Determination of antimony in soils and vegetables by hydride generation atomic fluorescence spectrometry and electrothermal atomic absorption spectrometry. Optimization and comparison of both analytical techniques

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Two sensitive analytical atomic spectrometry methods, electrothermal atomic absorption spectrometry (ET-AAS) and hydride generation coupled to atomic fluorescence spectroscopy (HG-AFS), were optimized for determining total antimony in soils and plant (alfalfa) matrices. The dry soils were digested with HNO_3–HCl–HF mixture, while, for the freeze dry alfalfa samples, HNO_3–H_2SO_4–H_2O_2 or HNO_3–H_2O_2 mixtures were used. The microwave oven digestion procedures chosen allowed the total dissolution of the matrices. The experimental parameters of both spectrometric techniques were optimized using standard solutions of Sb(III) and/or Sb(V), and digested solutions of soil and alfalfa samples. Since in the antimony determination by HG-AFS the kinetic of the hydride generation is dependent on the antimony oxidation state, a chemical reduction of Sb(V) to Sb(III) was carried out prior to the stibine generation. For this purpose, KI and L-cysteine were used as reducing agents, assaying different experimental conditions. The reduction of Sb(V) in plant solutions by a KI–ascorbic acid mixture can be performed at room temperature, while the Sb(V) reduction from soils solutions was quantitative when the procedure was accomplished in a microwave oven or at 90 °C in a water bath. For antimony determination by HG-AFS, the simple calibration mode was used, because this technique is less sensitive to interferences. For antimony determination by ET-AAS the use of a chemical modifier is unavoidable. Similar amounts of nickel or palladium were effective in stabilizing the antimony species present in soils and plant solutions; however, the best analytical signals were obtained using mixtures of this metals with $NH_4H_2PO_4$ and citric acid. Due to the matrix interference for determining antimony by ET-AAS, the standard additions method was used. The accuracy of the proposed methods were assessed by analyzing two certified reference soils (CRM) from NIST, San Joaquín soil (SRM 2709) and Montana soil (SRM 2710) and a reference vegetal material, Virginia tobacco leaves (CTA-VTL-2). In all cases the results obtained by both techniques agreed with the certified values. Under the optimized conditions, a detection limit of 0.08 μg l^{-1} of Sb(III) was achieved by HG-AFS, with a precision of 4.3% for 0.5 μg l^{-1}Sb(III); the calibration graph was linear from 0.25 to 250 μg l^{-1}. The detection limit obtained by ET-AAS, [injecting 20 μl Sb(III) solution and 10 μl chemical modifier mixture (2 μg Ni + 100 μg $NH_4H_2PO_4$ + 50 μg citric acid)] was 9 pg Sb, with a precision of 4.7% for 100 pg Sb. The proposed methods were successfully applied to the Sb determination in soils and alfalfa samples, from the Valparaíso region in Chile. In all samples the antimony concentrations found were higher than the average reported for Sb concentration in soils and vegetable.

Introduction

Antimony is an element which has received relatively little environmental attention, with only few studies in soils, sediments and biological material. This is due to the fact that antimony is recognized as a non-essential element for life and also because its content in most environmental matrices is very low, implying the use of very sensitive analytical techniques for its determination.[1] In comparison to arsenic, little information is available on the environmental chemistry of antimony.[2] Nevertheless, antimony is a cumulative toxic element that has chemical and toxicological properties similar to those of arsenic.[3] Indeed, As(III) is known as a carcinogen and Sb(III) oxide has been shown to cause lung cancer.[4] Chronic exposure to antimony compounds has been associated with myocardial effects and heart trouble.[5,6] However the carcinogenic effect of antimony is not completely understood.[7,8]

The US Environmental Protection Agency (EPA) considers antimony and its compounds as priority pollutants and the Council of European Community established the maximum admissible concentration of antimony in surface and drinking water at 10 μg l^{-1}. The natural concentration of antimony in soils is low, its abundance in the earth crust is estimated at 0.2–0.3 mg kg^{-1} (ref. 1). However, these levels are increased by natural (*e.g.*, volcanic activity) or industrial sources. It has been estimated that 3.8×10^{10} g of antimony per year are released into the environment from industrial activities such as manufacturing of semiconductor products, the fabrication of glasses, dyestuffs ceramics and fire retardants. Mining activities, especially emissions from smelters, and fossil fuel combustion have also contributed to increase the antimony concentration in the surrounding zones where these activities are developed.[9,10]

The determination of total antimony in environmental

matrices needs the selection of appropriate analytical methodologies, with adequate protocols for samples digestion and the application of sensitive and selective analytical techniques. Inductively coupled plasma mass spectrometry (ICP-MS) or ICP coupled to optical emission spectrometry (ICP-OES) are techniques that exhibit good analytical performances (high sensitivity, low detection limits and accuracy) for determining antimony at ultra-trace levels.[11–14] However, in spite of the analytical performances of these techniques, the high cost of the instrumentation and its maintenance make their use very expensive for routine analysis. In addition, the necessary instrumentation to apply these techniques is not always available in all analytical laboratories. Other analytical techniques that are widely used for determining trace elements in all kinds of matrices are atomic absorption spectrometry coupled to hydride generation, with atomization in a flame heated quartz tube (HG-QT-AAS) and electrothermal atomic absorption spectrometry (ET-AAS). These techniques have been applied to the antimony determination, especially in water samples.[15–18] However, the application of these techniques to determine Sb in solid environmental samples, like soils and plants, has been less frequent.[19–21]

Recently, atomic fluorescence spectroscopy coupled to hydride generation (HG-AFS) has received special attention as a trace-elemental analytical technique, because it is not very expensive and it offers good analytical performance in terms of linearity, low detection limits and better selectivity. In addition, the measurements by HG-AFS have greater tolerance to matrix interferences. However, there are few applications of this technique to determine total antimony in solid environmental samples; it has been mainly applied to quantify antimony in liquid samples such as tap water, seawater and environmental air samples.[22]

The aim of this study was the development and optimization of analytical methodologies based on digestion procedures and the subsequent precise, reliable, and accurate determination of antimony in soils and vegetable samples using two sensitive atomic spectrometry techniques, based on different chemical–physical principles: electrothermal atomic absorption spectrometry (ET-AAS) and atomic fluorescence spectrometry coupled to stibine generation (HG-AFS). To reach this goal the different experimental parameters of each technique that influence the analytical signal obtained in the antimony determination were optimized, using synthetic solutions of Sb(III) and Sb(V), and solutions obtained after total digestion of natural soils and plant samples. The effect of the antimony oxidation state on the respective spectroscopic signals was also evaluated. The accuracy of these methods was assessed by analyzing two reference soils from NIST, San Joaquín soil (SRM 2709) and Montana soil (SRM 2710) and a reference vegetal material Virginia tobacco leaves (CTA-VTL-2). The optimized methodologies were then applied to the antimony determination in soils and alfalfa samples from the Valparaíso region in Chile.

Experimental procedures

Instrumentation

Antimony was atomized using an ATI-Unicam 939 QZ atomic absorption spectrometer equipped with Zeeman and deuterium arc background correctors, a graphite furnace GF90 and an auto-sampler. For this work, the deuterium device was used as background corrector; the Zeeman corrector was employed only for comparative purposes. The antimony boosted-discharge hollow cathode lamp (BDHCL) was operated at 8.5 mA. The wavelength was set to 217.6 nm and a slit width of 0.5 nm was used throughout. Antimony was atomized from the surface of the pyrolytic graphite tubes purchased from ATI-Unicam (Part no. 9423 393 95041) after stopping the flow gas. In the other steps, nitrogen was used as purge gas at a flow rate of 200 ml min^{-1}. 10 μl of chemical modifier (Ni(II) + $NH_4H_2PO_4$ + citric acid) were injected simultaneously with 20 μl of sample solution. All measurements were performed in the absorbance peak height mode.

In the HG-AFS measurements, a continuous flow system was used for the stibine generation. The hydride generation system consisted of a peristaltic pump, Teflon tubes of 0.5 mm internal diameter, pumping tubes and connectors. The stibine was generated using $NaBH_4$ in hydrochloric acid media and purged with argon. This system was coupled to a commercial dryer membrane (Perma Pure product, dryer Model MD-110-12 FP), joined to an Excalibur atomic fluorescence spectrometer (PS Analytical Ltd, Orpington, Kent, UK), equipped with an antimony boosted-discharge hollow cathode lamp (BDHCL). The atomisation flame was sustained with H_2 obtained in the stibine generation reaction between $NaBH_4$ and HCl, and carried to the place of atomization by argon.

Reagents

High quality water obtained from a Milli-Q system was used throughout. Stock solutions of 1000 mg l^{-1} Sb(III) and 1000 mg l^{-1} of Sb(V) were prepared by dissolving solid antimony potassium tartrate, $K(SbO)C_4H_4O_6H_2O$ (Aldrich, 99.95% purity) and potassium pyroantimonate, $KSb(OH)_6$ (Prolabo, for analysis) in water, respectively. Working solutions of Sb(III) and Sb(V) were prepared daily by appropriate dilution with water.

High purity nitric, hydrochloric, hydrofluoric and sulfuric acids (Suprapur®, Merck) were used for digestion of soils and plant samples. Diluted solutions of different concentrations were obtained from these acids.

Stock solutions of different chemical modifiers were prepared: a 7000 mg l^{-1} Ni(II) solution was obtained by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (Prolabo); the 500 mg l^{-1} Pd(II) was prepared by dissolving $Pd(NO_3)_2$ (Sigma) in concentrated nitric and hydrochloric acids, diluted with deionised water; a mixture of 10000 mg l^{-1} of citric acid (Merck, Darmstadt) and 50000 mg l^{-1} of ammonium dihydrogenphosphate ($NH_4H_2PO_4$, Carlo Erba) was prepared by dissolving the respective salts. Working modifier solutions were obtained by diluting or mixing these solutions.

Sodium borohydride solution (1.5% m/v) was prepared by dissolving $NaBH_4$ powder (Fluka Chemica) in 1% m/v NaOH solution (Merck, Darmstadt). This solution was prepared daily just before use or stored for up to three days at 4 °C.

Sb(V) was reduced to Sb(III) using a mixture of KI and ascorbic acid (Rectapur® Prolabo) or an L-cysteine solution (Merck).

The certified reference materials San Joaquín and Montana soils (NIST 2709 and NIST 2710, respectively) were obtained from the National Institute of Standards and Technology (Washington DC); and the Virginia tobacco leaves (CTA-VTL-2) was purchased from the CTA Polish Academy of Sciences.

Optimization for determining total antimony

The experimental parameters of each technique were optimized with Sb(III) standard solutions, a Chilean soil solution (La Greda) and a Chilean alfalfa solution (Campiche). A Sb(V) solution was also used in the optimization by HG-AFS.

To determine Sb by ET-AAS, 20 μl of a sample solution (standard solutions or soil and vegetable diluted samples) and 10 μl of matrix modifier were injected automatically into the graphite furnace. The parameters optimized were composition and quantity of the matrix modifier and the respective furnace programs. Nickel and palladium nitrates and mixtures of these reagents with citric acid and ammonium dihydrogenphosphate were assayed as chemical modifiers.

To determine Sb by HG-AFS, the stibine was generated in a continuous flow system. The Sb(III) standard solution (or the sample solution) was pumped simultaneously to the mixture chamber (at a rate of 6 ml min^{-1}) with HCl and $NaBH_4$ solution streams (pumping rates 3 ml min^{-1}). The sample or the Sb standard solutions were prepared in HCl medium of the same concentration as the HCl stream. The parameters optimized were HCl and $NaBH_4$ concentrations, carrier gas flow (Ar) and the lamp intensities. When the experiments were carried out with Sb(V) standard solutions (or digested samples solutions), Sb(V) was reduced to Sb(III) before the stibine generation by mixing an aliquot of these solutions with the reducing solution. The composition and concentrations of reagents, time and experimental conditions to carry out this reduction were optimized. When the reduction was made at high temperature, the solution was placed into a hot water bath (90 °C) and cooled to room temperature before the analysis.

The optimized spectrometric techniques were then applied to the total Sb determination in four Chilean soils and two Chilean alfalfa samples. These samples were collected from sites located near a smelter of copper ores, located in the Valparaíso region of Chile.

Samples digestion procedure

All Teflon PTFE and glass vessels, and polyethylene storage vessels, were soaked in 10% v/v nitric acid for several days to leach trace metals, rinsed with deionised water and stored in polyethylene bags. The digestion of soil and plant samples (or certified reference materials) was performed in a microwave oven operating system (Microdigest A300, Prolabo) with an energy output of 0–200 W (0–100% potency, respectively). Soil matrices were digested using HNO_3–HCl–HF acid mixtures and the vegetal matrices were digested with HNO_3–H_2SO_4–H_2O_2 or HNO_3–H_2O_2 mixtures. Approximately 1.0 g of dry soils or lyophilised alfalfa samples (Lyovac GT 2) were placed into the Teflon or glass microwave digestion vessels, respectively, then 6 ml of concentrated HNO_3 was added to each sample. These samples were left to stand overnight at room temperature. Soils and vegetable samples were digested using the optimized microwave programs detailed in Table 1.

After cooling to room temperature, the digested samples were filtered through paper filters (Advantec no. 2, pore size 5–10 μm), and washed with ultra-pure water. The soil solutions were made up to 50 ml and the alfalfa solutions to 25 ml with water. Blank samples were prepared simultaneously. These solution were stored in polyethylene bottles in a refrigerator at 4 °C until the analysis was carried out.

To determine total antimony by HG-AFS, an aliquot of the sample solutions was placed into a volumetric flask, and 5 ml of KI (15% m/v) + ascorbic acid (3% m/v) solution and 6 ml of concentrated HCl were added. The final volume was made up to 50 ml with water. The sample size to be used for analysis depends on the concentration of antimony.

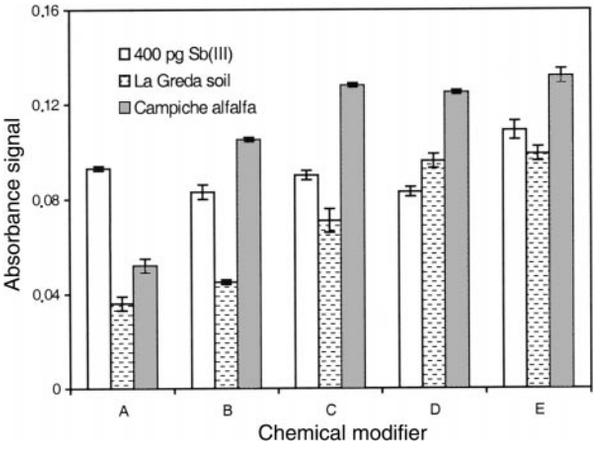

Fig. 1 Effect of different chemical modifiers on the absorbance signal of antimony for Sb(III) standard, soil and alfalfa solutions; (A) without chemical modifier, (B) 2 μg Ni(II), (C) 2 μg Pd(II), (D) 2 μg Ni(II) + 100 μg $NH_4H_2PO_4$ + 50 μg citric acid, (E) 2 μg Pd(II) + 100 μg $NH_4H_2PO_4$ + 50 μg citric acid.

Results and discussion

Optimization of parameters

The optimization of ET-AAS and HG-AFS parameters was carried out using the method of a one-factor-at-a-time-approach, in which each variable but one is held at the same level and the responses are evaluated at different levels of the factor being tested. Each variable is treated in turn, until the response is maximized.

Optimization of ET-AAS parameters

Chemical modifiers. The furnace program recommended by the equipment manufacturer was used for these experiments, performed without and with different matrix modifiers. The effects of single modifiers and modifier combinations of nickel and palladium nitrates with citric acid and ammonium dihydrogenphosphate (the modifier frequently used for Sb determination by ET-AAS[16,19–21,23]) were examined for 400 pg of Sb(III) standard solution (20 μl of 20 μg l^{-1} Sb) or 20 μl of soil and alfalfa samples solutions. As can be seen in Fig. 1, the presence of different matrix modifiers has similar effects on the Sb(III) signal. Pd was more effective than Ni for preventing the loss of Sb from soil. However the highest Sb signal for the soil sample solution was obtained when Ni(II) or Pd(II) was mixed

Table 1 Microwave oven programs used for the digestions of soils, and alfalfa samples for the antimony determination by HG-AFS or by ET-AAS

STEP	1	2	3	4	5	6	7	8	9	10
Soil samples										
Reagent	—	HCl	HF	—	HCl	H_2O	—	—	—	—
Volume/ml	—	5	10	—	3	20	—	—	—	—
Power/W	20	40	40	170	30	70	—	—	—	—
Time/min	5	5	5	20	10	10	—	—	—	—
Alfalfa samples by HG-AFS										
Reagent	—	H_2SO_4	—	—	—	H_2O_2	—	H_2O	—	—
Volume/ml	—	4	—	—	—	4	—	10	—	—
Power/W	20	90	110	130	150	130	150	120	—	—
Time/min	2	4	2	4	6	2	2	2	—	—
Alfalfa samples by ET-AAS										
Reagent	HNO_3	—	—	—	—	H_2O_2	—	H_2O_2	—	H_2O
Volume/ml	7	—	—	—	—	5	—	3	—	10
Power/W	20	90	110	130	150	130	150	130	150	110
Time/min	1	2	1	2	2	1	2	2	1	2

with $NH_4H_2PO_4$. This fact could be explained by taking into account that all soil solutions contain chloride and this species can complex antimony producing compounds that can be lost during the ashing step. The presence of $NH_4H_2PO_4$ may have two different effects; NH_4^+ ions form NH_4Cl with chloride, a compound that is easily eliminated in the ashing step, thus preventing the loss of Sb as chloride complexes. On the other hand, in spite of the slight increase in the background signal, the presence of phosphate in the chemical modifier produces a sharp peak in the atomization step, where the height peak is not affected by the background increase. The phosphate seems to stabilise Sb, forming stable compounds. Furthermore, citric acid can help to eliminate the interference produced by some transition metals, by lowering the atomization temperature. This effect has been observed with ascorbic and oxalic acids.[23] Peak height absorbance measurements were found to be adequate in all cases (for 100 pg Sb the standard deviation was 4.7%). The measurement of integrated absorbance was less precise (the standard deviation in this mode was always higher than 10%). These effects were similar when nickel was substituted by palladium in the chemical modifier mixture, but we chose the nickel mixture as chemical modifier due to its lower cost. A similar behaviour was observed for the Sb signal from the alfalfa solution.

As the presence of $NH_4H_2PO_4$ had an important effect on the Sb absorbance signal, the influence of different quantities of this compound in the chemical modifier was investigated (Fig. 2). A 100 μg amount of $NH_4H_2PO_4$ (10 μl of 10 g l^{-1}) was chosen as the optimal quantity to determine Sb in soil and plant samples by ET-AAS.

Furnace program. The temperatures and times of the ashing and atomization steps were optimized with the Sb solutions previously described. The effect of the ashing and the atomization temperatures on the Sb absorbance peak height are presented in Fig. 3. The optimized furnace program for Sb determination in soils and plant samples is given in Table 2. These conditions were considered to be better for routine analysis, because lower ashing temperatures and times are less destructive to the graphite tube.

Optimization of HG-AFS parameters

All chemical and physical parameters that affect the stibine generation and the AF signal were optimized using 1 μg l^{-1} of Sb(III), 1 μg l^{-1} of Sb(V) and soil and plant solutions. Before the stibine generation, the reduction of Sb(V) to Sb(III) was carried out using KI–ascorbic acid; however this reduction was also optimized for the real samples.

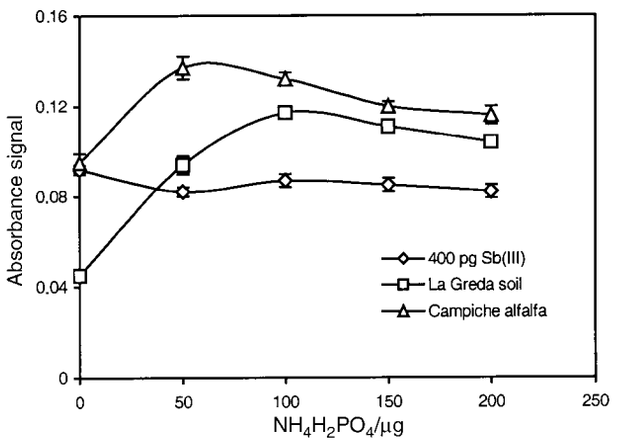

Fig. 2 Effect of $NH_4H_2PO_4$ amounts in the chemical modifier mixture 2 μg Ni(II) + 50 μg citric acid on the antimony absorbance signal for Sb(III) standard, soil and alfalfa solutions.

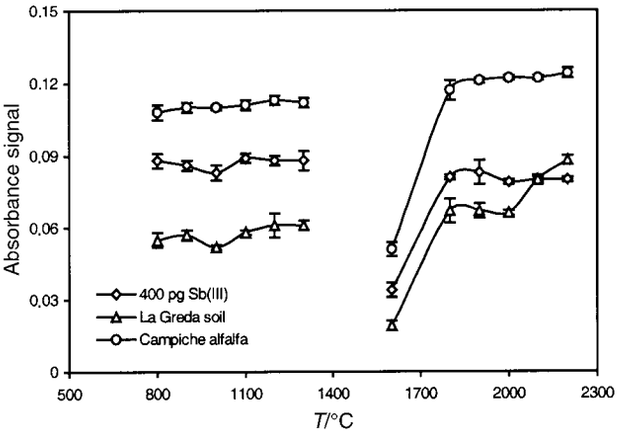

Fig. 3 Effect of the ashing and atomization temperatures on the antimony absorbance signal of Sb(III) standard, soil and alfalfa solutions.

Table 2 Furnace program used for determining antimony in soils and alfalfa samples by ET-AAS

Step	Temperature/ °C	Ramp/ °C s^{-1}	Duration/ s	N_2 Gas flow/l min^{-1}	Function
1	90	—	15	2	Dry
2	120	10	5	2	Dry/ramp
3	500	100	0	2	Ash/ramp
4	1100	250	6	2	Ash/hold
5	2100	—	3	0	Atom/hold
6	2500	—	2	0	Clean

Antimony BDHCL intensities. The excitation source intensities were optimized with the criterion that the maximum signal-to-noise ratio can be obtained without reducing the lifetime of the lamp. Thus, at a recommended constant primary intensity of 15 mA, the boosted intensity was varied between 10 and 25 mA, and then the primary intensity was varied in the same range at a constant boosted intensity of 20 mA. The boosted intensities had no effect on the signal-to-noise ratio, however maximal ratios were obtained for a primary intensity higher than 20 mA. The retained values for both intensities were 20 mA. The results obtained with Sb(V) solutions were similar.

Carrier gas. The carrier gas flow rate was optimized with the same criterion. The optimal carrier gas flow rate was 250 ml min^{-1}, independent of the Sb oxidation state.

Sodium borohydride and HCl concentrations. The experiments were carried out with 1 μg l^{-1} Sb(V) and 1 μg l^{-1} Sb(III) solutions. The $NaBH_4$ concentration was optimized using the same criterion for the maximum signal-to-noise ratio. The $NaBH_4$ concentration was varied within the range 1–3% m/v using 2 mol dm^{-3} HCl in the sample and carrier solutions. A 1.5% $NaBH_4$ concentration produced the highest signal-to-noise ratio. Higher concentrations of $NaBH_4$ did not improve this ratio and the AF signal was practically constant while the noise was high [Fig. 4(A)]. The effect of HCl concentration on stibine generation was also investigated by measuring the AF signal for Sb(III) and Sb(V) solutions [Fig. 4(B)]. It was found that the acid concentration effect is not appreciable; 1.5 mol dm^{-3} HCl concentration was retained for carrier and sample solutions.

Antimony(V) reduction. Hydride generation for the antimony determination requires Sb to be present in the 3+ oxidation state for optimum production of stibine. It can be seen in Fig. 5 that, under the experimental reducing conditions, Sb(V) is only

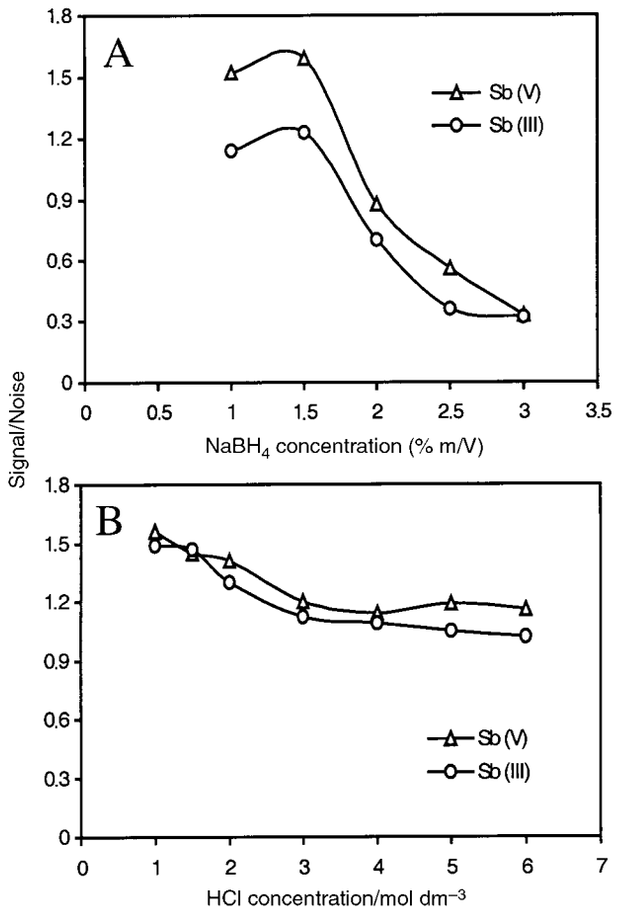

Fig. 4 Effect of $NaBH_4$ (A) and HCl (B) concentrations on the fluorescence signal of 1 $\mu g\,l^{-1}$ Sb(III) and 1 $\mu g\,l^{-1}$ Sb(V). The experi mental conditions were: carrier gas flow 250 ml min^{-1}, currents lamp 20 mA and reduction of Sb(V) using KI–ascorbic acid.

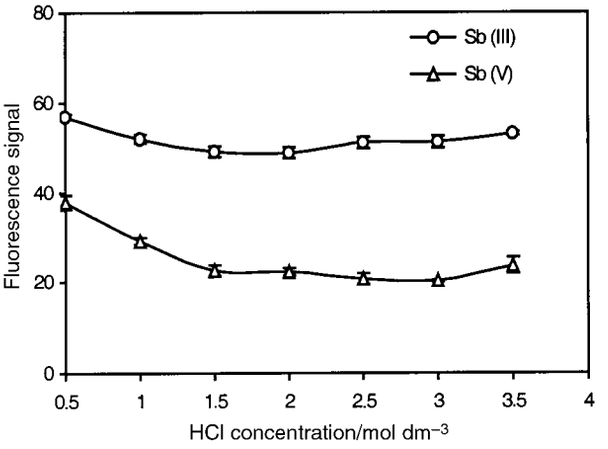

Fig. 5 Effect of the HCl concentration in the sample solution on the fluorescence signal of 1 $\mu g\,l^{-1}$ Sb(III) and 1 $\mu g\,l^{-1}$ Sb(V) without reduction by KI.

partially reduced by sodium borohydride. Independent of the HCl concentration used as the medium for this reaction, the Sb(V) AF signals yield approximately 50% of the respective Sb(III) signal. For this reason, the chemical reduction of Sb(V) to Sb(III) is unavoidable for the Sb(V) determination by hydride generation. In order to reach this chemical reduction, different methods using KI or L-cysteine as reducing agent have been proposed.[22–26] In this work, the experimental conditions to carry out the Sb(V) reduction by KI or L-cysteine were optimized, because Sb(V) is the specie obtained when the solid matrices are digested by acid–oxidant mixtures. The assays were performed with reference material solutions, using 1.5 mol dm^{-3} HCl as reaction medium. The AF signals of these solutions were compared to the respective AF Sb(III) signal. The experimental conditions assayed are summarized in Table 3. In Fig. 6 are presented the Sb concentrations found for the reference material used (San Joaquin soil, with a certified concentration of 7.9 ± 0.6 mg Sb kg^{-1}). These results permit the conclusion that the chemical reduction, in this kind of matrix, can be carried out using KI or L-cysteine, by heating the sample solution in a microwave oven for at least 3 min at 120 W or in a water bath at 90 °C for 40 min. The Sb recovery under these conditions was quantitative.

In order to demonstrate if there was a kinetic hindrance for the experiments with KI 1.5% m/v, the reaction time at room temperature was tested between 10 min and 6 days. It can be seen (Fig. 7) that Sb(V) reduction from alfalfa and standard solutions is reached after very short times. For soil solution, Sb(V) was quantitatively reduced only after an elapsed time of 3 days. This reaction can be speeded up with a hot water bath or in a microwave oven. Similar results have been reported by Petrick and Krivan,[25] who found that the Sb(V) reduction to Sb(III) in the presence of hydrofluoric acid by KI or by KI + ascorbic acid mixture was not possible at room temperature. To perform this reduction, it is necessary to heat the solution to 80 °C.

Summarizing, the final retained conditions for determining Sb in soils and plant samples were: primary and boosted BDHCL intensities 20 mA; HCl concentration 1.5 mol dm^{-3} (flow rate 6 ml min^{-1}); $NaBH_4$ concentration 1.5% m/v (flow rate 3 ml min^{-1}); and argon as carrier gas, at a flow rate of 250 ml min^{-1}. The sample solutions were reduced by KI 1.5% m/v + ascorbic acid 0.3% m/v in HCl 1.5 mol dm^{-3} at 90 °C in a water bath for 40 min for soil solutions, and at room temperature for 30 min for plant solutions.

Analytical quality control of the proposed methodologies

The accuracy and precision of the developed analytical methodologies for soils and vegetal samples (digestion and analytical techniques) were assessed by analyzing different certified reference materials with certified total antimony

Table 3 Experimental conditions assayed for Sb(V) reduction in the CRM San Joaquín soil solution (digestion made with HNO_3–HCl–HF)

		Concentration of reagents in the sample solution			
Method	Treatment	KI–ascorbic acid (% m/v)	L-Cysteine (% m/v)	HCl/mol dm^{-3}	H_3BO_3/mol dm^{-3}
1	30 min, room temperature	1.5/0.3	—	1.5	0.08
2	2 min microwave, 120 W	1.5/0.3	—	1.5	0.08
3	3 min microwave, 120 W	1.5/0.3	—	1.5	0.08
4	3 min microwave, 120 W	1.5/0.3	—	1.5	—
5	40 min, water bath 90 °C	1.5/0.3	—	1.5	—
6	30 min, room temperature	—	1	1.5	0.08
7	40 min, water bath 90 °C	—	1	1.5	0.08
8	3 min, microwave, 120 W	—	1	1.5	—

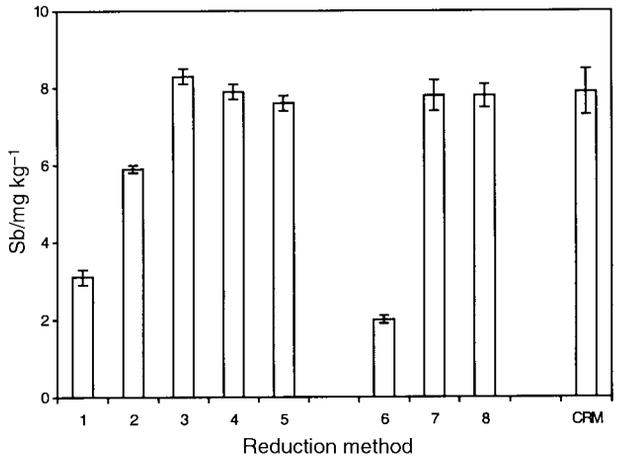

Fig. 6 Antimony concentration determined for the CRM San Joaquín soil (digested with HNO_3–HCl–HF acid mixture). Sb(v) reduced in the experimental conditions summarized in Table 3.

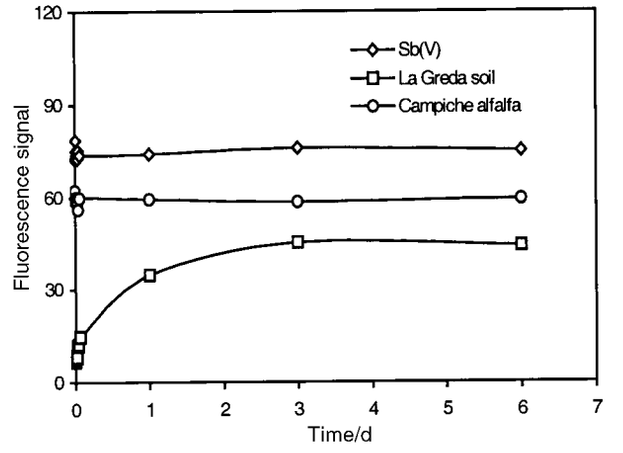

Fig. 7 Effect of the Sb(v) reduction time on the fluorescence signal for 1 μg l^{-1} Sb(v) standard solution and soil and alfalfa solutions (reduction performed at room temperature).

concentrations and matrices similar to the environmental samples to be analyzed. As can be seen in Table 4 the results obtained for the reference materials (San Joaquín and Montana soils and the Virginia Tobacco Leaves) are in good agreement with the certified values.

Antimony determination in environmental samples

The proposed methodologies based on ET-AAS and HG-AFS techniques were applied to determine total antimony in four Chilean soils and two Chilean alfalfa samples. The matrix effects on the ET-AAS and HG-AFS analytical signals were evaluated by comparing the conventional calibration slopes with the standard additions slopes. Significant matrix effects were detected for soils and alfalfa samples in the antimony determination by the ET-AAS method, whereas no significant differences were found between the slopes obtained by both calibration procedures when using HG-AFS. Therefore, to determine total antimony in all samples by this analytical technique, the conventional calibration mode was used. The antimony concentrations found in the soils and plant samples analyzed are given in Table 5. All Sb concentration values are higher than those reported as average concentrations for soils (1 mg kg^{-1}) and herbaceous vegetables (0.2 mg kg^{-1}).[27] These data possibly reflect the degree of contamination of the sampling sites. Samples were collected in zones affected by the emissions of mining complexes of copper ores. The antimony determination by ET-AAS in alfalfa samples with low antimony content and/or digested with the sulfuric acid mixture was not possible, owing to the high matrix effect produced in the atomization step, but no interference was detected in these samples when antimony was determined by HG-AFS. This shows that the sample digestion procedure must be selected by taking into account the analytical technique to be applied.

Table 4 Concentration of antimony (mg kg^{-1}) in the CRM analyzed by ET-AAS and HG-AFS methods ($n=4$)

Reference material	Certified values	Experimental values ETAAS	Experimental values HG-AFS
San Joaquin soil (NIST 2709)	7.9±0.6	8.0±0.3	7.9±0.1
Montana soil (NIST 2710)	38±4	38±2	38±2
Virginia tobacco leaves (CTA-VTL-2)	312±25[a]	377±28[a]	291±8[a]

[a]Measured in μg kg^{-1}.

Table 5 Antimony concentrations in soils and alfalfa from different sites of Valparaíso region, Chile ($n=4$)

Sample	Site	Sb concentrations ET-AAS	Sb concentrations HG-AFS
Soils/mg kg^{-1}	La Greda	6.7±0.3	6.8±0.4
	Puchuncaví	5.7±0.4	5.5±0.1
	Campiche	12±1	13±1
	Maitenes	6.6±0.4	6.4±0.5
Alfalfa/μg kg^{-1}	La Greda	—	393±30
	Campiche	1691±70	1667±88

Table 6 Comparative analytical characteristic of ETAAS and HG-AFS methods for Sb(III)

Analytical characteristic	ET-AAS[a]	HG-AFS
Linear range	0–50 μg l^{-1}	0–250 μg l^{-1}
Sensitivity	0.0045 μA l g^{-1} (22 pg characteristic mass)	0.021 l μg^{-1}
Detection limit	0.45 μg l^{-1} (9 pg)	0.08 μg l^{-1}
Precision[b]	4.7% for 100 pg	4.3% for 0.5 μg l^{-1}

[a]20 μl solutions injected. [b]Expressed in terms of variation coefficient.

Analytical characteristics of the methods

After the proposed methods were successfully applied to determining total antimony in solid matrices of environmental interest, the analytical characteristics of both techniques were established and compared. The detection limit was calculated as $LOD = (the\ blank\ signals\ mean + 3\sigma)/m$ where σ is the standard deviation of 10 measurements of a blank solution and m is the slope of the calibration graphs. The precision (expressed in terms of variation coefficient) was determined for six Sb(III) determinations and the sensitivity was calculated from the slope of each calibration graph. In Table 6 are summarized the analytical characteristics of both the ET-AAS and HG-AFS methods.

Conclusions

The proposed methods allow the determination of antimony in environmental solid samples like soils and plants. The microwave digestion of soils and plant by mixtures of HNO_3–HCl–HF and HNO_3–H_2O_2, respectively, are favorable for trace antimony determination by HG-AFS and ET-AAS;

the digestion of plant samples by HNO_3–H_2SO_4–H_2O_2 mixtures is only suitable for antimony determination by HG-AFS. The combination of stibine generation coupled with atomic fluorescence spectrometry provides a relatively rapid, simple and very sensitive method for the determination of total antimony in soils and plants samples. Since the AF analytical signal is dependent on the antimony oxidation state, a chemical reduction of Sb(v) species present in the digested samples, prior to the hydride generation, must be carried out. For this purpose the use of a KI and ascorbic acid mixture in HCl medium, at room temperature or heating at 90 °C in a water bath, is adequate. This technique is less sensitive to interfering species than ET-AAS, permitting the use of a simple calibration mode to quantify antimony.

For antimony determination by ET-AAS the use of a chemical modifier is unavoidable. Similar amounts of nickel or palladium were effective in stabilizing the antimony species present in soils and plant digested samples; however the best analytical signals were obtained using mixtures of these metals with $NH_4H_2PO_4$ + citric acid. Due to the matrix interference the quantification of antimony must be carried out by the standard additions method.

The optimized digestion and determination procedures allowed the accurate analysis by both methods of antimony in soils and vegetable standard reference materials and in similar environmental matrices. The HG-AFS method shows exceptional potential and there are many reasons to be optimistic regarding the use of this technique in routine analysis of a variety of environmental samples, and in the determination of antimony and other hydride forming elements.

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