis and atomization curves for Ag using the filter sample LDC-6 and an aqueous standard with 101 μg Ag, without and with 400 μg Ru as permanent modifier; atomization temperature used for the pyrolysis curves: 2,000 $^{\circ}\text{C}$; pyrolysis temperature used for the atomization curves: 1,000 $^{\circ}\text{C}$.

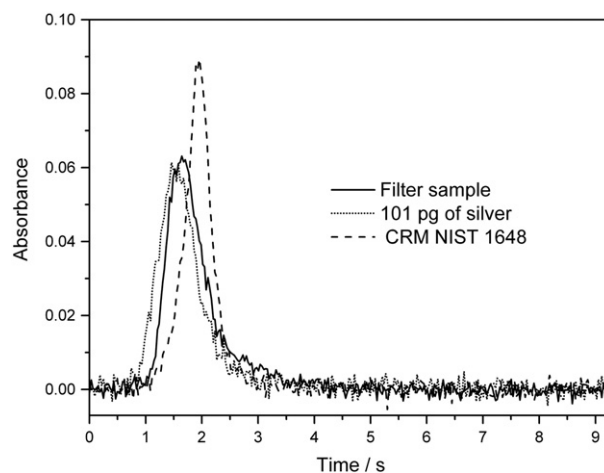


Fig. 2. Superimposed transient signals of silver for the filter sample LDC-6 (solid line; 116 μg Ag), an aqueous standard solution (dotted line; 101 μg Ag) and urban particulate matter NIST SRM 1648 (dashed line; 107 μg Ag) using a pyrolysis temperature of 1,000 $^{\circ}\text{C}$ and an atomization temperature of 2,000 $^{\circ}\text{C}$.

background absorption and/or emission are corrected automatically [11]. Fig. 3 shows the transient signals obtained for 0.090 mg of filter sample with APM (LDC-6) without and with automatic background correction at the center pixel at 338.268 nm using 400 μg Ru as a permanent modifier. The background is very low and could be corrected without any problems. This is actually according to expectation for a pyrolysis temperature of 1,000 $^{\circ}\text{C}$ and an atomization temperature of 2,000 $^{\circ}\text{C}$, where most of the matrix (SiO_2) remained in the graphite tube up to the cleaning stage.

3.3. Figures of merit

The figures of merit for the proposed method are summarized in Table 3. The characteristic mass (m_0), defined as the mass of the analyte that produces a PVSA of 0.0044 s, was found to be 4.4 μg Ag. This is in agreement with the literature [11], considering that the secondary line of silver 338.289 nm is about a factor of two less sensitive than the main line at 328.068 nm.

A calibration curve has been established using a blank and six calibration solutions in the concentration range 2.5–19.0 $\mu\text{g L}^{-1}$ Ag (mass range: 50–380 μg Ag) prepared in 0.07 mol L^{-1} HNO_3 . Calibration curves were also obtained using increasing masses of the NIST SRM 1648 urban particulate matter. The slope obtained for Ag was in good agreement with that obtained for aqueous standard solutions,

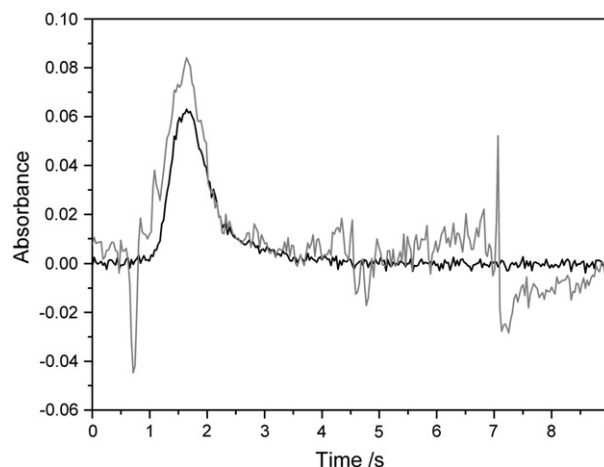


Fig. 3. Transient signals for 0.090 mg of filter + APM sample LDC-6 using a pyrolysis temperature of 1,000 $^{\circ}\text{C}$ and an atomization temperature of 2,000 $^{\circ}\text{C}$; gray line: without correction; black line: with automatic correction for spectrally continuous events.

Table 3

Figures of merit for the determination of Ag by HR-CS SS-GF AAS and 400 µg of ruthenium as permanent modifier; pyrolysis temperature: 1,000 °C; atomization temperature: 2,000 °C.

Parameters	Values
Analytical range	50–380 pg/2.5–19.0 µg L ⁻¹
Calibration curve aqueous	$A_{\Sigma 3, \text{int}} = 0.001037m_{\text{Ag}} + 0.0043$
Correlation coefficient/ <i>r</i>	0.9996
Calibration curve (NIST 1648)	$A_{\Sigma 3, \text{int}} = 0.001007m_{\text{Ag}} + 0.0034$
Correlation coefficient/ <i>r</i>	0.9959
<i>m</i> ₀	4.4 pg
LOD ^a on filter	17 ng g ⁻¹
LOD ^b in APM	0.5 µg g ⁻¹
LOD ^c in air	0.05 ng m ⁻³
LOQ ^a on filter	58 ng g ⁻¹
LOQ ^b in APM	1.6 µg g ⁻¹
LOQ ^c in air	0.16 ng m ⁻³

^a Based on 0.34 mg of sample mass.

^b Based on 3.89 g of filter and 0.13 g of APM.

^c Based on 1,440 m³ of air.

as shown in Table 3, indicating that calibration against aqueous standards is possible. This is in agreement with earlier work by Dittert et al. [19], who determined silver in geological materials using a similar procedure and calibration against aqueous standards.

The limit of detection (LOD) was calculated as three times the standard deviation of 10 measurements of the blank divided by the slope of the calibration curve. A “zero mass response” [20], obtained by repeatedly submitting the empty SS platform to the temperature program given in Table 2, was taken as the blank. The LOD in Table 3 has been calculated for a sample mass of 0.34 mg, the maximum filter mass with APM that has been used in this work, and for Ag in the sampled air, based on a 24 h sampling interval, i.e., 1,440 m³ of air and 0.14 g of APM collected on the filter. The limit of quantification (LOQ) is defined as 10 times the standard deviation of 10 measurements of the blank divided by the slope of the calibration curve.

3.4. Analysis of APM collected on filters

The accuracy of the proposed method has been verified analyzing the CRM NIST 1648 - Urban Particulate Matter. A value of $6.04 \pm 0.37 \mu\text{g g}^{-1}$ Ag (average ± confidence interval instead of standard deviation, *n* = 10) has been found, which is not statistically different compared to the informed value of $6 \mu\text{g g}^{-1}$, based on a Student *t*-test at a confidence level of 95% ($t_{\text{calculated}} = 0.40$; $t_{\text{value}} = 2.62$, *n* = 10, degrees of freedom = 09).

The correlation between the filter mass with APM introduced into the graphite furnace and the integrated absorbance (PVSA, $A_{\Sigma 3, \text{int}}$) is shown in Fig. 4 for the filter LDC-6. The sample mass has been varied in the range from 0.057 to 0.281 mg (*n* = 23); each measurement point corresponds to an individual sample weighing and measurement, and is hence an indication for the precision of the entire procedure. The reasonably good linear correlation (*r* = 0.93) shows that at least up to about 0.3 mg of filter sample with APM can be introduced and measured with the proposed procedure.

The proposed method was applied for the determination of Ag in four filter samples collected in the urban area of Buenos Aires, Argentina, as shown in Table 4. The filters were loaded with a mass between 51.3 and 136.9 mg of APM, and containing between 44.0 and 95.1 µg APM per cubic meter of air. The silver content found in these filter samples was between 0.60 ± 0.03 and $1.18 \pm 0.07 \text{ ng g}^{-1}$, corresponding to 30.2 ± 0.6 and $48.9 \pm 2.8 \mu\text{g g}^{-1}$ Ag in the collected APM, and $1.99 \pm 0.11 \text{ ng m}^{-3}$ and $4.54 \pm 0.26 \text{ ng m}^{-3}$ Ag in the air, respectively. The precision, expressed as relative standard deviation (RSD) of the measured values, was between 1.6% and 7.1% (*n* = 5), which is

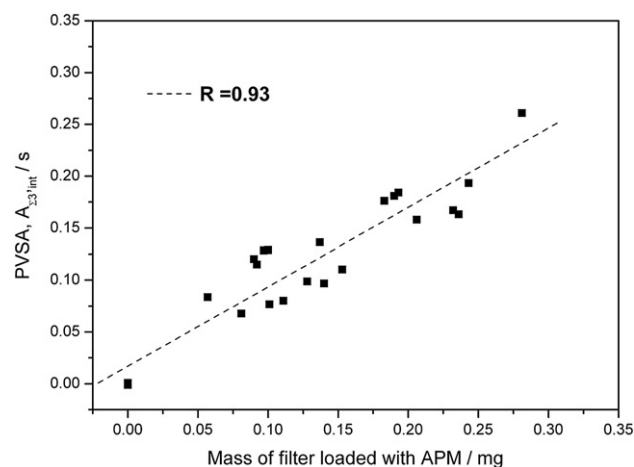


Fig. 4. Correlation between the filter sample mass introduced into the graphite furnace and the integrated absorbance. Pyrolysis temperature: 1,000 °C; atomization temperature: 2,000 °C; 400 µg Ru as permanent modifier (*n* = 23).

quite acceptable for the direct analysis of solid samples. The silver content in all samples collected in Buenos Aires City are below the maximum allowable concentration according to the National Institute of Occupational Safety and Health (NIOSH) and The American Conference of Governmental Industrial Hygienists (ACGIH) for silver (0.01 mg m^{-3}) and silver metal (0.1 mg m^{-3}), respectively, although these limits were established for the workplace and not for outdoor air.

4. Conclusion

A simple, fast and reliable procedure for the determination of silver in airborne particulate matter collected on glass fiber filters has been developed using HR-CS SS-GF AAS and calibration against aqueous standards with 400 µg Ru as the permanent modifier. The proposed method appears to be suitable for routine applications. Among the main advantages of direct solid sampling compared to conventional techniques, including slurry sampling, is that no corrosive and toxic acids, such as nitric or hydrofluoric acid are used, and that essentially no sample preparation is required, which contributes significantly to the sample throughput.

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Table 4

Results obtained for the determination of silver on the glass fiber filter, in the airborne particulate matter (APM) and in the air, using HR-CS SS-GF AAS and calibration against aqueous standards with Ru as permanent modifier.

Sample	Ag on filter ^a / µg g ⁻¹	Ag in APM ^a / µg g ⁻¹	Ag in air ^a / ng m ⁻³	RSD/% (<i>n</i> = 5)
LDC-5	0.84 ± 0.02	30.2 ± 0.6	2.30 ± 0.05	1.6
LDC-6	1.18 ± 0.07	48.9 ± 2.8	4.54 ± 0.26	4.6
LDC-7	0.60 ± 0.03	45.3 ± 2.5	1.99 ± 0.11	4.5
LDC-8	0.64 ± 0.06	35.8 ± 3.2	2.48 ± 0.22	7.1

^a Average of five determinations ± confidence interval (at the 95% level).

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