Talanta 84 (2011) 593–598

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

Antimony speciation in soils: Improving the detection limits using post-column pre-reduction hydride generation atomic fluorescence spectroscopy (HPLC/pre-reduction/HG-AFS)

Waldo Quiroz[a,*], David Olivares[a], Manuel Bravo[a], Jorg Feldmann[b], Andrea Raab[b]

[a] Laboratorio de Química Analítica y Ambiental, Instituto de Química, Pontificia Universidad Católica de Valparaíso, Avenida Parque Sur 330 Curauma, Valparaíso, Chile
[b] Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3TU, UK

ARTICLE INFO

Article history:
Received 11 November 2010
Received in revised form
30 December 2010
Accepted 7 January 2011
Available online 15 January 2011

Keywords:
Antimony speciation
Soils
HG-AFS

ABSTRACT

HG-AFS is highly sensitive and low cost detection system and its use for antimony chemical speciation coupled to HPLC is gaining popularity. However speciation analysis in soils is strongly hampered because the most efficient extractant reported in the literature (oxalic acid) strongly inhibits the generation of SbH_3 by Sb(V), the major species in this kind of matrix, severely affecting its detection limits. The purpose of this research is to reduce the detection limit of Sb(V), by using a post column on-line reduction system with L-cysteine reagent (HPLC/pre-reduction/HG-AFS). The system was optimized by experimental design, optimum conditions found were 2% (w/v) and 10 °C temperature coil. Detection limits of Sb(V) and Sb(III) in oxalic acid (0.25 mol L^{-1}) were improved from 0.3 and 0.1 μg L^{-1} to 0.07 and 0.07 μg L^{-1}, respectively. The methodology developed was applied to Chilean soils, where Sb(V) was the predominant species.

1. Introduction

Antimony speciation in different matrices has received growing attention in recent years because the toxicity and biological effects caused by antimony compounds depend on its chemical form. Inorganic antimony compounds are more toxic than organic antimony compounds, and Sb(III) is ten times more toxic than Sb(V) [1]. Therefore, the total antimony concentration may not sufficiently describe the toxicity, bioavailability, biotransformation and other relevant aspects of this metalloid [2].

Methodologies for antimony speciation in environmental samples based on high performance liquid chromatography (HPLC) separation have been developed and are summarized in critical reviews published since 1998 [3–11]. HPLC coupled to inductively coupled plasma mass spectrometry (ICP-MS) is one of the most commonly used methods due to its good analytical performance [7,12–20]. However, HPLC using hydride-generation atomic fluorescence spectroscopy (HG-AFS) as a detection system seems to be a good alternative because of its low running cost, the affordability of its instruments. It offers good analytical performance in terms of linearity and detection limits and its potential to be field-deployable. HPLC–HG-AFS has been applied to the antimony speciation in different environmental matrices, such as fresh water [21,22], sea water [23], terrestrial plants [24], marine sediments [25], soils [26], coal fly ash [27] and marine biota [28].

Although HG-AFS offers good detection limits and selectivity, its analytical figure of merits depends dramatically on the hydride-generation step. For instance, the quantitative reduction of Sb(V) is mandatory before the hydride-generation step to improve the method sensitivity of the total antimony determination. The difference in sensitivity between Sb(V) and Sb(III) is partially due to the slower reduction of the pentavalent form.

In the early 1980s, the pre-reduction of Sb(V) to Sb(III) required use of the following reagents: KI, either alone or mixed with ascorbic acid, thiourea [29,30] and more recently L-cysteine [31–35]. L-Cysteine is particularly attractive because of its low toxicity and the low acid concentrations required in the hydride-generation step [22]. L-Cysteine has been reported to increase the Sb(V) sensitivity by a factor of seven [36].

When antimony chemical speciation is performed by HPLC coupled with a HG-AFS detector, the sensitivity problem of Sb(V) still remains, and the detection limit is generally higher for Sb(V) than Sb(III) [23,28]. The major problems in HPLC–HG-AFS antimony speciation analysis of soil are the low kinetics in the generation of SbH_3 from Sb(V) and the inhibition of the Sb(V) chromatographic signal by complexing agents such as oxalic acid or citric acid, both of which are efficient extracting agents reported in the literature for antimony speciation in soil and sediments [25,37]. On the other hand, Sb(V) can be found naturally, either in its oxalic acid complex or its

* Corresponding author. Tel.: +56 32 2274925; fax: +56 32 2274939.
E-mail address: waldo.quiroz@ucv.cl (W. Quiroz).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.01.018

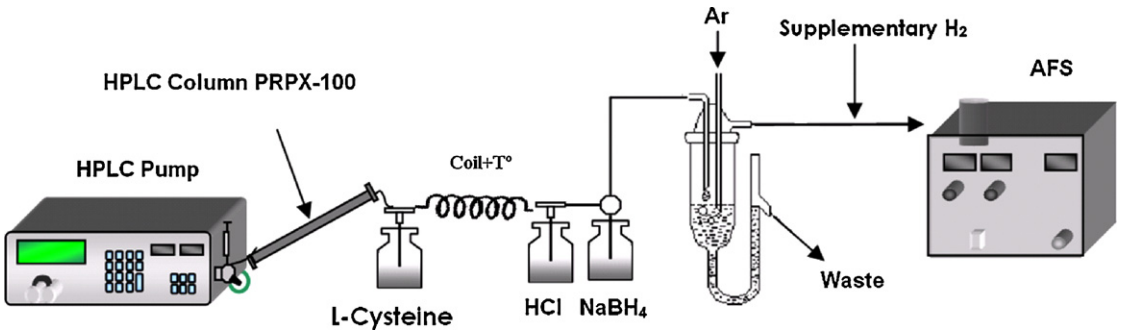

Fig. 1. HPLC/pre-reduction/HG-AFS system with post-column pre-reduction step.

citric acid complex, in matrices such as citrus juice [38] or organic soil matter [39].

When determining total antimony by HG-AFS, the pre-reduction of Sb(V) to Sb(III) can be performed using L-cysteine as the reducing agent; with this understanding, we postulated that incorporating an online post-column pre-reduction into the HPLC–HG-AFS system would allow for the reduction of Sb(V) to Sb(III) before the hydride-generation system. This incorporation would increase Sb(V) sensitivity and allow the system to reach similar detection limits as those for Sb(III). The reducing agent selected for these purposes was L-cysteine.

Here we describe an efficient methodology for antimony speciation by HPLC–HG-AFS coupling online a post-column pre-reduction step. Sb(V) was pre-reduced to Sb(III) before the hydride-generation system by L-cysteine in a HCl medium. We used the experimental design to optimize the experimental conditions of the pre-reduction step. We applied this methodology to the antimony speciation analysis of soil extracts. Our method is the first method that incorporates a post-column pre-reduction step.

2. Experimental

2.1. Instrument

We determined the total antimony content of the diluted extracts using ICP-MS monitoring ^{121}Sb and ^{123}Sb with ^{103}Rh as the internal standard.

An HPLC Hewlett Packard 1050 quaternary pump with an autosampler, a 100 μL loop, and a PRPX-100 Hamilton (100 mm × 4.1 mm; 5 μm particle diameter) anion-exchange column were used for the chromatographic separation. Previous studies have described both the gradient elution program and the hydride-generation atomic fluorescence conditions used [23].

The post-column pre-reduction step was performed by mixing the mobile phase online with 2% (w/v) L-cysteine in 1.5 mol L^{-1} HCl using a coil (4 m in length and 0.5 cm i.d.) at 10 °C (Fig. 1).

2.2. Chemicals and reagents

All chemicals and reagents used in this study had purities at or exceeding analytical grade. De-ionized water (18.2 MΩ cm) was obtained from a Nanopure system (Barnstead, Dubuque, IA, USA). Glass and polyethylene wares were cleaned by soaking them in 10% (v/v) nitric acid (analytical grade) for one day and rinsing them several times with de-ionized water before use. High-purity nitric, hydrochloric, hydrofluoric and sulphuric acids (Suprapur, Merck) and concentrated tetrafluoroboric acid HBF_4, purchased from Sigma, USA were used for soil digestion.

Individual stock solutions of antimony species were prepared from potassium hexahydroxy-antimoniate $KSb(OH)_6$ (99.95%), potassium antimonyl tartrate $K(SbO)C_4H_4O_6H_2O$ (99.95%) and trimethylantimony dichloride $(CH_3)_3SbCl_2$ (96%) purchased from Sigma–Aldrich (USA) and are referred to as Sb(V), Sb(III) and TMSb(V), respectively. We prepared the stock solutions of Sb(V) (100 mg L^{-1}) and TMSb(V) (100 mg L^{-1}) by dissolving the respective compounds in de-ionized water and storing the solutions in the dark at 4 °C. We prepared a fresh standard solution of Sb(III) before each use by dissolving potassium antimonyl tartrate in de-ionized water. The working antimony standards solutions at lower concentration levels (e.g., individual species and mixed species) were prepared as needed by diluting the stock solutions with their respective extracting solutions.

2.3. Samples collection

During 2009, soil samples were collected in 5 different places in Valparaiso region a central zone of Chile. Los Andes, San Felipe, San Esteban, Chagres and Catemu were the location selected. All soils samples selected were favorable for agriculture, on the other hand, all these places are surrounded by industrial mining and cement industry activities.

Approximately 10 kg of soil were collected from first 5 cm from the surface, which were transferred to laboratory facilities to be ground and sieved to 2 mm. After that soil samples were dried at 50 °C for 48 h and then stored in plastic bags until analysis. Respective geographic coordinates of the sampling sites are given in Table 1.

Table 1
Geographic coordinates and chemical characteristics of soil samples.

Code	Samples location	Coordinates			pH	(%)Organic matter
		°	′	″		
A1	Los Andes	32	49	0.01	6.2	3.7
		70	35	34.7		
A2	Los Andes	32	48	44.5	6.5	3.7
		70	36	03.9		
B	San Esteban	32	49	16.6	6.3	4.6
		70	35	28.9		
C	San Felipe	32	41	25.7	6.9	4.1
		70	47	25.7		
D	San Felipe	32	41	56.9	6.7	1.9
		70	45	40.3		
E	San Felipe	32	44	12.4	6.4	5.0
		70	46	21.0		
F	Chagres	32	48	24.2	7.1	1.9
		70	57	08.7		
G	Chagres	32	48	03.1	6.9	2.9
		70	57	36.2		
H	Catemú	32	46	20.7	6.5	6.2
		70	59	20.5		
I	Catemú	32	46	39.5	6.4	3.1
		70	58	50.0		
J	Catemú	32	46	39.6	7.1	3.2
		70	58	49.9		

Table 2
Experimental design in the optimization of the signal/background ratio response for Sb(V) and Sb(III) in HPLC/pre-reduction/HG-AFS system.

	Factors	
	Temperature (°C)	L-Cysteine (%, w/v)
Coded factors	A	B
Level −1	10	0
Level 0	50	1
Level +1	90	2

2.4. Total antimony determination

The total antimony concentration in soil was determined by using HG-AFS under the conditions previously reported by our group [40]. The total antimony extracted from the soil was determined by measuring the appropriate dilutions of the extracts using ICP-MS.

2.5. Antimony extraction from soil

Dry Chilean soil (0.1 g; 38.4 ± 3.0 mg kg^{-1}) was weighed and combined with 5 mL of the extracting solutions in 15 mL polypropylene vessels. The mixture was shaken at room temperature in a horizontal shaker (junior orbit shaker, Labline Instruments, Melrose Park, IL, USA) at 150 rpm for 2 h and centrifuged for 30 min at 5000 rpm (HERMLE Z 300K). After centrifuging, the supernatants were filtered through an HA-type 0.45 μm membrane filter and cleaned using C-18 cartridges (Millipore). ICP-MS was used to determine the total antimony concentration of the extracts.

Oxalic solutions (0.25 mol L^{-1}, pH 1.3) have been used to extract antimony from soil samples. The extracting yields of each solution were evaluated by applying the extraction procedure previously described for the soil samples.

2.6. Antimony speciation in soil

Sb(V), Sb(III) and TMSb(V) in soil extracts were determined by using anion-exchange high-performance liquid chromatography (HPLC–HG-AFS). Our HPLC–HG-AFS analysis included a post-column pre-reduction step that mixed online the eluent with L-cysteine (2% w/v). Standard addition method, incorporating peak-area measurements, was performed to determine each antimony species.

3. Results and discussion

3.1. Optimization of pre-reduction step

The parameters evaluated in this study were L-cysteine concentration (in HCl 1.5 mol L^{-1}) and coil temperature. The selected response in this study was signal/noise ratio for both Sb(V) and Sb(III). Because most soil contains inorganic species [26,37,41–43], the TMSb(V) response was not considered for the optimization calculation. The parameter range and its codification are presented in Table 2.

Table 3 shows the signal/noise responses obtained during the optimization step for Sb(V), Sb(III) and TMSb(V). A linear model was fitted with results, and the response predicted for the "0"-level point was compared with the predicted values. Both results are statistically similar, which explain the absence of curvature in the experimental domain studied. The statistical significance of the coded parameters is shown in the Pareto charts (see Fig. 2). Of all the factors considered, only the L-cysteine concentration was a significant and positive effect for the signal/noise response of Sb(V) (see Fig. 2A), which supports our hypothesis about increasing the sensitivity of Sb(V) by adding an online pre-reduction step. In Sb(III) (see Fig. 2B), only temperature showed a significant and negative effect, while the L-cysteine concentration does not significantly increase the signal/noise response of Sb(III). This result is expected because this species does not need to be reduced to generate SbH_3 in the hydride generation system. In TMSb(V) (see Fig. 2C), only temperature showed a significant and negative effect. Finally, the interaction (AB) between temperature and the L-cysteine concentration had no significant effect on any species studied.

Table 3
Signal/noise responses for Sb(V), Sb(III) and TMSb(V).

Temperature	L-Cysteine	Signal/noise		
		Sb(V)	Sb(III)	TMSb(V)
−1	−1	11.54	24.97	6.78
−1	1	42.88	37.65	4.50
1	−1	9.87	12.35	2.96
1	1	16.13	8.87	2.71
0	0	26.47	14.83	4.03
0	0	22.77	17.02	3.40
0	0	30.00	16.29	3.39
Centers points[a]		26 ± 7	16 ± 4	4 ± 1
Predicted centers		22.8	18.9	4.0

[a] Mean values ± confidence interval ($\alpha = 0.05$).

Fig. 3 shows the response surfaces obtained for the linear fitting of the Sb(III), Sb (V) and TMSb(V) signal/noise ratios (see Table 3).

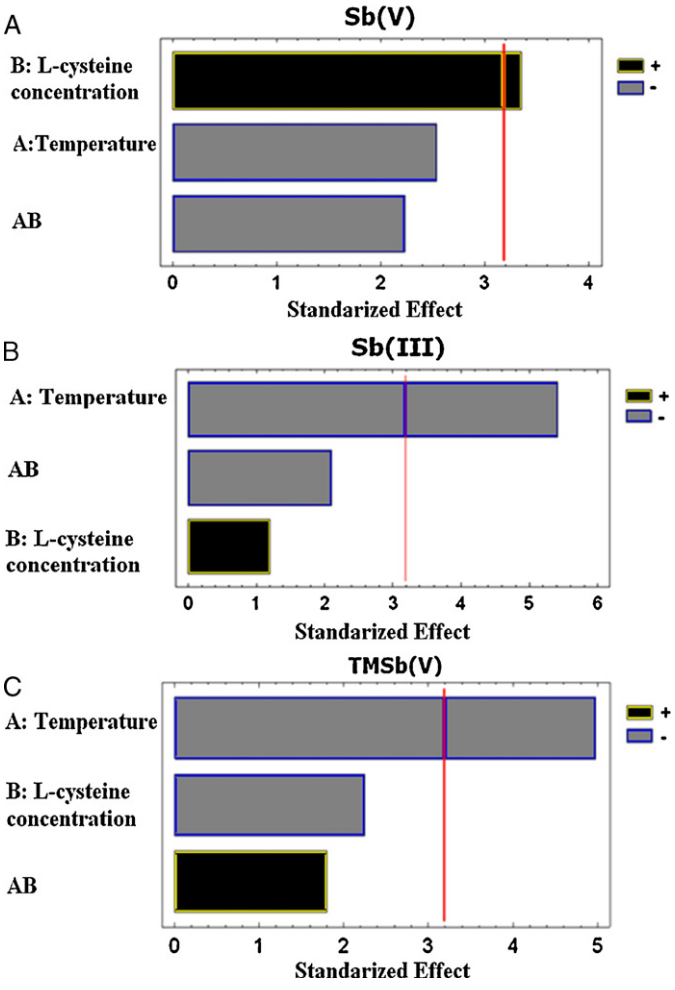

Fig. 2. Pareto chart for evaluate the effect of L-cysteine concentration and coil temperature over signal/noise response of (A) Sb(V), (B) Sb(III) and (C) TMSb(V).

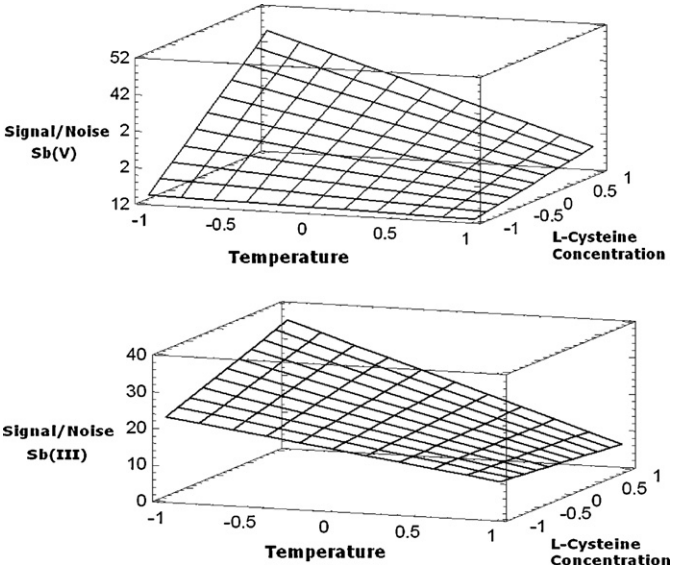

Fig. 3. Surface signal/noise responses of Sb(V) and Sb(III).

Table 4
Theoretical and experimental values (±95% confidence limit) for signal/noise response of Sb(V) and Sb(III) by HPLC/pre-reduction/HG-AFS in optimum conditions.

Specie	Signal/noise Predicted value	Signal/noise Experimental value
Sb(V)	46	45 ± 3
Sb(III)	36	36 ± 2

These surfaces explain 91% and 93% of total variability of the experimental response obtained for inorganic antimony [R^2 = 0.91 and 0.93 for Sb(V) and Sb(III), respectively]. As shown in Fig. 3, the maximum response for Sb(V) was obtained when the temperature and L-cysteine concentration were set to the "−1" and "+1" level (10 °C and 2%, w/v, respectively); these conditions are the optimal conditions for Sb(III); therefore, 10 °C and 2% (w/v) were the conditions selected for further investigation.

The fit of the polynomial model was evaluated by comparing the model's predicted response to the model's experimental response under optimal conditions. As the results in Table 4 show, the model responses to Sb(V) and Sb(III) were statistically similar to the experimental responses at a 95% level of confidence. The similarities between the model responses and the experimental responses assure both the quality of the model and the prediction.

Table 5
Analytical figures of merit.

Specie	LOD ($\mu g L^{-1}$)	LOQ ($\mu g L^{-1}$)	RSD (%)	Linear range ($\mu g L^{-1}$)
Sb(V)	0.07	0.25	4.9	1–200
Sb(III)	0.07	0.23	5.1	1–200
TMSb(V)	1.0	2.5	4.5	1–200

Table 6
Recovery of Sb(V), Sb(III) and TMSb (V) from soils H and F.

Soil	Specie	Spiking ($\mu g g^{-1}$)	Recovery ($\mu g g^{-1}$)	% recovery
H	Sb(V)	2.0	2.1 ± 0.4	105
	Sb(III)	2.0	1.8 ± 0.3	90
	TMSb	2.0	1.9 ± 0.4	95
F	Sb(V)	1.0	1.0 ± 0.2	100
	Sb(III)	1.0	0.92 ± 0.09	92
	TMSb	1.0	0.95 ± 0.10	95

3.2. Analytical figures of merit

Analytical figures of merit were found using the previously described optimal experimental conditions. Both the detection limit and the quantification limit were calculated according to the IUPAC (3 SD of blank signal/slope) for Sb(V) and Sb(III) for a 100 μL injection loop. The precision was expressed as the relative standard deviation (RSD) by analyzing solutions of 5 $\mu g L^{-1}$ of each standard solution for a cycle of injections made three times per day over 5 days. The analytical figures of merit are summarized in Table 5.

Using the pre-reduction step, both the detection limit and the quantification limit for Sb(V) are similar to those of Sb(III). This similarity is an analytical improvement because, in previous research, the Sb(V) detection limit was clearly higher than the Sb(III) detection limit [23]. Comparing our results with the results found in previous studies of the HPLC–HG-AFS system, our Sb(V) detection limit was lower than the Sb(V) detection limit reported by Sayago et al. of 0.8 $\mu g L^{-1}$ [44] and was similar to the detection limit reported by Miravet et al. of 0.04 $\mu g L^{-1}$ [45] and 0.06 $\mu g L^{-1}$ [22]. To show the clear increase of the Sb(V) sensitivity, Fig. 4 com-

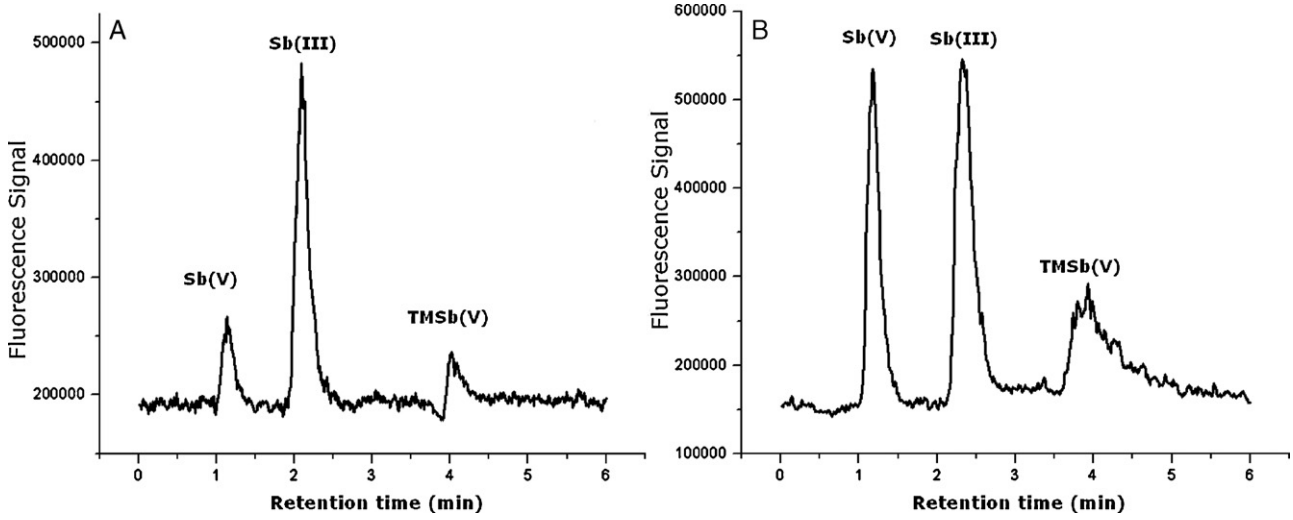

Fig. 4. Chromatograms of 10 $\mu g L^{-1}$ of Sb(V), Sb(III) and TMSb(V) in oxalic acid 0.25 mol L^{-1}, obtained (A) without pre-reduction and (B) with pre-reduction.

Table 7
Analysis of Chilean soils, total antimony, Sb(V) and Sb(III) determination.

Soil i.d.	Location	Total Sb ($\mu g\,g^{-1}$)	Sb extracted ($\mu g\,g^{-1}$)	% extracted	Sb(V) ($\mu g\,g^{-1}$)	Sb(III) ($\mu g\,g^{-1}$)
1	Los Andes	1.6 ± 0.2	0.32 ± 0.03	20	0.31 ± 0.03	<LOD
2	Los Andes	1.6 ± 0.3	0.32 ± 0.02	20	0.32 ± 0.02	<LOD
3	San Esteban	2.7 ± 0.1	0.37 ± 0.05	14	0.31 ± 0.05	<LOQ
4	San Felipe	2.7 ± 0.1	0.54 ± 0.05	20	0.49 ± 0.05	0.06 ± 0.02
5	San Felipe	2.0 ± 0.2	0.34 ± 0.02	17	0.29 ± 0.02	<LOQ
6	San Felipe	2.5 ± 0.2	0.6 ± 0.1	24	0.5 ± 0.1	<LOQ
7	Chagres	3.6 ± 0.2	1.1 ± 0.1	31	0.96 ± 0.08	0.06 ± 0.02
8	Chagres	2.7 ± 0.2	0.65 ± 0.05	24	0.56 ± 0.05	0.06 ± 0.03
9	Catemu	6.4 ± 0.5	1.9 ± 0.1	30	1.9 ± 0.1	0.19 ± 0.05
10	Catemu	1.5 ± 0.1	0.23 ± 0.02	15	0.19 ± 0.02	<LOD

LOD: Sb(III) 0.02 $\mu g\,g^{-1}$; Sb(V) 0.02 $\mu g\,g^{-1}$.

pares chromatograms obtained both with and without the online pre-reduction system.

When antimony speciation was performed at identical conditions without pre-reduction, detection limits of 0.3 $\mu g\,L^{-1}$, 0.1 $\mu g\,L^{-1}$, and 1.8 $\mu g\,L^{-1}$ for Sb(V), Sb(III) and TMSb(V) were founded, respectively. Compared to detection limits in previous experiments, these detection limits show that our methodology is an improvement on the developed methodology. This improvement holds true even in TMSb(V), which was not considered in the determination of the optimal conditions.

3.3. Accuracy

Validation of analytical methods for antimony speciation is difficult owing to the absence of certified reference material for the species of this element in soils. Therefore, a study on the recovery of Sb(V), Sb(III) and TMSb(V) species in soil samples during the extraction procedure was achieved. For this purpose two different soil samples (samples H and F according to Table 1) were spiked with 2.0 $\mu g\,g^{-1}$ and 1.0 $\mu g\,g^{-1}$, respectively of Sb(V), Sb(III) and TMSb(V). Native antimony species in soil samples were determined simultaneously using the optimized HPLC–HG-AFS method. Results are summarized in Table 6.

3.4. Application of the optimized methodology to antimony speciation in soil

The optimized methodology was applied to different Chilean soil samples located in the Valparaiso region. No TMSb(V) was detected in the soils analyzed. The results are summarized in Table 7.

As shown in Table 6, the total antimony concentration ranged between 1.5 $mg\,kg^{-1}$ and −3.6 $mg\,kg^{-1}$, which is higher than the worldwide average reported for this matrix (1 $mg\,kg^{-1}$) [46] but below the concentration of contaminated soil reported by Lintschinger et al. [43] in soil from Bavaria, Germany (73.4–196 $mg\,kg^{-1}$) or Scheinost et al. [47] in soil from Swiss shooting ranges (1300–17,500 $mg\,kg^{-1}$). This general enrichment can be explained by industrial activities such as mining and cement that are developed in the areas surrounding the sampling sites. For example in less than 20 km away from the sampling sites there is a copper industry, which emits atmospheric particulate matter contaminating for decades the soils and vegetables of the surrounding areas with copper and arsenic, both elements normally are related with antimony through composition of sulphide ores [48].

We found that the extraction percentages of antimony from soils were low (between 14% and 35%). However, similar results have been reported in the literature. For example, Fuentes et al. reported an extraction percentage between 9% and 17% using a 0.2 $mol\,L^{-1}$ oxalic acid/oxalate mixture, which demonstrates that antimony is found mainly in the residual fraction [37]. Fuentes et al. extracted only 0.4% and 8% of the total antimony content in Chilean soils by applying a 0.05 $mol\,L^{-1}$ EDTA at pH 7 [49]. Amereih et al. achieved less than 15% extraction using 0.1 $mol\,L^{-1}$ citric acid, pH 2.08, as the extractant [18]. About the problem of the low extraction yield, it could be useful for future considerations, to apply more energetic extraction methods such as microwave [50] or ultrasound [51] assisted extraction. However, in both strategies is fundamental to analyze the stability of species during the whole analytical process, especially considering that an extraction assisted by more energetic methods increases the risk of oxidation of Sb(III) to Sb(V).

Sb(V) was the predominant species found in each soil extract tested. The sum of the total extracted species varied between 82% and 100%, which demonstrates that most of the extracted antimony species were inorganic. Sb(III) was found between 0% and 14% in all soil extracts, which reveals that it is a minor species. We cannot determine whether the presence of the trivalent Sb in the extract reflects the presence of trivalent Sb in the soil or whether species transformations have taken place. To make this determination, isotopic studies or solid-state speciation methods such as XANES and EXAFS are necessary [52]. However, the possibility that Sb(III) will oxidize during the extraction procedure always exists. Regarding speciation analysis in soils, Fuentes et al. [37] reported that approximately 90% of the extracted antimony in Chilean soils was Sb(V) and that the percentage of Sb(III) varied between 5% and 21%. However, different results were obtained by Amereih et al., which reported that Sb(V) ranged between 30% and 85% of the total extracted antimony. In some extracts the presence of Sb(III) as the predominant species could be explained by the anthropogenic influence of vehicle traffic [18].

4. Conclusions

Our study confirms that antimony speciation in soil by HPLC–HG-AFS is severely hampered by oxalic-acid extracting media. Most of the problems come from the inhibition of SbH_3 due to the complexation of oxalic-acid with Sb(V). When determining inorganic species, a pre-reduction system that incorporates L-cysteine seems to overcome these problems. The optimized methodology shows an excellent performance for antimony speciation in soils. Only inorganic species, Sb(V) and Sb(III), were detected in extracts of Chilean soils, and Sb(V) was always the predominant species.

Further work should investigate the potential to increase extraction efficiency, including a systematic study on stability species.

Acknowledgements

The authors gratefully acknowledge the financial support of FONDECYT (project 11080084).

Manuel Bravo, David Olivares and Waldo Quiroz are especially thankful to Dr. Ida De Gregori and Dr. Hugo Pinochet for their high-

quality teaching in the field of analytical chemistry. We wish them a happy retirement.

References

[1] A. Guy, P. Jones, S.J. Hill, Analyst 123 (1998) 1513.
[2] S.X. Garbos, E. Bulska, A. Hulanicki, Z. Fijalek, K. Soltyk, Spectrochim. Acta B 55 (2000) 795.
[3] M. Filella, N. Belzile, Y.-W. Chen, Earth Sci. Rev. 57 (2002) 125.
[4] M. Filella, N. Belzile, Y.-W. Chen, Earth Sci. Rev. 59 (2002) 265.
[5] P. Smichowski, Y. Madrid, C. Cámara, Fresenius J. Anal. Chem. 360 (1998) 623.
[6] M. Krachler, H. Emons, J. Zheng, Trends Anal. Chem. 20 (2001) 79.
[7] M.J. Nash, J.E. Maskall, S.J. Hill, Analyst 131 (2006) 724.
[8] Y.W. Chen, N. Belzile, Anal. Chim. Acta 671 (2010) 9.
[9] R. Miravet, E. Hernández-Nataren, A. Sahuquillo, R. Rubio, J.F. López-Sánchez, Trends Anal. Chem. 29 (2010) 28.
[10] H.R. Hansen, S.A. Pergantis, J. Anal. At. Spectrom. 23 (2008) 1328.
[11] D. Sanchez-Rodas, W.T. Corns, B. Chen, P.B. Stockwell, J. Anal. At. Spectrom. 25 (2010) 933.
[12] J. Lintschinger, I. Koch, S. Serves, J. Feldmann, W.R. Cullen, Fresenius J. Anal. Chem. 359 (1997) 484.
[13] N. Ulrich, Anal. Chim. Acta 359 (1998) 245.
[14] M. Krachler, H. Emons, Anal. Chim. Acta 429 (2001) 125.
[15] J. Zheng, M. Ohata, N. Furuta, Anal. Sci. 16 (2000) 75.
[16] N. Ulrich, Anal. Chim. Acta 417 (2000) 201.
[17] N. Miekeley, S.R. Mortari, A.O. Schubach, Anal. Bioanal. Chem. 372 (2002) 495.
[18] S. Amereih, T. Meisel, R. Scholger, W. Wegscheider, J. Environ. Monit. 7 (2005) 1200.
[19] R. Miravet, J.F. López-Sánchez, R. Rubio, P. Smichowski, G. Polla, Anal. Bioanal. Chem. 387 (2007) 1949.
[20] J. Zheng, A. Iijima, N. Furuta, J. Anal. At. Spectrom. 16 (2001) 812.
[21] A. Sayago, R. Beltrán, M.A.F. Recamales, J.L. Gómez-Ariza, J. Anal. At. Spectrom. 17 (2002) 1400.
[22] R. Miravet, J.F. López-Sánchez, R. Rubio, J. Chromatogr. A 1052 (2004) 121.
[23] I. De Gregori, W. Quiroz, H. Pinochet, F. Pannier, M. Potin-Gautier, J. Chromatogr. A 1091 (2005) 94.
[24] R. Miravet, E. Bonilla, J.F. López-Sánchez, R. Rubio, J. Environ. Monit. 7 (2005) 1207.
[25] M. Potin-Gautier, F. Pannier, W. Quiroz, H. Pinochet, I. De Gregori, Anal. Chim. Acta 553 (2005) 214.
[26] S. Amereih, T. Meisel, E. Kahr, W. Wegscheider, Anal. Bioanal. Chem. 383 (2005) 1052.
[27] R. Miravet, J.F. López-Sánchez, R. Rubio, Anal. Chim. Acta 576 (2006) 200.
[28] I. De Gregori, W. Quiroz, H. Pinochet, F. Pannier, M. Potin-Gautier, Talanta 73 (2007) 458.
[29] Z.X. Li, Y.A. Guo, Talanta 65 (2005) 1318.
[30] Z.X. Li, X.M. Yang, Y.A. Guo, H.T. Li, Y.H. Feng, Talanta 74 (2008) 915.
[31] B. Welz, M. Sucmanova, Analyst 118 (1993) 1417.
[32] B. Welz, M. Sucmanova, Analyst 118 (1993) 1425.
[33] H.W. Chen, I.D. Brindle, S.G. Zheng, Analyst 117 (1992) 1603.
[34] A. Dulivo, L. Lampugnani, G. Pellegrini, R. Zamboni, J. Anal. At. Spectrom. 10 (1995) 969.
[35] A. D'Ulivo, L. Lampugnani, D. Faraci, D.L. Tsalev, R. Zamboni, Talanta 45 (1998) 801.
[36] B. Chen, M. Krachler, W. Shotyk, J. Anal. At. Spectrom. 18 (2003) 1256.
[37] E. Fuentes, H. Pinochet, M. Potin-Gautier, I. De Gregori, J. AOAC 87 (2004) 60.
[38] H.R. Hansen, S.A. Pergantis, J. Anal. At. Spectrom. 21 (2006) 731.
[39] M. Tella, G.S. Pokrovski, Geochim. Cosmochim. Acta 73 (2009) 268.
[40] I. De Gregori, H. Pinochet, E. Fuentes, M. Potin-Gautier, J. Anal. At. Spectrom. 16 (2001) 172.
[41] C. Casiot, O.F.X. Donard, M. Potin-Gautier, Spectrochim. Acta B 57 (2002) 173.
[42] E. Fuentes, H. Pinochet, I. De Gregori, M. Potin-Gautier, Spectrochim. Acta B 58 (2003) 1279.
[43] J. Lintschinger, B. Michalke, S. Schulte-Hostede, P. Schramel, Int. J. Environ. Anal. Chem. 72 (1998) 11.
[44] A. Sayago, R. Bcltrán, J.L. Gómez-Ariza, J. Anal. At. Spectrom. 15 (2000) 423.
[45] R. Miravet, E. Bonilla, J.F. López-Sanchez, R. Rubio, Appl. Organomet. Chem. 20 (2006) 12.
[46] M.J. Nash, J.E. Maskall, S.J. Hill, J. Environ. Monit. 2 (2000) 97.
[47] A.C. Scheinost, A. Rossberg, D. Vantelon, I. Xifra, R. Kretzschmar, A.K. Leuz, H. Funke, C.A. Johnson, Geochim. Cosmochim. Acta 70 (2006) 3299.
[48] R. Ginocchio, P.H. Rodriguez, R. Badilla-Ohlbaum, H.E. Allen, G.E. Lagos, Environ. Toxicol. Chem. 21 (2002) 1736.
[49] I. De Gregori, E. Fuentes, D. Olivares, H. Pinochet, J. Environ. Monit. 6 (2004) 38.
[50] M.M. Rahman, Z.L. Chen, R. Naidu, Environ. Geochem. Health 31 (2009) 93.
[51] M.N.M. Reyes, M.L. Cervera, R.C. Campos, M. de la Guardia, Talanta 75 (2008) 811.
[52] J. Feldmann, P. Salaun, E. Lombi, Environ. Chem. 6 (2009) 275.