

Optimization of methods to assess levels of As, Bi, Sb and Se in airborne particulate matter by FI-HG-ICP OES

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A study was undertaken to assess the level of selected trace elements namely, As, Bi, Sb and Se in airborne particulate matter collected on ash-free glass-fibre filters from urban and industrial areas of Argentina. For sample digestion, a simple acid treatment with HCl + HF is proposed with the aim to minimize contamination and reduce sample treatment steps. A flow injection-hydride generation system in combination with inductively coupled plasma optical emission spectrometry was used. While, Se and Bi could be determined directly from the digest, As and Sb needed a pre-reduction with KI, and H₃BO₃ to avoid the interference of F⁻ ions that may cause losses *via* volatile compounds such as AsF₃ and Sb(v) complexes. Limits of detection (3σ) of 0.3 ng m⁻³ for As; 0.09 ng m⁻³ for Bi, and 0.1 ng m⁻³ for Sb and Se were achieved. Precision resulted in better than 6.1% accuracy for all the elements determined. Accuracy test was assessed by means of the certified reference material, NIST 1648 (urban particulate matter).

1. Introduction

The issue of urban air quality is receiving increasing attention as a growing share of the world's population is now living in urban centers and demanding a cleaner urban environment. Metals and metalloids content in airborne particulate matter (APM), and especially in fine fractions, have been raising much concern with regards to their impact on human health.¹ Trace metals are a part of atmospheric pollutants and their determination offers useful information when evaluating the interaction between air pollutants and public health.²

In previous studies we have tested both, Nuclepore³ and glass-fibre filters⁴⁻⁷ to collect APM from urban areas of Buenos Aires city and different sample treatments were presented. These types of filters have been also used by other research groups.^{8,9} Many studies have focused on sampling and preparation of airborne samples for chemical analysis.¹⁰⁻¹² Microwave assisted digestion and further analysis by ICP-MS, is one of the most powerful approaches to determine trace elements in APM samples collected on filters.¹³ However, the complexity of the matrix and the addition of high amounts of different acids such as H₂SO₄, HNO₃, HCl and even HF, for digestion may introduce new sources of interferences.^{13,14} In addition, although microwave digestion methods are widely used and are faster than usual acid digestion procedures, the Teflon vessels used are static and can be easily contaminated by particles from the laboratory air.¹⁵

For elements such as As, Bi, Sb and Se the hydride generation technique coupled to an ICP OES presents a number of

advantages including the diminishing of interferences due to sample matrix constituents or digestion acids.¹⁶⁻²⁰ In this proposal, a procedure for the accurate determination of As, Bi, Sb and Se in APM by a flow injection (FI) HG-ICP OES is presented.²¹ Pretreatment of APM collected on filters included decomposition in a mixture of HCl and HF. The use of disposable test-tubes for sample dissolution with only a few steps minimized the possibility of contamination which resulted in an easy and suitable method for APM digestion. This flow injection analysis enabled the reduction of time, reagent and sample consumptions, beyond the minimization of matrix effects and analyte losses. To mitigate the interference caused by HF in the determination of As and Sb, H₃BO₃ was added. Once the conditions were optimized the method was successfully applied to the analysis of APM collected in urban and industrial areas of Buenos Aires city in Argentina.

2. Experimental

2.1. Standards and reagents

All solutions were prepared with Ultrapure water (18 MΩ cm) obtained from a Milli-Q, EASY pure RF (Barnsted, Iowa, USA). The acids used were HNO₃ from Fluka (Germany), HCl from Merck (Darmstadt, Germany), and HF also from Merck (Darmstadt, Germany). A saturated solution of boric acid was prepared by dissolving 48.7 g of H₃BO₃ in 1000 ml of ultrapure water. A 10% m/v KI solution from Mallinckrodt (Charlotte, NC) was prepared in ultrapure water. All lab materials were cleaned in 10% HNO₃, Fluka (Germany) and rinsing with ultrapure water. Synthetic standard stock solutions (1000 mg l⁻¹) of As, Bi, Sb and Se, were from Fluka (Switzerland). For checking accuracy, aliquots of the Standard Reference Material SRM NIST 1648 (Urban Particulate Matter) were subjected to the same treatment as the samples and included in the over-all analytical process.

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2.2. Instrumentation

The measurements were performed with a sequential ICP OES; model ICP 2070 from BAIRD (Bedford, MA, USA) operated at 1 KW (forward power). The analytical lines employed were 188.978, 223.060, 206.833 and 196.026 nm for As, Bi, Sb and Se respectively. The FI system used is shown in Fig. 1. Minipulse 3 peristaltic pumps were from Gilson (Villiers-Le-Bell, France). Sample and eluent lines were selected using a Reodyne (Cotai, CA, USA) Model 50, four-way rotary valve. The hydride unit used was a hydride generator (PS Analytical Ltd.) and the flow rate of the reagents was controlled by a Watson-Marlow 303X peristaltic pump. The flow rates used were 9 ml min⁻¹ and 4 ml min⁻¹ for NaBH₄ and HCl respectively. Carrier gas flow rate was 650 ml min⁻¹. The glass gas-liquid separator had a PTFE-coated capillary to introduce the samples with remnants of HF. Tygon-type pump tubing (Ismatec, Cle-Parmer, Vernon Hills, IL, USA) were employed to propel the sample and reagents. An ultrasonic bath from Astrason Ultrasonic Clear, Farmingdale (N.Y., USA), was employed for sample preparation.

2.3. Sample collection

Seven samples were collected during a 12 days measuring campaign at two sampling sites A and B) covering an area of about 10 km². The samplers were situated at about 1 m from the road edge. Rainy and windy days were, as possible, avoided. Airborne particulate matter samples were collected on ash-free glass-fibre filters (20.3 cm × 25.4 cm, ADVANTEC, GB100R, 0.6 μm nominal rating) with a high-volume air sampler (SIBATA, HV 1000F, Japan) with a PM-10 sampling head. The sampling flow rate used was 1000 L min⁻¹ and the average total sampling time was 24 h (approximately from noon to noon of consecutive days) to achieve a concentration of the analytes sufficient for their quantification. Selection of representative monitoring points, operation, treatment and handling of samples and data validation were carried out according to QA/QC guidelines of the World Health Organization.²²

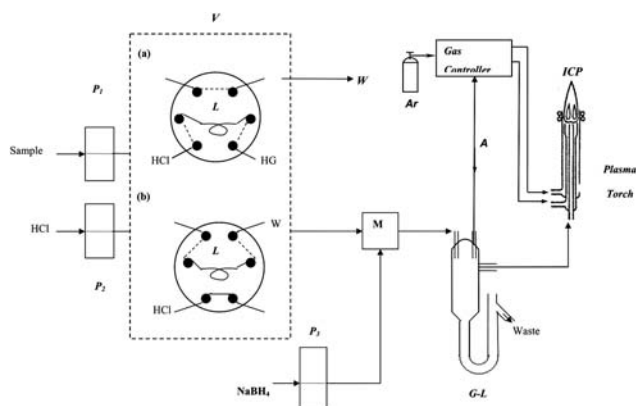


Fig. 1 Schematic diagram of the experimental setup: P1, P2 and P3, peristaltic pumps; V, six-port rotary valve (a, load position; b, injection position); L, PTFE injection loop; M, mixer chamber of the hydride generator; G-L, modified gas liquid separator with PTFE capillaries; A, Argon line with a ball-flowmeter.

2.4. Filter handling

Filters were handled in ways to minimize contamination. Blanks were prepared with unexposed ash-free glass-fibre and were handled identically to the samples. After sampling, filter cassettes were delivered to the laboratory in clean, sealed plastic bags. Once in the laboratory, filters loaded with airborne particulate matter (about 1440 cm², 4.50 g) and blank filters were folded and cut with a disposable stainless steel knife blades into strips using a polyethylene template which made strips sized 2.5 × 17 cm.¹¹ Cutting the filter into smaller sections was necessary to get the sample mass below 0.3 g. Individual filter strips loaded with APM were transferred carefully to disposable polyethylene centrifuge tubes.

2.5. Sample preparation

Individual filter strips were placed into disposable polyethylene tubes to which the acid mixture was added. For Se and Bi determination, tubes were placed in a water bath and 10 ml of concentrated HCl was added, then the temperature was raised to approximately 80 °C (30 min) and homogenized into an ultrasonic bath during 30 min. Next, 1.5 ml of concentrated HF was added and the solution was made up to 50 ml with ultrapure water. Finally, small aliquots (from 0.5 to 2.0 ml) of the digested samples were submitted to the hydride generation system (Fig. 1). For As and Sb determination, the same procedure was used and subsequently 5 ml of KI was added and kept for 30 min to assure total reduction. After that, 25 ml of H₃BO₃ were added. The solution was made up to 50 ml with ultrapure water. Unless some samples were collected in polluted areas, the addition of an oxidizing acid such as HNO₃, was unnecessary for total dissolution. According to our experience, the addition of nitric acid is mandatory when samples under study are collected in highly polluted areas. Nitric acid completes organic compound decomposition and breaks down metal-hydrocarbon complexes into H₂O, CO₂ and oxidized metals.

Finally, small aliquots of the digested samples and blank solutions were introduced into the hydride generation system (Fig. 1). Both, aqueous calibration and analyte addition methods were employed for quantification. About 0.3 g of the Standard Reference Material, SRM NIST 1648 was weighed onto a blank filter and subjected to the same treatment as the samples.

3. Results and discussion

3.1. Optimization of the flow injection hydride generation process

Different variables involved in the hydride generation of the analytes and their determination by FI-HG-ICP OES were studied. It is well known that for each different analyte, the reagent concentrations and other parameters should be carefully optimized when samples other than aqueous solutions are analyzed. The effect of HCl and NaBH₄ concentration on As, Bi, Sb and Se signals were studied separately. The outcome of these studies is that the optimal conditions were found to be: concentrations of HCl above 15% m/v for As, 10% m/v for Sb, and 5% m/v for Bi and Se. On the other hand, the optimal concentrations of the NaBH₄ were above 0.7% m/v for all

analytes. Since the highest NaHB_4 concentration tolerated by the ICP was 0.7% m/v due to the high amount of H_2 gas introduced, this compromise concentration of reductant reagent was employed in all cases.²³

The superiority of the overall performance of a FI system over batch procedures is obvious, the decrease in sample and reagent consumption and the increased tolerance to interferences being the most dramatic. Taking this point into account, the volume of the injected sample was also studied. Then, the peak height obtained for each transient signal was compared with that obtained when a standard was passed continuously with the HCl solution. The experimental observations (Fig. 2) showed that either As, Bi, Sb or Se, 2 ml was enough to generate transient signals that reached the same level as the continuous ones. Obviously, to increase sensitivity of the FI mode, the volume of sample injected can be increased to reduce the dispersion. For sufficiently high injected volume, steady-state signals can be reached. However, when the injected volumes of treated filters are high enough to modify the chemical composition in the gas-liquid separator, a suppressing effect is observed due to matrix effects (increasing the concentration of HNO_3 and HF).

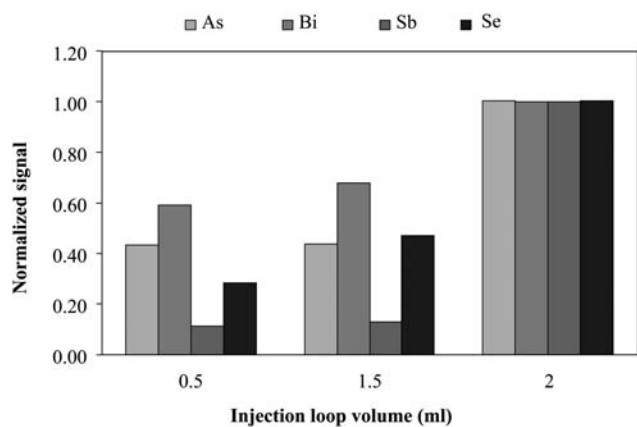


Fig. 2 Effect of injected volume on analyte signal.

3.2. Effect of HNO_3

Despite the fact that HNO_3 is a regular acid used to dissolve these kinds of samples, in this case its use was restricted due to the interfering effect that may occur on the hydride generation process. It could be inferred that while in the case of Bi, the HNO_3 added at the beginning did not affect the analytical signal, there are different suppressing effects for As, Sb and Se. On one hand, there is a progressive negative effect on the Se signal beyond a HNO_3 concentration of 10% v/v; and on the other hand, for As and Sb, there is a strong suppressing effect even at low HNO_3 concentrations (<5% v/v). Since it was experimentally observed that total dissolution of samples is achieved even without using this acid, its addition is recommended only when samples coming from highly polluted areas are analyzed in order to completely dissolve carbonaceous or organic matter that could be collected into the filters. Otherwise, poor recoveries may be achieved since the analytes are not completely released from the filter.²⁴

3.3 Effect of HF

After the acid treatment with gently heating and ultrasound agitation, the addition of hydrofluoric acid is mandatory to dissolve completely the silica in the reagent vessel. However, there is an interfering effect of fluoride on As and Sb signals. In the case of As this is mainly attributed to analyte losses *via* formation of volatile AsF_3 and for Sb, volatile complexes between fluoride and Sb(v) can be expected. This effect was experimentally corroborated by analyzing blank filters spiked with standards of As and Sb and treated with increasing amounts of HF. The objective of this study was to establish the minimum HF concentration necessary to dissolve silicates. It was observed (Fig. 3), that the analytical response was progressively suppressed (more than 2-fold) for both analytes at HF concentrations higher than 30 g l^{-1} . On the other hand, Bi and Se signals were not influenced by fluoride ions. The strong suppressing effect of fluorine on As and Sb could be overcome by the addition of H_3BO_3 which is a masking agent for fluoride ions. It was demonstrated that the addition of 25 ml of a saturated solution

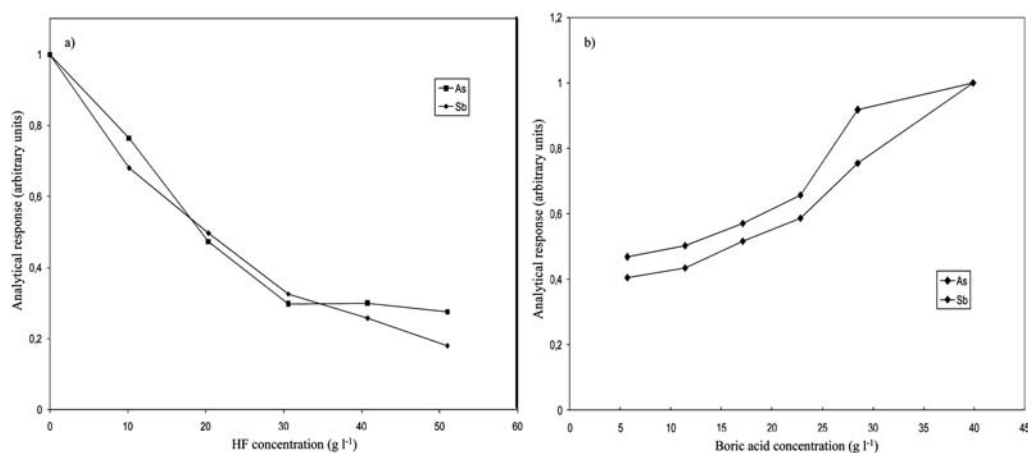


Fig. 3 a, Suppressing effect of F^-/HF on As and Sb signal; b, Analytical response as a function of the H_3BO_3 added in presence of 50 g l^{-1} of HF.

Table 1 Analytical performance

	As	Bi	Sb	Se
Calibration curve ^{ab}	y = 20.4x R ² = 1	y = 27.875x - 145.83 R ² = 0.9915	y = 24.5 x + 33 R ² = 0.9991	y = 6.56 x - 65.5 R ² = 0.9988
LoD/ng m ^{-3c}	0.3	0.09	0.1	0.1
LoQ/ng m ^{-3d}	0.8	0.2	0.4	0.4
RSD (%) ^e	< 4.5	< 5	< 6.1	< 3

^a y [=] emission intensity in counts per second. ^b x [=] concentration in µg l⁻¹. ^c three times the standard deviation of the blank (3σ). ^d ten times the standard deviation of the blank (10σ). ^e n = 10.

of boric acid allowed an efficient hydride generation of As and Sb.

3.4. Effect the of oxidation state and pre-reduction

The effectiveness of the hydride generation processes depends strongly on the oxidation state of the elements. Thus, these procedures involve a pre-reduction stage (As(v) to As(III), Sb(v) to Sb(III), Se(vI) to Se(IV)). There is a large list of pre-reductants and in this work we have selected KI to determine the total concentration of As and Sb. It was verified that after the recommended sample pretreatment, the addition of 5 ml of KI was necessary to achieve the accurate determination of total As and Sb concentrations. Successful applications have been found for pre-reducing Se(vI) when high temperatures and HCl have been used.¹⁷ Consequently, heating the samples in a water bath at 80 °C during 30 min to facilitate the reduction is recommended.

3.5. Analytical performance and application to real samples

On the basis of the findings of this study, FI-HG-ICP OES combined with an efficient sample digestion method involving the use of disposable test tubes was a fully adequate method to determine selected elements in airborne particulate matter collected on filters. The figures of merit for each individual analyte were calculated on digested strips of blank filters of approximately 0.3 g, presented in Table 1. Since the hydride generation was carried out in a continuous flow injection mode

Table 2 Accuracy verification: analysis of the certified reference material NIST 1648 (urban particulate matter) and application to real samples. Concentrations are expressed in ng m⁻³.

Sample ^{ab}	As	Bi	Sb	Se
A1	< 0.8	< 0.2	30.3	< 0.4
A2	5.4	< 0.2	29.1	< 0.4
A3	1.1	< 0.2	30.0	< 0.4
A4	3.7	< 0.2	26.4	< 0.4
B1	0.8	0.4	24.7	< 0.4
B2	3.0	5.5	27.0	< 0.4
B3	< 0.8	< 0.2	33.9	< 0.4
Certificate	115 ± 10	— ^c	45 ^d	27 ± 1
Experimental	116 ± 4	34.1 ± 2.2	45.4 ± 1.4	27.9 ± 1.5

^a A: APM sampled collected in the district of Ezeiza, between Buenos Aires Province and Buenos Aires city. (1, Thursday; 2, Wednesday; 3, Friday; 4, Saturday). ^b B: APM sampled collected in San Nicolás, Buenos Aires province in the nearest of a coal power plant (1, Friday; 2, Sunday; 3, Tuesday). ^c Neither certified nor reference values are available for Bi in the SRM used for checking accuracy. ^d informed value.

(Fig. 1), the time of analysis, reagent and sample consumptions, matrix effects and contamination risks were minimized. The entire signal acquiring process was about 35 s, allowing a sampling frequency of 100 determinations h⁻¹. After a thorough study of the experimental conditions for sample pre-treatment, the possible non-spectral interferences were suitably handled. Accuracy was evaluated by means of the analysis of a Standard Reference Material (SRM NIST 1648—urban particulate matter). Table 2 shows the experimental results for each analyte and the certified values. Calibration against simple aqueous standards was used in all cases. In spite of the complexity of the matrix analyzed, the analyte addition method was not necessary.

Table 2 collects the results achieved when samples of APM collected in industrial and urban areas were analyzed. In all cases, very low levels of As, Bi and Se were detected. On the contrary, Sb concentrations ranged from 24.7 to 33.9 ng m⁻³. Antimony is a traffic-related element and the uniformity of the results confirms that samples were collected in sites with a similar traffic pattern. Bismuth was only detected in two samples that were collected close to a thermal power plant that burns coal.

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