

# Redox speciation analysis of antimony in soil extracts by hydride generation atomic fluorescence spectrometry

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## Abstract

A sensitive atomic spectrometric method for the redox speciation analysis of antimony in soils is described. The method is based on the selective generation of stibine from Sb(III) in a continuous flow system using atomic fluorescence spectrometry for detection. Sb(V) is masked by citric or oxalic acid in HCl medium. The procedure was optimized with synthetic solutions of Sb(III) and Sb(V). The effect of carboxylic acid and HCl concentration on the recovery of Sb(III) and Sb(V) species from standard solutions, and on the fluorescence signal were studied. Both species were extracted from soil with H<sub>2</sub>O, 0.05 mol l<sup>-1</sup> EDTA and 0.25 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Since the soil samples were collected from sites impacted by copper mining activities, the effect of Cu<sup>2+</sup> on the determination of antimony in synthetic solutions and soil extracts was studied. Cu<sup>2+</sup> decreased the Sb(III) signal, but had no effect on the total antimony determination. Therefore, the selective determination of Sb(III) was carried out in citric acid–HCl medium, using the analyte addition technique. Total antimony in soil extracts was determined using the standard calibration technique after reducing Sb(V) to Sb(III) at room temperature with KI–ascorbic acid. The Sb(V) concentration was calculated from the difference between total antimony and Sb(III). The limits of detection (PS Analytical, Excalibur Millennium model) were 17 and 10 ng l<sup>-1</sup> for Sb(III) and total antimony, respectively, and the R.S.D. at the 0.5-μg l<sup>-1</sup> level were 2.5 and 2.4%, respectively. The total antimony concentration of soils is in the mg kg<sup>-1</sup> range; the Sb recovery from the different soils by the extracting solutions was between less than 0.02% and approximately 10%. Similar recoveries were obtained using EDTA and sulfuric acid solutions. Sb(V) was found to be the main antimony species extracted from soils.

*Keywords:* Antimony; Speciation analysis; Soil extracts; Hydride generation atomic fluorescence spectrometry

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## 1. Introduction

Antimony has chemical and toxic properties similar to those of arsenic; however, the carcino-

genic effect of antimony is not completely understood [1]. Compared to arsenic, this element has received little environmental attention. There are only a few of studies in soils, sediments and biological materials. The natural concentration of antimony in soils is <1 mg kg<sup>-1</sup> [2]. However,

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this level might be substantially increased due to inputs from natural or industrial sources [3]. The US Environmental Protection Agency listed antimony as one of the pollutants of concern. The toxicity of antimony and its environmental cycle depend on its chemical form. Antimony is found in two oxidation states, Sb(III) and Sb(V), in inorganic and organic components in environmental samples. It has also been realized that determining the total concentration in a given sample for estimating its physiological or environmental risks is not enough, and the importance of speciation analysis of antimony has been recognized.

Speciation studies in soils need the selection of appropriate analytical methods. Inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES) coupled with high performance liquid chromatography (HPLC) have been used for the speciation analysis of antimony in synthetic water samples and soil extracts [4–8]. However, the high cost of instrumentation and its maintenance make their use expensive for routine analysis.

Another frequently applied technique to determine trace levels of antimony is hydride generation atomic absorption spectrometry (HG-AAS) [6,9–11] or hydride generation atomic fluorescence spectrometry (HG-AFS) [12–17]. This last technique is not very expensive and it offers good analytical performance in terms of linearity and limits of detection. Thompson [12] was the first to describe a dispersive atomic fluorescence system to determine hydride-forming elements (As, Se, Sb and Te) with detection limits approximately  $0.1 \mu\text{g l}^{-1}$ . Guo et al. [14] using a non-dispersive AFS system obtained similar performance. Hydride generation techniques have been applied to determine antimony in samples such as tap water, seawater, airborne particles, sediment and soils [15,17–19]. Controlling the borohydride reduction stage, HG permits discrimination between Sb(III) and Sb(V). Several authors have used the pH dependence of stibine generation for the separate determination of antimony species [20–26]. The same effect can be achieved under a highly acidic condition using carboxylic acids to suppress hydride formation from Sb(V), so that

Sb(III) can be determined selectively [9,11,27]. Mohammad et al. [9] proposed citric acid (12% m/v) for this procedure. Guy et al. [28] demonstrated the association of Sb(V) with three  $\alpha$ -hydroxy acids (citric, mandelic and malic) by NMR, ESI-MS and HPLC–ICP-OES. Sb(V) is quantitatively complexed with citric acid in a 1:1 molar ratio. However, the selection of appropriate conditions for the selective generation of stibine from Sb(III) is not an easy task. The hydride generation efficiency depends on the experimental conditions and the matrix composition. The technique suffers from interferences caused by metallic ions, such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  [29–31], and hydrofluoric acid concentrations as low as  $0.02 \text{ mol l}^{-1}$  were found to suppress the stibine generation from Sb(V), but not that from Sb(III) [32–34].

Chile is a producer and exporter of copper, molybdenum and other metals and ores. But copper mining activities are a constant source of environmental contamination. The objective of the present work was to assess the antimony toxicity and its accessibility to plants from soils contaminated by mining activities. A method for redox speciation analysis of antimony in soil extracts, based on the selective generation of stibine from Sb(III) using HG-AFS is described. The stibine generation from Sb(V) is avoided by complexation with citric and oxalic acids in HCl medium. The effect of these reagents on the fluorescence signal from synthetic solutions of Sb(III) and Sb(V) and from soil extracts was studied. Since soil samples were collected from sites contaminated by copper mining, the  $\text{Cu}^{2+}$  concentration effect on the fluorescence signal, in the presence of citric acid, was also studied. The approach was applied for speciation analysis of antimony in  $\text{H}_2\text{O}$ , EDTA and  $\text{H}_2\text{SO}_4$  soil extracts.

## 2. Experimental

### 2.1. Instrumentation

For the HG-AFS antimony determinations, PSA Analytical (Orpington, Kent, UK) Excalibur model (10033) or Millennium model (10055) atomic fluorescence spectrometers, were used. These

instruments have a continuous flow system for hydride generation coupled to a commercial dryer membrane (Perma Pure product, dryer model MD-110-12 FP), which is joined to the fluorescence spectrometer. The stibine was purged to the atomization flame by an argon flow; the flame is sustained with  $H_2$  produced in the hydride generation reaction between  $NaBH_4$  and  $HCl$ . Both instruments are equipped with an antimony boosted discharge hollow cathode lamp (BDHCL), Photon PTY Ltd (Victoria, Australia), operated at 15–20 mA.

## 2.2. Reagents

High purity water with a resistivity of 18  $M\Omega$  cm, obtained from a NANOpure ultrapure water system (Barnstead, Dubuque, IA) was used for all dilutions. Stock solutions of 1000  $mg\ l^{-1}$  Sb(III) and 1000  $mg\ l^{-1}$  of Sb(V) were prepared dissolving solid potassium antimony tartrate  $K(SbO)C_4H_4O_6 \cdot H_2O$  (Aldrich, 99.95% purity) and potassium pyroantimonate  $KSb(OH)_6$  (Prolabo, for analysis) in 1% m/v ascorbic acid (Merck) and water, respectively, and stored at 4 °C in polyethylene bottles. Working solutions of Sb(III) and Sb(V) were prepared daily by appropriate dilution with 0.1% m/v ascorbic acid and water, respectively.  $Cu^{2+}$  solutions were prepared from a standard solution of 1000  $mg\ l^{-1}$  (Titrisol® Merck).

High purity nitric, hydrochloric, hydrofluoric and sulfuric acids (Suprapur®, Merck) were used for digestion of soils.

Sodium borohydride solution was prepared dissolving  $NaBH_4$  powder (Merck) in  $NaOH$  solution (Merck). This solution was prepared daily just before use or stored for up to 3 days at 4 °C.

Citric acid monohydrate or oxalic acid dihydrate (Merck, pro analysis) were used to mask Sb(V). A mixture of KI and ascorbic acid (Merck) was used in the pre-reduction of Sb(V) to Sb(III).

The mild extractions of antimony from soils were carried out with deionized water, 0.25  $mol\ l^{-1}$   $H_2SO_4$  and 0.05  $mol\ l^{-1}$  EDTA (di-sodium salt of ethylenediaminetetraacetic acid, Merck, pro analysis), pH 7.0.

## 2.3. Samples

Soil samples were collected at Puchuncaví valley, an agricultural zone (located at the north of Valparaíso city) that receives the impact of the industrial complex 'Las Ventanas', where a smelter and electro-refinery plant of Cu ore, as well as a coal-fired thermoelectric power plant are located.

## 2.4. Procedures

### 2.4.1. Digestion and determination of total Sb in soil

The sample digestion and the experimental parameters to determine total antimony in soil by HG-AFS has been described in detail elsewhere [35].

### 2.4.2. Soil extraction procedure

Aliquots of 1.0 g of dry soil were accurately weighed into 50-ml polypropylene vessels. The extraction solutions (10 ml of  $H_2O$ , 20 ml 0.25  $mol\ l^{-1}$   $H_2SO_4$  or 10 ml of 0.05  $mol\ l^{-1}$  EDTA, pH 7.0) were added and the vessels were covered and shaken at room temperature in a horizontal shaker (Junior orbit shaker, Labline instrument, Melrose Park, IL) at 150 rpm for 24, 1 and 2 h for  $H_2O$ , EDTA and  $H_2SO_4$ , respectively. The slurries were centrifuged (Kubota 1720, Kubota Corporation, Tokyo, Japan), at 10 °C for 30 min at 4000 rpm. The supernatant was decanted off.

### 2.4.3. Redox speciation analysis of antimony

The determination of Sb(III) and Sb(V) in the synthetic solutions and in the soil extracts was carried out in two steps. For the selective determination of Sb(III), an aliquot of the soil extract (1–5 ml) was placed into a 25-ml volumetric flask, mixed with 5 ml of 20% m/v citric acid and 3 ml of concentrated  $HCl$ , and completed to volume with water. The determination of Sb(III) concentrations in soil extracts was carried out using the analyte addition technique. For the determination of total antimony, a volume of 0.2–1.0 ml of the extracts (depending on the total Sb concentration) was mixed in a 25-ml volumetric flask with 2.5 ml of 15% m/v KI+3% m/v ascorbic acid and 3 ml of concentrated  $HCl$  and

Table 1

Operating conditions employed to determine antimony by HG-AFS, with the PS Analytical Excalibur and Excalibur Millennium models

Parameter	Excalibur model	Excalibur Millennium model
Sb BDHCL current (mA)		
Primary	20	17.5
Boosted	20	15
Concentrations		
HCl ( $\text{mol l}^{-1}$ )	1.5	1.5
$\text{NaBH}_4$ (% m/v)	1.5	0.7
Flow rates ( $\text{ml min}^{-1}$ )		
HCl	6	9
$\text{NaBH}_4$	6	3
Sample	6	9
Carrier gas/argon	250	300
Drier	600	2500
Instrument conditions		
Delay period (s)	10	10
Analysis period (s)	30	30
Memory period (s)	40	40
Filter <sup>a</sup>	32	32
Amplification range <sup>b</sup>	10	100

<sup>a</sup> Sets the smoothness of the signal by box car integration. The higher the filter number the smoother the signal. Available filters 1–64.

<sup>b</sup> Available ranges are 1, 10, 100 and 1000.

then completed to volume with deionized water. The mixture was left to stand at room temperature for 30 min to ensure complete reduction of Sb(V) to Sb(III) before the stibine generation. The determination of total antimony was performed by the standard calibration technique, using the experimental conditions in Table 1, which have been described in detail elsewhere [35]. The pre-reduction of Sb(V) to Sb(III) by KI/ascorbic acid in the soil extracts was quantitative at room temperature, whereas the digested soil solutions had to be heated at 90 °C, 40 min in a water bath or in a microwave oven. This different behavior might be due to the presence of residual concentrations of HF in the acid digested soil solutions [32–34]. The concentration of Sb(V) was calculated from the difference between the total concentration and the concentration of Sb(III).

### 3. Results and discussion

#### 3.1. Optimization of the redox speciation analysis of antimony

The determination of the redox species of antimony by HG-AFS in soil extracts was based on the selective generation of stibine from Sb(III) by reaction with borohydride in citric acid–HCl medium. As was described elsewhere [35], the Sb(V) fluorescence signal yield was approximately 50% of the respective Sb(III) signal in HCl medium, whereby the latter was practically independent of the HCl concentration. Similar results have been described by Mohammad et al. [9] in the speciation analysis of antimony in water by HG-AAS.

Two carboxylic acids, citric acid ( $\alpha$ -hydroxy acid) and oxalic acid, both in HCl medium, were investigated as masking agents to inhibit stibine generation from Sb(V), making possible the selective determination of Sb(III). Citric acid has been proposed for the speciation analysis of antimony and arsenic by HG-AAS, with or without pH control [9,22], and it has been shown that Sb(V) was quantitatively complexed by citric acid in highly acidic medium [28]. Oxalic acid has not yet been described as a masking agent for Sb(V) to determine Sb(III) selectively in acid medium.

The effect of citric and oxalic acid concentration (in 2.5  $\text{mol l}^{-1}$  HCl) on the fluorescence signal obtained after hydride generation from Sb(III) and Sb(V) is shown in Fig. 1. Both acids at concentrations greater than 3% m/v effectively suppressed the hydride generation from Sb(V), suggesting stable complexation of this species by both masking agents. The fluorescence signal from Sb(III) remained practically constant, independent of the citric or oxalic acid concentration. Thus, an effective discrimination between Sb(III) and Sb(V) could be obtained, and a selective determination of Sb(III) could be achieved by using either acid. Similar results have been obtained by Mohammad et al. [9], who used 12% citric acid in 3- $\text{mol l}^{-1}$  HCl medium, whereas in our work the citric acid concentration chosen was only 4% (m/v). However, the citric acid/antimony molar ratio employed in our work was approximately 70-fold greater than that employed by Mohammad et al.

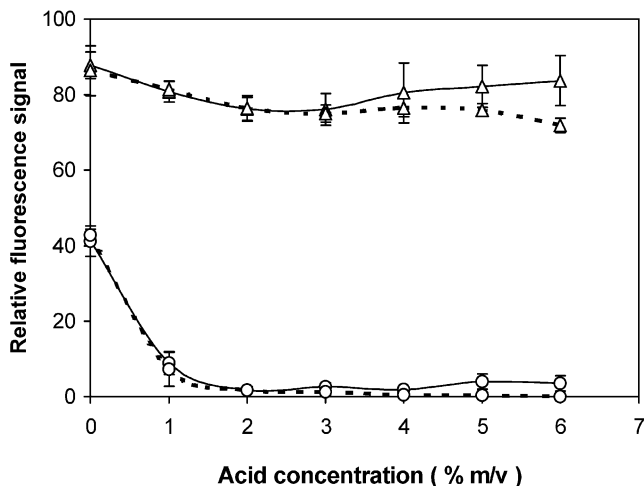


Fig. 1. Effect of (—) citric and (----) oxalic acid concentration on the fluorescence signal from ( $\Delta$ )  $2 \mu\text{g l}^{-1}$  Sb(III) and ( $\circ$ )  $2 \mu\text{g l}^{-1}$  Sb(V) in  $2.5\text{-mol l}^{-1}$  HCl medium. (Results expressed as mean  $\pm$  S.D.,  $n=4$ .)

( $5 \times 10^7$  compared to  $7 \times 10^5$ ), as the Sb concentration levels employed in this work ranged between  $0.1$  and  $1 \mu\text{g l}^{-1}$  due to the greater sensitivity of HG-AFS compared to HG-AAS.

The effect of HCl concentration on the fluorescence signal in the presence of 4% m/v citric or oxalic acid was also investigated. Fig. 2 shows that the HCl concentration had essentially no effect on the yield of hydride generation from Sb(III). For Sb(V), no AF signal at all was obtained for HCl concentrations between  $0.5$  and  $2 \text{ mol l}^{-1}$ , but a small signal was obtained at higher HCl concentrations. This is probably due to a competition in Sb(V) complexation between the carboxylic acid and the chloride ions from HCl. Stable complexes between Sb(V) and  $\text{Cl}^-$  ( $\text{SbCl}_6^-$  or  $\text{Sb}(\text{OH})_x\text{Cl}_y^{+(5-x-y)}$ ) have been described in aqueous media [36].

The effect of increasing Sb(V) concentrations on the fluorescence signal obtained from  $0.5 \mu\text{g l}^{-1}$  Sb(III), in 4, 8 and 12% (m/v) citric and 4% oxalic acid in  $1.5\text{-mol l}^{-1}$  HCl medium is shown in Table 2; the yield of hydride formation from Sb(III) remained practically constant, even when the Sb(V)/Sb(III) ratio in the solution was as high as 50. The results with 8 and 12% (m/v)

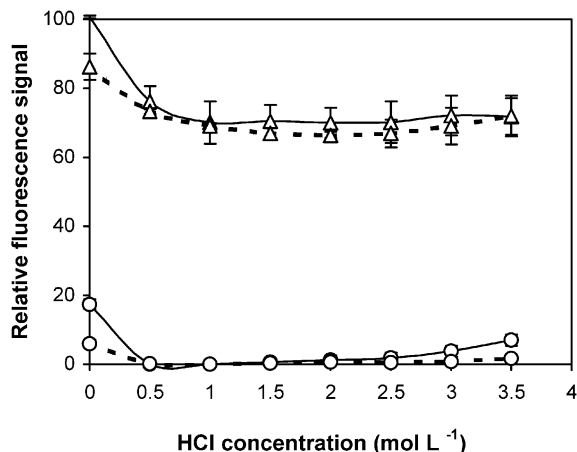


Fig. 2. Effect of HCl concentration on the fluorescence signal from ( $\Delta$ )  $2 \mu\text{g l}^{-1}$  Sb(III) and ( $\circ$ )  $2 \mu\text{g l}^{-1}$  Sb(V) in (—) 4% m/v citric and (----) 4% m/v oxalic acid medium. (Results expressed as mean  $\pm$  S.D.,  $n=4$ .)

citric acid were statistically similar to those obtained with 4% (m/v) citric or oxalic acid, suggesting that the latter concentration is sufficient to achieve quantitative complexation of Sb(V).

Because of the similar results obtained with the two acids, 4% (m/v) citric acid in  $1.5\text{-mol l}^{-1}$  HCl medium was chosen for the selective determination of Sb(III). Recovery studies from five different synthetic mixtures, containing different ratios of Sb(V)/Sb(III) were performed, applying the above method; total antimony was determined using the experimental conditions detailed in Table 1, and Sb(V) was calculated from the difference.

Table 2

Effect of Sb(V) concentration on the fluorescence signal obtained for  $0.5 \mu\text{g l}^{-1}$  Sb(III), containing different concentrations of oxalic or citric acid, in  $1.5 \text{ mol l}^{-1}$  HCl

Sb(V)/Sb(III) ratio	Citric acid (% m/v)			Oxalic acid 4% (m/v)
	4	8	12	
0	$628 \pm 11$	$679 \pm 16$	$690 \pm 10$	$491 \pm 14$
1	$680 \pm 23$	$668 \pm 37$	$679 \pm 47$	$507 \pm 20$
5	$632 \pm 10$	$656 \pm 10$	$688 \pm 21$	$486 \pm 10$
10	$685 \pm 15$	$714 \pm 10$	$687 \pm 22$	$530 \pm 10$
20	$691 \pm 26$	$752 \pm 10$	$681 \pm 12$	$537 \pm 11$
50	$753 \pm 28$	$723 \pm 40$	$741 \pm 16$	$568 \pm 19$

Results expressed as mean  $\pm$  S.D.,  $n=4$ .

Table 3  
Recovery of Sb(III) and Sb(V) from synthetic solution mixtures

Prepared concentration ( $\mu\text{g l}^{-1}$ )		Measured concentration ( $\mu\text{g l}^{-1}$ )		Recovery (%)	
Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)
0.25	1.75	$0.27 \pm 0.02$	$1.71 \pm 0.07$	$108 \pm 7$	$98 \pm 4$
0.50	1.50	$0.50 \pm 0.03$	$1.45 \pm 0.06$	$101 \pm 5$	$97 \pm 4$
1.00	1.00	$0.95 \pm 0.06$	$0.90 \pm 0.03$	$95 \pm 6$	$90 \pm 3$
1.50	0.50	$1.41 \pm 0.06$	$0.50 \pm 0.04$	$94 \pm 1$	$100 \pm 8$
1.75	0.25	$1.66 \pm 0.08$	$0.24 \pm 0.02$	$95 \pm 2$	$96 \pm 7$

Results expressed as mean  $\pm$  S.D.,  $n=4$ .

As can be seen in Table 3 the Sb(III) and Sb(V) recoveries from the different synthetic mixtures was between 90 and 108%, and was essentially independent of the Sb(V)/Sb(III) ratio.

The analytical characteristics obtained for the determination of Sb(III) and total antimony under these experimental conditions are presented in Table 4. The detection limits were calculated as  $\text{LOD} = 3s/S$ , where  $s$  is the S.D. of 10 measures of a blank solution and  $S$  is the slope of the standard calibration curve. The results show that the analytical performance of the Excalibur Millennium model was better than that the older model. It is important to note the low detection limits obtained with this model for total antimony ( $10 \text{ ng l}^{-1}$ ) and for Sb(III) ( $17 \text{ ng l}^{-1}$ ), values comparable to those obtained by ICP-MS.

### 3.2. Effect of the $\text{Cu}^{2+}$ concentration on the antimony signal

Since the soil samples were collected from sites impacted by copper mining activities, and consid-

ering that high transition metals concentrations, such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  have interferences in the hydride generation [29–31], the effect of the  $\text{Cu}^{2+}$  concentration on the hydride generation from Sb(V) and Sb(III) in synthetic solutions and soil extracts was studied. In order to evaluate the Cu concentrations to be considered in this study, copper was determined in the acid digested solutions and in  $\text{H}_2\text{O}$ , EDTA and  $\text{H}_2\text{SO}_4$  extracts of La Greda soil, by AAS. Hence, the  $\text{Cu}^{2+}$  concentration effect on the determination of total antimony and Sb(III) in  $\text{H}_2\text{O}$ , EDTA and  $\text{H}_2\text{SO}_4$  solutions was carried out by measuring the signal from  $0.5 \mu\text{g l}^{-1}$  Sb(V) or Sb(III) in these synthetic solutions, containing Cu concentrations up to  $2500 \mu\text{g l}^{-1}$ .  $\text{Cu}^{2+}$  had no effect on the fluorescence signal of total antimony from synthetic solutions, independent of the chemical composition of the extracting solution. In contrast, the hydride generation from Sb(III) was affected by the presence of  $\text{Cu}^{2+}$  in all synthetic solutions, particularly in water, as shown in Fig. 3. The different behavior could be explained by the high concentration of iodide present when total antimony is determined. It is well known that  $\text{Cu}^{2+}$  is reduced by iodide with the formation of tri-iodide and  $\text{Cu}^+$ , species that can be stabilized by chloride ions from the HCl solution employed in the hydride generation. This reaction can produce a significant decrease in the  $\text{Cu}^{2+}$  concentration, avoiding the possible reaction between  $\text{Cu}^{2+}$  and borohydride.

A similar study was carried out with the acid digested and extracted solutions from La Greda soil. In spite of transition metal interference in HG depending only on the absolute concentration of the interfering ion [31], in this case, results of the effect of Cu concentration on the Sb(III) and total

Table 4  
Analytical characteristic for total antimony and Sb(III) determination by HG-AFS

Analytical characteristic	Excalibur model		Excalibur Millennium model	
	Total antimony	Sb(III)	Total antimony	Sb(III)
Sensitivity <sup>a</sup>	48	39	1318	1280
LOD ( $\mu\text{g l}^{-1}$ ) <sup>b</sup>	0.020	0.042	0.010	0.017
RSD ( $n=6$ ) for $0.5 \mu\text{g l}^{-1}$	4.3%	8.7%	2.4%	2.5%

<sup>a</sup> Expressed in fluorescence units  $\text{l } \mu\text{g}^{-1}$ .

<sup>b</sup>  $\text{LOD} = 3s/S$ ,  $s$  standard deviation of 10 blank measures,  $S$  slope.

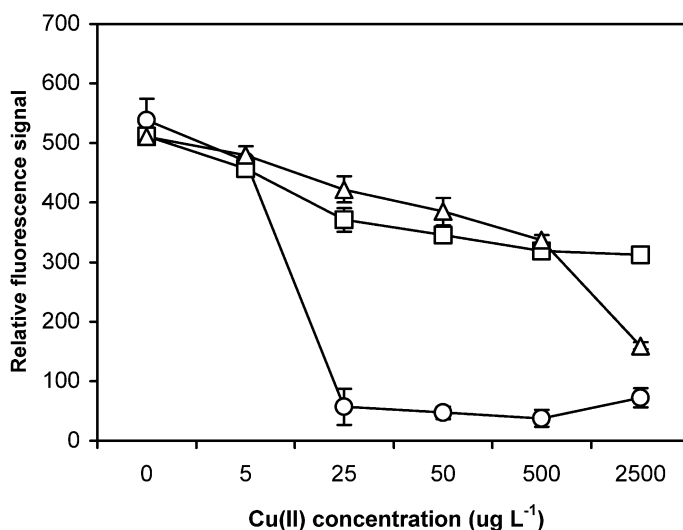


Fig. 3. Effect of copper concentration on the fluorescence signal from synthetic solutions (○) H<sub>2</sub>O, (□) 0.05 mol l<sup>-1</sup> EDTA pH 7.0 and (△) 0.25 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> of 0.5 µg l<sup>-1</sup> Sb(III) (4% m/v citric acid in 1.5-mol l<sup>-1</sup> HCl medium). (Results expressed as mean ± S.D., *n* = 4.)

Sb fluorescence signals are presented on the function of Cu/Sb ratio present in solution (Fig. 4a and b). The Cu/Sb was selected as abscissa axis because the initial Cu and Sb concentrations in each extract were different, as well as the aliquot of sample taken to perform the Sb determinations. Ratios were calculated from the values of the Sb and Cu concentrations previously determined and the respective copper amount added. As can be seen in Fig. 4a, the presence of Cu<sup>2+</sup>, as in the synthetic solutions, had no effect on the fluorescence signals of total antimony determination, whereas high Cu/Sb ratios decreased the Sb(III) fluorescence signal from all soil extracts (Fig. 4b). Taking into account these results, the effect of the matrix composition on the fluorescence signal of Sb(III) was studied by comparing the slopes obtained by the standard calibration and by the analyte addition technique for La Greda soil extracts. The slope of the calibration curves for synthetic solutions was  $1277 \pm 100$  fluorescence units µg<sup>-1</sup> l and the slopes for water, EDTA and H<sub>2</sub>SO<sub>4</sub> soil extracts were  $1256 \pm 125$ ,  $1105 \pm 100$  and  $883 \pm 50$  fluorescence units µg<sup>-1</sup> l, respectively. These results show a matrix effect on the hydride generation from Sb(III) in EDTA and

H<sub>2</sub>SO<sub>4</sub> soil extracts, whereas the slope from water extract is statistically similar to the slope obtained for the standard calibration curve. The different behavior must be due to the lower metal extracting power of water compared to EDTA and sulfuric acid. This fact was in accordance with the copper recovery obtained with the different extracting solutions (Table 5). According to these results, the determination of Sb(III) in all soil extracts was performed by the analyte addition technique, and the determination of total antimony was carried out by the standard calibration technique.

### 3.3. Applications

The methodology developed in this work is based on mild extraction procedures, the selective determination of Sb(III) and the total antimony determination by HG-AFS was applied to five Chilean agricultural soils, collected from sites impacted by copper mining. The total concentration of copper in the soils and soil extracts was also determined, and the results are given in Table 5 (the recoveries were calculated on basis of the total antimony determined by HG-AFS; copper was determined by flame AAS). From these results

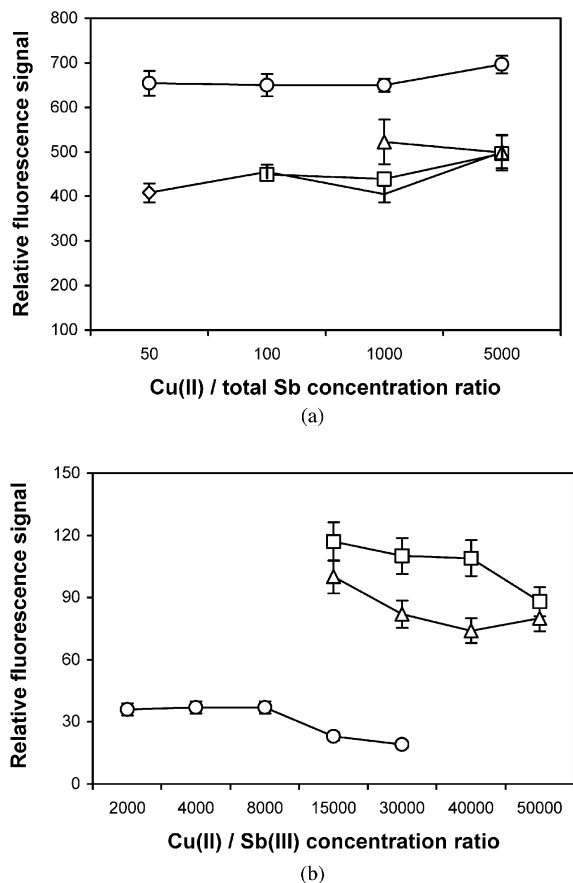


Fig. 4. Effect of copper concentration on the fluorescence signal from (◇) digested solutions (HNO<sub>3</sub>/HCl/HF) and (O) H<sub>2</sub>O, (□) EDTA and (Δ) H<sub>2</sub>SO<sub>4</sub> extracts from La Greda soil. (a) total antimony (pre-reduction 1.5% m/v KI+0.3% m/v ascorbic acid in 1.5-mol l<sup>-1</sup> HCl medium, 40 min at 90 °C for digested solution); (b) Sb(III) (4% m/v citric acid in 1.5-mol l<sup>-1</sup> HCl medium). (Results expressed as mean ± S.D., n = 4.)

several remarks can be made: first, in all cases the total antimony and copper concentrations in these soils are higher than those reported for agricultural soils [2], reflecting the degree of contamination caused by the copper industries located near to the sampling zone. Relative to the total antimony (and copper) in soil extracts, the results clearly show that the % recovery of total antimony extracted by H<sub>2</sub>SO<sub>4</sub> is similar to EDTA and higher than water. These results can be explained taking into account that H<sub>2</sub>SO<sub>4</sub> can release antimony (and copper)

from soil carbonaceous compounds and also from others insoluble compounds, whose solubility is increased in acid medium. It is also well known that EDTA is one of the strongest synthetic chelating reagents and forms stable complexes with most metals ions (especially at neutral pH). EDTA is mainly used to evaluate the mobile fraction and the availability of metals in soils. The fact that the total antimony extracted by both extracting solutions was similar should indicate that both reagents act on the same soil compounds, sulfuric acid could react with the anions and EDTA with the cations present in these compounds. Results show that both, Sb(III) and Sb(V) compounds were extracted by the solutions employed, but in all cases the recovery of total antimony was low. Under the conditions used in this work, which were assumed to be mild enough to preserve the oxidation states, Sb(V) was the main antimony species extracted from soils (except for Nogales soil). Lintschinger et al. [37], using HPLC-ICP-MS, demonstrated that the antimony oxidation states are preserved in water and EDTA extracts from contaminated soils, although Sb(III) was not detected. In our work, Sb(III) was detected in EDTA and sulfuric acid soil extracts, which might be due to the better LOD obtained in this work (Table 4), compared to that reported by those authors (Sb(III), 0.8 μg l<sup>-1</sup>).

#### 4. Conclusions

The proposed method based on mild extraction procedures and redox speciation analysis of antimony, coupling the selective stibine generation from Sb(III), masking Sb(V) with citric acid in HCl medium, with detection by AFS, provides a rapid and sensitive analytical technique for liquid samples, such as soil extracts. This approach could probably be extended to other hydride-forming elements in solid environmental samples.

The results showed that, in spite of the low recovery of total antimony, the solutions employed extract antimony compounds of both oxidation states. The results also show that neutral EDTA solution and diluted sulfuric acid have comparable extracting power to separate antimony from contaminated soils, in spite of their different chemical



Table 5

Total antimony and copper concentrations in soils from Valparaíso region in Chile, and recovery of Sb(III), Sb(V) and copper from water, EDTA and H<sub>2</sub>SO<sub>4</sub> soil extracts

Site	Total Sb (mg kg <sup>-1</sup> )	Total Cu (mg kg <sup>-1</sup> )	% Recovery								
			H <sub>2</sub> O			EDTA			H <sub>2</sub> SO <sub>4</sub>		
			Cu(II)	Sb(III)	Sb(V)	Cu(II)	Sb(III)	Sb(V)	Cu(II)	Sb(III)	Sb(V)
Campiche	13 ± 1	329 ± 26	1.9	<0.02	4.0	64	0.02	9.1	79	0.1	7.7
La Greda	6.8 ± 0.4	530 ± 38	1.3	<0.02	1.8	26	0.1	3.9	79	0.5	4.9
Maitenes	6.4 ± 0.5	282 ± 10	0.8	<0.02	0.8	51	<0.02	2.1	66	0.1	3.0
Puchuncaví	5.5 ± 0.1	255 ± 6	0.9	<0.02	0.9	60	0.1	3.5	64	0.3	2.2
Nogales	1.8 ± 0.2	104 ± 4	0.4	<0.02	0.1	38	0.5	0.7	44	0.7	0.7

Results expressed as mean ± S.D., *n* = 4.

behavior. The results also show that the available antimony in the contaminated soils considered in this study is less than 10% of the total antimony.

The HG-AFS method presented good analytical performance and a LOD comparable to ICP-MS. Thus, there is much reason to be optimistic about the use of this technique in routine redox speciation analysis, principally owing to its low cost, simplicity and low limits of detection.

Finally, taking into account the promising results obtained with oxalic acid to mask quantitatively Sb(V) in acidic medium, further detailed studies to demonstrate its potential in speciation analysis of antimony are underway.

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