

Analytical Strategies for Determination and Environmental Impact Assessment of Inorganic Antimony Species in Natural Waters Using Hydride Generation Atomic Fluorescence Spectrometry (HG AFS)

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This study proposes an optimized procedure for the determination of inorganic antimony species in natural waters using hydride generation atomic fluorescence spectrometry (HG AFS) and continuous flow system. The variables of the hydride generation system, such as pre-reduction time, hydrochloric acid concentration and sodium tetrahydroborate concentration, were evaluated using full factorial design at two levels and Doehlert design. After optimized experimental conditions, the method allowed the determination of antimony with limits of detection and quantification of 9 and 30 ng L⁻¹, respectively. The precision (RSD) of the method was < 5% and the accuracy was confirmed by the analysis of certified reference material (SLRS-4, River water for trace metals). The method was successfully applied for inorganic antimony speciation in water samples collected in Salvador City, Bahia State, Brazil. In mineral water, total Sb concentrations ranged from 0.26 to 0.30 µg L⁻¹, whereas the concentrations of Sb^{III} were below 0.03 µg L⁻¹. On the other hand, in natural surface waters, the quantifiable concentration of total Sb and Sb^{III} ranged from 0.41 to 1.23 µg L⁻¹ and 0.23 to 1.04 µg L⁻¹, respectively. The highest average concentrations of Sb were obtained in regions with the largest urban influence, ratifying the anthropogenic impact in water bodies.

Keywords: speciation, antimony, natural waters, multivariate optimization, HG AFS

Introduction

Antimony is considered, among other elements such as As, Pb and Hg, a toxic chemical element of global concern that has unknown biological functions.^{1,2} Its presence in aquatic environments is mainly due to anthropogenic activities and also as a result of natural processes, such as rock weathering and soil runoff.³ Among its applications, it is possible to mention the use of antimony in flame retardants, pharmaceutical products, as a component of brake linings and as a catalyst in the manufacture of polyethylene terephthalate (PET) containers. Antimony, in the environment, is mainly found in two oxidation states, Sb^{III} and Sb^V, which can be present as different organic and inorganic species. Inorganic species are more

toxic and Sb^V compounds are less toxic than those of Sb^{III} compounds.^{2,4-6}

In recent years, an increase in the number of studies on total antimony determination and their inorganic species, Sb^{III} and Sb^V, has been observed in environmental samples and drinking waters. These studies are encouraged by the toxicity of the element, as well as the considerable different toxicity of antimony species and by low permissible concentrations of this element in the environment, which are stipulated by regulatory agencies in many countries. The World Health Organization (WHO)⁷ establishes the concentration of 20 µg L⁻¹ as a maximum permissible limit of antimony in drinking water. On the other hand, the maximum concentrations allowed in drinking water by the United States Environmental Protection Agency (USEPA)⁸ and Brazilian regulations^{9,10} are 6 and 5 µg L⁻¹, respectively. For freshwater bodies, the maximum admissible limit is

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5 $\mu\text{g L}^{-1}$, according to the resolution of the National Council of the Environment of Brazil (CONAMA).¹¹ Thus, the development of reliable, sensitive and accurate analytical procedures is extremely important for the determination and monitoring of total Sb, Sb^{III} and Sb^V in environment samples, as natural waters.

Among the detection techniques used for speciation antimony studies in natural waters, the most used are atomic absorption spectrometry (AAS)¹²⁻¹⁴ and atomic fluorescence spectrometry (AFS), coupled to hydride generation (HG).¹⁵⁻²⁰ The popularity of hydride generation atomic fluorescence spectrometry (HG AFS) is growing, due to its low instrumental cost, when compared with sophisticated techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) coupled to high performance liquid chromatography (HPLC), great sensitivity in the determination of antimony at trace levels and wide dynamic range.⁶ Wen and Zhu¹⁴ developed a method for antimony speciation, Sb^{III} and Sb^V, in soil and water samples, using ultrasound-assisted emulsification of solidified floating organic drop microextraction (USE-SFODME) and electrothermal atomic absorption spectrometry (ETAAS). The concentrations of Sb^{III} and Sb^V were 0.37 and 1.05 $\mu\text{g L}^{-1}$ for lake water and, for tap water, the concentrations of both species were below the detection limit (9.89 ng L^{-1}). Wu *et al.*²⁰ performed the simultaneous speciation of inorganic As and Sb in natural water, using online solid-phase extraction and HG AFS, and a limit of detection of 2.1 ng L^{-1} was achieved for Sb^{III}. Sea water, river water, lake water and groundwater samples were analyzed, the highest concentration of total antimony was found in groundwater (0.271 $\mu\text{g L}^{-1}$), and 0.213 $\mu\text{g L}^{-1}$ corresponded to Sb^{III}.

Deng *et al.*¹⁵ performed antimony speciation using HG AFS and 8-hydroxyquinoline as a masking agent. The speciation analysis was conducted in surface waters of three lakes, and Sb^{III} concentrations were low or non-detectable, whereas Sb^V concentrations ranged from 39.6 to 72.5 ng L^{-1} . Carneado *et al.*¹⁹ evaluated the influence of storage time and temperature on Sb migration from PET bottles into mineral water. Total antimony in mineral waters was determined using HG AFS and the speciation analysis was performed by high performance liquid chromatography hyphenated inductively coupled plasma mass spectroscopy (HPLC-ICP-MS). In this study, it was observed that Sb^V was the predominant species in the measured water and that, when bottles were stored at 60 °C, significant amounts of Sb migrated into the water, exceeding the maximum content established by the European Union²¹ (5.0 $\mu\text{g L}^{-1}$) after 15 days of storage.

Thus, this paper reports a rapid and sensitive analytical method, without a separation/pre-concentration step, for

the determination of total Sb and Sb^{III} in mineral water and natural surface water, using continuous flow of hydride generation and atomic fluorescence spectrometry. Multivariate design was applied for the optimization of variables that influence the system. The concentrations of antimony determined in natural waters collected in Salvador, Bahia, Brazil, were evaluated and discussed, taking into account the national and international current regulations and other data reported in the literature.

Experimental

Reagents and solutions

All reagents used in the experiments were of analytical grade. The solutions were prepared using ultrapure water obtained by purification system of a Milli-Q system (Millipore, Bedford, MD, USA). Standard antimony solutions used in the experiments were prepared by diluting a 1000 mg L^{-1} Sb^V stock solution (Merck, Germany). A 3 mol L^{-1} HCl solution used in all experiments was prepared from concentrated HCl (37% v v⁻¹, Merck). The reducing solution of 1.4% (m v⁻¹) sodium tetrahydroborate was prepared daily by dissolving appropriate amounts of solid NaBH₄ (Merck) in 0.5% (m v⁻¹) NaOH (Merck). For total Sb determination, pre-reducing solutions containing 2.0% (m v⁻¹) ascorbic acid and 10% (m v⁻¹) potassium iodide were used and daily prepared with ultrapure water. A certified reference material of river water to trace metal (SLSR-4) from the National Research Council of Canada (Ottawa, Canada) was used to evaluate the accuracy of the method.

Natural water sample: collection and storage

The proposed method was applied for the determination of total Sb and Sb^{III} in mineral water and natural surface water samples. Four mineral water samples (M1; M2; M3 and M4) were purchased in supermarkets of Salvador (Bahia, Brazil). These samples were stored at room temperature until analysis in their own marketing containers. Ten samples of surface natural water were collected on the same day in different water bodies of Salvador (Figure 1). Two samples were collected in Abaeté Lake, five in the pond of Pituacú Metropolitan Park and three in Tororó Lake. These samples were collected in decontaminated plastic bottles and, after collection, the samples were placed in a refrigerated container and transported to the laboratory, where they were analyzed on the same day.

Abaeté Lake is a pond much used for entertainment and tourism and is located in the environmental protection area

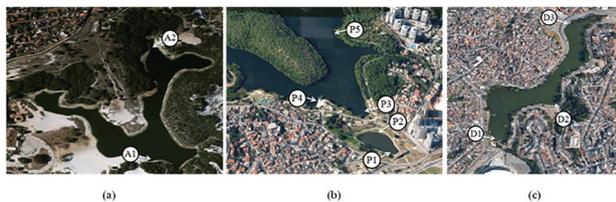


Figure 1. Surface natural water samples collected from: (a) Abaeté Lake; (b) Pituacú Metropolitan Park; (c) Tororó Lake. Images taken by Google Maps, 2016.

of the Metropolitan Park of Ponds and Dunes of Abaeté in Salvador, Bahia, Brazil. Pond of Pituacú is located in Pituacú Metropolitan Park, which is situated on the seafront and corresponds to the largest ecological reserve in the city of Salvador, Bahia. Tororó Lake is a lake artificially located in the city center and limited by different neighborhoods. It is a well wooded sports and leisure area.

Instrumentation

An Aurora Lumina 3300 atomic fluorescence spectrometer (Vancouver, Canada) fitted with an antimony hollow cathode lamp (HCL) of high intensity and with a quartz tube atomizer, was used to measure antimony fluorescence intensity. Argon with a purity degree of 99.996% (White Martins, São Paulo, Brazil) was used as the carrier gas of the generated hydride. The experimental conditions and operating parameters are summarized in Table 1.

Table 1. Settings and operating conditions of HG AFS for Sb determination

Parameter	Condition
Atomizer height / mm	8
Sb-HCL, wavelength / nm	217
Lamp current / mA	100
Flame composition	H ₂ /air
Argon flow rate (carrier gas) / (mL min ⁻¹)	400
Argon flow rate (auxiliary gas) / (mL min ⁻¹)	800
NaBH ₄ flow rate (reducing solution) / (mL min ⁻¹)	4
Sample flow rate / (mL min ⁻¹)	4
Read time / s	6

General procedure

The developed method used a continuous flow system for hydride generation. In this system, a peristaltic pump was used to drive the acidified sample and 1.4% (m v⁻¹) NaBH₄ solution, both at a flow rate of 4 mL min⁻¹, for a hydride generator, simultaneously. The volatile antimony hydride (SbH₃) and the hydrogen formed were transported

to gas-liquid separator and to the quartz cell (atomizer) with the aid of argon and finally, after the decomposition of the hydride in H₂/air flame, Sb was detected by AFS. The speciation analysis is based on the different kinetics of antimony hydrides generation from their different inorganic species. The inorganic Sb^{III} species reacts faster with sodium tetrahydroborate, preferably forming SbH₃.

For the determination of total Sb, 3.0 mL of the water sample, as well as 3.0 mL of 3 mol L⁻¹ HCl and 1 mL of pre-reducing solution (10% KI + 2% ascorbic acid), were added into a 10 mL volumetric flask. After 20 min, ultrapure water was added to reach a volume of 10 mL and this solution was then analyzed using the continuous flow system for hydride generation and AFS. For the determination of Sb^{III}, 3.0 mL of the water sample were acidified with 3 mL of 3 mol L⁻¹ HCl and diluted with 6 mL ultrapure water in a volumetric flask (10 mL), and then subjected to analysis. Sb^V was determined by the difference between the concentrations of total Sb and Sb^{III}.

Results and Discussion

Optimization of the experimental conditions for hydride generation

The experimental conditions were evaluated, firstly using a two-level full factorial design, which included the following factors: pre-reduction time (RT), hydrochloric acid concentration [HCl] and sodium tetrahydroborate concentration [NaBH₄]. The evaluated chemometric response was fluorescence intensity (FI), and the real and coded values of the factors along with the responses are shown in Table 2. All experiments were performed in a random order and employing 3 µg L⁻¹ Sb^{III} solutions.

Table 2. Full two-level factorial design, optimization of the procedure for Sb determination by HG AFS^a

Experiment	HCl / (mol L ⁻¹)	NaBH ₄ / % (m v ⁻¹)	RT / min	FI
1	-1 (3)	-1 (1)	-1 (10)	178.4
2	-1 (3)	-1 (1)	1 (30)	167.5
3	-1 (3)	1 (3)	-1 (10)	225.7
4	-1 (3)	1 (3)	1 (30)	218.1
5	1 (5)	-1 (1)	-1 (10)	86.6
6	1 (5)	-1 (1)	1 (30)	91.0
7	1 (5)	1 (3)	-1 (10)	195.6
8	1 (5)	1 (3)	1 (30)	189.2
9 (CP)	0 (4)	0 (2)	0 (20)	137.5
10 (CP)	0 (4)	0 (2)	0 (20)	135.7
11 (CP)	0 (4)	0 (2)	0 (20)	137.8

^a(CP): central point. RT: pre-reduction time; FI: fluorescence intensity.

The obtained data were processed using the Statistica 7.0 computer program. An evaluation of these results, considering the studied experimental dominions, revealed that the concentrations of sodium tetrahydroborate (effect: 76.27 ± 3.45) and hydrochloric acid (effect: -56.82 ± 3.43) were the factors that had the greatest significant effects on the generation of antimony hydrides. The interaction of these factors was also significant (effect: 27.32 ± 3.46), but the pre-reduction effect and all other interactions had a lower influence on the system. On the basis of these results, a Doehlert design, involving HCl and NaBH₄ concentrations, was performed, to find the critical conditions for antimony hydride generation. All experiments were conducted by fixing the pre-reduction time in twenty minutes and investigating the most significant factor (concentration of NaBH₄) in five levels and the concentration of HCl in three levels. The coded and real values established in the Doehlert design are shown in Table 3.

Table 3. Doehlert design, optimization of the procedure for Sb determination by HG AFS^a

Experiment	HCl / (mol L ⁻¹)	NaBH ₄ / % (m v ⁻¹)	FI
1	0.866 (5)	0.5 (1.8)	367
2	0.866 (5)	-0.5 (1.4)	660
3	0 (4)	-1 (1.2)	762
4	-0.866 (3)	-0.5 (1.4)	787
5	-0.866 (3)	0.5 (1.8)	434
6	0 (4)	1 (2.0)	167
7 (CP)	0 (4)	0 (1.6)	651
8 (CP)	0 (4)	0 (1.6)	643
9 (CP)	0 (4)	0 (1.6)	652

^a(CP): central point. FI: fluorescence intensity.

After processing the obtained results in a statistical program, a quadratic model without lack of fit was generated, which exhibited a response surface with a maximum fluorescence intensity at the experimental conditions of 3.07 mol L⁻¹ HCl and 1.24% (m v⁻¹) NaBH₄. Considering the optimization studies, the critical conditions for antimony hydride generation using continuous flow system and AFS were 20 min for pre-reduction time, 3 mol L⁻¹ for hydrochloric acid concentration and 1.2% for sodium tetrahydroborate concentration.

Analytical characteristics of the method

Several analytical parameters, such as limits of detection and quantification (LOQ), sensitivity, linearity and precision, were evaluated for the proposed method. With the use of optimized experimental conditions, the

method allowed the direct determination of antimony in natural waters with limits of detection and quantification of 9 and 30 ng L⁻¹, respectively. The precision of the method in terms of relative standard deviation (RSD, n = 7) was 3.3, 2.8 and 2.1% for standard antimony solutions of 5, 7 and 10 µg L⁻¹, respectively, and 4.4% for certified reference samples of river water with an antimony content of 0.23 ± 0.04 µg L⁻¹, showing good repeatability data. The calibration curve was linear in the range from 30 ng L⁻¹ to 10.0 µg L⁻¹, which showed the following regression equation $FI = 71.77C_{Sb} + 11.52$ (where C_{Sb} is reference at antimony concentration), with a correlation coefficient (r) of 0.9993. The accuracy of the proposed method was evaluated by the analysis of certified reference samples of river water (SLRS-4). There are no certified reference material available for analyses of speciation for Sb^{III}. Maybe the predominance of Sb^V in water samples is caused by species transformation after the sampling. The problematic are on the instability of Sb^{III} regarding oxidation. In certified reference material only the total Sb is available and this was used. The obtained result demonstrates agreement between the certificate (0.23 ± 0.04 µg L⁻¹) and found values (0.30 ± 0.09 µg L⁻¹), indicating that the proposed method is reliable and can be applied in studying matrices.

Application to natural waters

The proposed method was applied for speciation analysis of inorganic antimony in water samples. The chemical speciation of antimony consisted in the determination of total Sb after adding a pre-reducing solution (KI with ascorbic acid) into the sample and Sb^{III}, without adding this solution into the water sample. The concentration of Sb^V is achieved by the difference between the concentrations of total Sb and Sb^{III} in the analyzed samples. The results obtained for mineral and natural surface waters are shown in Table 4.

The results demonstrate that, for the analyzed mineral water, the concentration of total Sb that ranged from 0.26 ± 0.04 to 0.30 ± 0.08 µg L⁻¹ was lower than the maximum permissible values endorsed by the USEPA,⁸ which provides a reference value of 6 µg L⁻¹, as well as by Brazilian regulations,^{9,10} which stipulate a value of 5 µg L⁻¹, both for potable and bottled water. With the use of the developed method, it was not possible to estimate Sb^{III} concentrations in the samples, which were below the limit of quantification (0.03 µg L⁻¹). These results are in agreement with data reported in the literature for mineral water, for which average concentrations that ranged from 0.123 to 0.137 µg L⁻¹ for total Sb and 0.029 to 0.027 µg L⁻¹ for Sb^{III} was observed, when storage time in PET containers

Table 4. Determination of total Sb and Sb^{III} in mineral and natural surface waters collected in Salvador, Brazil (n = 3)

	Sb determined / ($\mu\text{g L}^{-1}$)	
	Total Sb	Sb ^{III}
Mineral water sample		
Mineral water 1 (M1)	0.27 ± 0.04	< 0.03 (LOQ)
Mineral water 2 (M2)	0.29 ± 0.04	< 0.03 (LOQ)
Mineral water 3 (M3)	0.26 ± 0.06	< 0.03 (LOQ)
Mineral water 4 (M4)	0.30 ± 0.08	< 0.03 (LOQ)
Natural surface water sample		
Abaeté Lake (A1)	0.41 ± 0.09	< 0.03 (LOQ)
Abaeté Lake (A2)	0.83 ± 0.10	< 0.03 (LOQ)
Pond of Pituauçú (P1)	0.82 ± 0.31	< 0.03 (LOQ)
Pond of Pituauçú (P2)	1.10 ± 0.07	< 0.03 (LOQ)
Pond of Pituauçú (P3)	0.62 ± 0.21	0.23 ± 0.11
Pond of Pituauçú (P4)	0.70 ± 0.12	< 0.03 (LOQ)
Pond of Pituauçú (P5)	0.87 ± 0.17	0.27 ± 0.09
Tororó Lake (D1)	1.22 ± 0.09	< 0.03 (LOQ)
Tororó Lake (D2)	0.99 ± 0.15	0.33 ± 0.07
Tororó Lake (D3)	1.23 ± 0.11	1.04 ± 0.18

LOQ: limit of quantification.

was extended. Extended storage results in sample contamination with Sb and in a significant conversion of Sb^{III} to Sb^V, the less toxic species.¹³

For natural surface water samples, the total Sb content ranged from 0.41 ± 0.09 to 1.23 ± 0.11 $\mu\text{g L}^{-1}$ and, for Sb^{III}, it ranged from < 0.03 (LOQ) to 1.04 ± 0.18 $\mu\text{g L}^{-1}$. The values found in this study are similar to those reported for natural waters in other studies,^{12,14,22} although the distribution and speciation of antimony in aquatic systems depend on the nearness of pollution sources and the physicochemical conditions of the environment. In general, the level of Sb^V depends on the redox status of the aquatic environment and Sb^{III} is characteristic of water with a low oxygen content.²²⁻²⁶ Finally, antimony concentrations did not exceed the maximum admissible content in freshwater bodies established by the Brazilian regulation (5.0 $\mu\text{g L}^{-1}$).¹¹

Average total Sb content in Abaeté Lake was 0.62 $\mu\text{g L}^{-1}$, presenting the lowest average among the locations studied. Pond of Pituauçu samples had an average value equivalent to 0.822 $\mu\text{g L}^{-1}$. Already, Tororó Lake samples had the highest average concentration of total Sb (1.15 $\mu\text{g L}^{-1}$). This result is likely because the Tororó Lake is the region with the largest urban influence and anthropogenic impact.

Conclusions

The present study presented a sensitive, accurate, fast and reliable procedure for the non chromatographic speciation of

inorganic antimony species in natural waters using continuous flow system and HG AFS. The multivariate techniques used in this study provided a quick and efficient optimization of the investigated factors that influence the determination of antimony using hydride generation. The concentrations of total Sb and Sb^{III} found in the analyzed natural surfaces and mineral waters were below the recommended by national and international regulatory agencies, and consistent with the results obtained by other studies involving watercourse bodies and mineral water.

Acknowledgments

The authors gratefully acknowledge the Brazilian agencies Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for grants and fellowships.

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Submitted: April 20, 2017

Published online: July 7, 2017