http://dx.doi.org/10.5935/0103-5053.20150062

J. Braz. Chem. Soc., Vol. 26, No. 5, 985-991, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Noteworthy Method for Direct Determination of Sb^{III} and Total Inorganic Antimony in Natural Waters

Thaís S. Neri,[a] Dayene C. Carvalho,[a] Vanessa N. Alves[b] and Nívia M. M. Coelho*,[a]

[a]*Institute of Chemistry, University of Uberlândia, Av. João Naves de Ávila 2121,*
38400-902 Uberlândia-MG, Brazil

[b]*Department of Chemistry, University of Goiás, Av. Dr. Lamartine Pinto de Avelar,*
1120 Setor Universitário, 75704-020 Catalão-GO, Brazil

A procedure was developed for the direct determination of Sb^{III} and total inorganic Sb in water samples by hydride generation atomic absorption spectrometry (HG AAS), without pre-reduction of Sb^{V}. The $NaBH_4$ concentration was maintained at 0.4% (m/v) to perform the selective generation of stibine from Sb^{III} and online stibine generation was carried out with 5.0% (m/v) $NaBH_4$ to obtain the total antimony concentration. Sb^{V} was calculated as the difference between the values obtained for total Sb and Sb^{III}. In both cases, the procedure did not appear to be adversely affected by potential interferents such as Sb^{V}, As^{III}, As^{V}, Ca^{II}, Na^{I}, chloride and phosphate at a concentration of 0.5 mg L^{-1}. For the proposed procedure, the detection limits were 0.2 µg L^{-1} for Sb^{III} and 0.3 µg L^{-1} for total Sb, while the relative standard deviations were 0.1% for 10.0 µg L^{-1} Sb^{III} and 0.4% for 10.0 µg L^{-1} total Sb. A sampling rate of approximately 30 determinations *per* hour was achieved, requiring 300 mL of $NaBH_4$, and the amount of waste generated was in order of 960 mL, indicating that this analytical procedure can be considered as green. The method was shown to be satisfactory for the determination of trace levels of antimony in water samples. The result obtained for the assaying of certified drinking water samples was 9.7 ± 0.1 µg L^{-1} (certified value 10.0 ± 0.5 µg L^{-1}).

Keywords: antimony speciation, selective generation, HG AAS, water analysis

Introduction

The toxicity of antimony and its compounds is a matter of concern worldwide.[1] The World Health Organization[2] and United States Environmental Protection Agency[3] have established maximum admissible concentrations for antimony in drinking water of 20 and 6 µg L^{-1}, respectively. In general, inorganic antimony is more toxic than organic antimony and, moreover, the trivalent species is 10 times more toxic than the pentavalent species. This is because Sb^{III} shows a high affinity for red blood cells and sulfhydryl groups in cell constituents, while erythrocytes are almost impermeable to Sb^{V}.[4]

Nowadays, this metalloid is widely employed in several applications including in brake linings and as an additive in the rubber vulcanization process.[5-8] Also, organic antimony compounds are used for the preparation of flame retardants. In the biomedical field, antimony compounds are used as therapeutic agents to treat parasitic diseases such as *Leishmaniasis* and *Bilharziasis*.[9] Antimony is found in nature mainly as sulfide stibnite (Sb_2S_3). Considering the widespread industrial use of the various forms of Sb and their differences in toxicity, it is essential to develop analytical methods for their quantification.

Some previous papers describe experimental procedures for the determination of Sb^{III} and Sb^{V}, where Sb^{V} was determined after pre-reduction to Sb^{III}.[10,11] The reducing agents typically applied to convert Sb^{V} to Sb^{III} are potassium iodide and L-cysteine, and the former is the most widely used even though it is associated with several problems.[12] Potassium iodide requires relatively strong acidic conditions for both the sample and the reducing medium and the high concentrations applied can lead to the generation of considerable levels of iodine, which is especially disadvantageous in cases where the quantification of the analyte is carried out via hydride generation (HG) and atomic absorption spectrometry (AAS). In addition, the use of L-cysteine as a pre-reductant is advantageous

---

*e-mail: nmmcoelho@ufu.br

because it allows the reduction to proceed under mildly acidic conditions.[13-15]

HG combined with AAS as the detection technique has been frequently used for the direct determination of Sb in several different types of samples.[16-23] Some authors have demonstrated that the response obtained for Sb^V is around 50-80% lower than that obtained for Sb^{III} and it has been suggested that in the process of stibine formation from Sb^V, the Sb^V is firstly reduced to Sb^{III} with the subsequent formation of SbH_3.[24]

The aim of this study was to develop a method for the direct determination of trace amounts of Sb^{III} and total Sb by hydride generation atomic absorption spectrometry (HG AAS) without an Sb^V pre-reduction step. The determination of inorganic antimony species in water matrices using the proposed method is recommended, based on the fact that the Sb^{III} species shows significantly higher signal intensity at low sodium tetrahydroborate ($NaBH_4$) concentrations than the Sb^V species. The sodium tetrahydroborate concentration used for the determination of Sb^{III} was 0.4% (m/v) and notable interference was not observed at a concentration of 0.5 mg L^{-1} Sb^V. Since a flow system was employed, it is possible to perform the online generation of stibine with 5.0% (m/v) $NaBH_4$ in the same system used to obtain the total antimony concentration. The Sb^V is determined as the difference between the values obtained for the total antimony and Sb^{III}. The optimal conditions for the hydride generation and atomization of Sb^{III} were investigated. The method is suitable for application in routine analysis and monitoring studies.

Experimental

Instrumentation

For the antimony determination, a flame atomic absorption spectrophotometer (Varian, SpectrAA-220, Victoria, Australia) equipped with a continuous flow Varian VGA 77 vapor generation accessory was used. The VGA system consists of a three-channel peristaltic pump equipped with Tygon and polyethylene tubes that carry the sample through a reaction coil, where it is acidified and mixed with a suitable reductant. The stibine vapor formed is transferred to an absorption cell for determination by the spectrometer. The antimony hollow cathode lamp (Varian, Victoria, Australia) was operated at 7.0 mA, the wavelength was set at 217.6 nm and the spectral band pass was set at 0.1 nm. The analysis was carried out with a burner height of 17 mm, acetylene flow rate of 2.0 L min^{-1} and air flow rate of 13.5 L min^{-1}. The sample, HCl, $NaBH_4$, and nitrogen gas were introduced at flow rates of 4.0, 7.0, 5.0 and 100 mL min^{-1}, respectively. The instrumental parameters used for the VGA 77 were those recommended by the manufacturer. The reaction time obtained after optimization was 60 s.

Reagents and solutions

All chemicals and reagents used were of analytical grade or higher purity and deionized water obtained from a water purification system (Gehaka, São Paulo, Brazil) was used throughout. Before use, laboratory glassware was kept overnight in 10% (v/v) nitric acid (aqueous solution) followed by ultra-sonication for 1 h and final rinsing with deionized water. Working standard solutions of Sb^{III} and Sb^V were all prepared daily through the appropriate dilution of 1000 mg L^{-1} $SbCl_3$ (Merck, Darmstadt, Germany) and 1000 mg L^{-1} $SbCl_5$ (Merck, Darmstadt, Germany) stock solutions, respectively. These solutions were stored in polyethylene bottles in a refrigerator at 4 °C. Sodium tetrahydroborate solutions were prepared daily from 97% $NaBH_4$ (Fluka, Switzerland) in 0.4% (m/v) NaOH (Merck, Darmstadt, Germany) solution to give stability since $NaBH_4$ decomposes easily. A solution of 5% (v/v) HCl was prepared through dilution of concentrated hydrochloric acid in water (Merck, Darmstadt, Germany).

Study of the experimental variables

Since $NaBH_4$ is used directly in the HG system for stibine generation and high concentrations of reductant are able to reduce total Sb to Sb^{III} and, in turn, to stibine, a study was conducted to compare the analytical signal obtained from Sb^V and Sb^{III} solutions, separately. In order to evaluate the effect of sodium tetrahydroborate concentration on the analytical signal for solutions containing 10 µg L^{-1} Sb^{III} or Sb^V, the sodium tetrahydroborate concentration was evaluated in the range of 0.1 to 10.0% (m/v). The sodium tetrahydroborate flow rate was maintained at 5.0 mL min^{-1} and the HCl concentration at 5.0% (v/v). The optimization of the parameters affecting the antimony determination by HG AAS was performed using a univariate method. Other variables studied were the sample and sodium tetrahydroborate flow rates and the HCl concentration.

Study on interfering ions

In order to investigate the selectivity of the proposed method, the determination of Sb^{III} in the presence of possible interferences was investigated. For this purpose, experiments were conducted using a 2^{7-3} fractional factorial design and the results analyzed by calculating the interference factor. The influence of potentially interfering ions (Sb^V, As^{III}, As^V,

Ca^{II}, Na^{I}, Cl^{-}, PO_4^{3-}) was verified by comparing the analytical signals of a solution containing only Sb^{III} and a solution containing Sb^{III} ions together with potentially interfering ions. In this study, a specie was considered as an interferent in the Sb^{III} determination by the proposed procedure when the difference between the analytical signal for the solution containing only Sb^{III} ions and that also containing the possible interfering ions was higher than 10%. Thus, the interference factor, IF, is defined by equation 1:

$$IF = A'/A \qquad (1)$$

where A' is the analytical signal for the solution containing the analyte in the presence of possible interferents, and A is the analytical signal for the solution containing Sb^{III} in the absence of possible interferents. An interference factor of 1.00 indicates that there is no interference, while factors greater than 1.10 or smaller than 0.90 indicate an increase or a decrease in the analytical signal due to interference. Other ions present in the certified sample (APS 1075), such as Ni, Cu and Zn, showed no interference in amounts 6, 2 and 7-fold higher than the total Sb value, respectively.

Samples

Mineral water samples were obtained from local store. For the recovery tests, the samples were spiked with Sb^{III} and Sb^{V} at a concentration of 10.0 μg L^{-1}. The accuracy was also determined using samples of certified drinking water (APS-1075). This certified reference material was obtained from Alpha Resources Inc. (Stevensville, Michigan, USA). The proposed procedure was also applied to sea water samples from Itaguá Beach (Ubatuba, SP, Brazil), Lamberto Beach (Ubatuba, SP, Brazil) and Fortaleza Beach (Ubatuba, SP, Brazil) and river water samples of two different locations along the Uberabinha River, which runs through an urban zone in the city of Uberlândia (Minas Gerais, Brazil). In addition, the proposed procedure was also applied to sediment samples collected from Itaguá Beach (Ubatuba-SP). These samples were subjected to the Bureau Commune de Reference (BCR) sequential extraction method (4th extraction stage) proposed by the European Community Bureau of Reference.[25]

Results and Discussion

Evaluation of antimony hydride generation conditions

The conditions for HG were optimized to obtain maximum sensitivity and reproducibility of the method. Figure 1 shows the results for the system.

The efficiency of the antimony hydride generation was investigated using 6.0% (v/v) HCl at different flow rates from 1.0 to 9.0 mL min^{-1}. The results indicate an increase in the absorbance signal with an increase in the flow rate up to 7.0 mL min^{-1} (Figure 1a). At higher flow rates, the signal decreased since the sample and the reagent did not have sufficient time to mix. Lower flow rates were not sufficient to generate atomic hydrogen in adequate quantities to react with BH_4^- efficiently,[26] while at higher flow rate, excessive formation of H_2 occurs interfering in the analytical signal.[26-28] Thus, the most appropriate hydrochloric acid flow to ensure the formation of a sufficient amount of stibine was 7.0 mL min^{-1}.

Sodium tetrahydroborate flow rates ranging from 1.0 to 12.0 mL min^{-1} were evaluated. The analytical signal was relatively low when the sodium tetrahydroborate flow rate was less than 5.0 mL min^{-1}. For flow rates above 5.0 mL min^{-1} there was a slight decrease in the analytical signal, and above 7.0 mL min^{-1} a sharp decrease was observed (Figure 1b). This can be explained by the formation of H_2 gas in excess, resulting in dilution of the stibine formed, allowing the hydrides to reach the atomization cell. Thus, the flow of sodium tetrahydroborate solution was maintained at 5.0 mL min^{-1}.

Another important factor to be studied is the sample flow rate. Although a high flow rate is preferable in order to achieve higher sampling frequency, the sample flow rate is limited by the reaction in the hydride generation system and the capacity of the pumping system to maintain a stable flow under high pressures. The sample flow rate was studied in the range of 1 to 10 mL min^{-1}. The analytical signal increased until a sample flow rate of 4.0 mL min^{-1} and from then on, it remained almost constant up to 8.0 mL min^{-1}, after which it decreased (Figure 1c). This decrease is related to the greater amount of Sb^{III} introduced into the gas-liquid separator when high sample flow rates are used, and the $NaBH_4$ is not sufficient to reduce the whole amount of sample present and generate stibine. Thus, the sample flow was set at 4.0 mL min^{-1}.

The experimental conditions for the determination of Sb^{III} and Sb^{V} were established for the selective generation of stibine from Sb^{III} and online stibine generation to obtain the total antimony concentration. The hydride generation parameters evaluated were the $NaBH_4$ and HCl concentrations. Each parameter was evaluated for each antimony species using 10 μg L^{-1} Sb^{III} and Sb^{V} solutions.

The $NaBH_4$ concentration is an important parameter for the generation of stibine, because it is formed in the presence of hydrogen generated by $NaBH_4$ in an acidic medium. In this case, H_2 acts as a stripping gas, besides acting in the formation of stibine. Since the amount of H_2

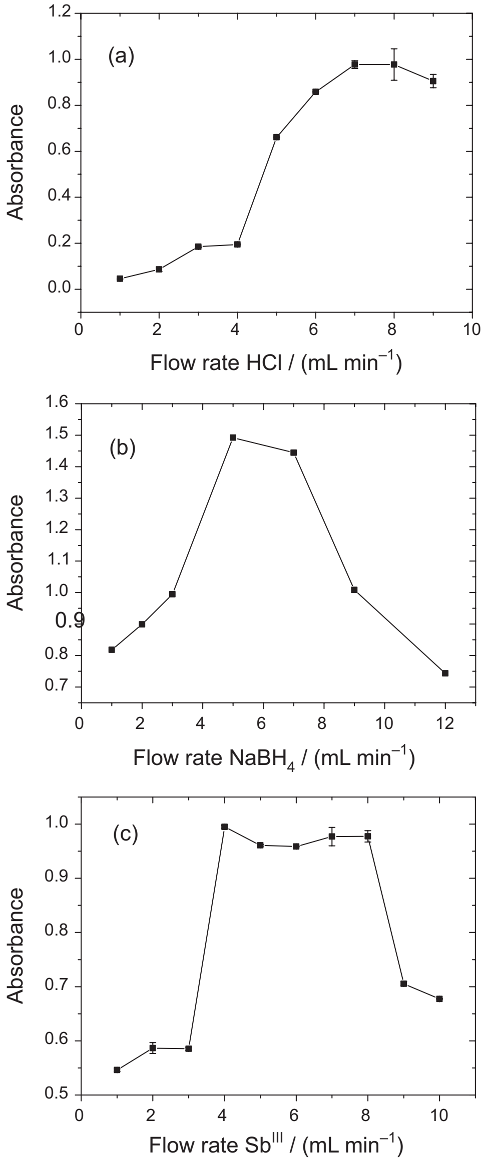

Figure 1. Optimization of the following HG conditions: (a) HCl flow rate, (b) NaBH$_4$ flow rate and (c) sample flow rate.

present is dependent on the NaBH$_4$ and HCl flow rates and concentrations, all of these parameters need to be studied. Figure 1 shows that the generation of hydride from Sb^{V} leads to slower stibine generation compared with Sb^{III}, making it necessary to increase the NaBH$_4$ concentration in order to compare the results obtained for the two species. Results show that the absorbance increases with an increase in the NaBH$_4$ concentration in the determination of both inorganic antimony forms (Figure 2). However, the response obtained for Sb^{V} is lower than that obtained for Sb^{III}. The results of previous studies suggest that in the process of stibine formation from Sb^{V}, there is firstly the reduction of Sb^{V} to Sb^{III} with the subsequent formation of SbH$_3$.[24] A NaBH$_4$ concentration higher than 0.4% (m/v) is required to obtain complete antimony hydride generation from both Sb^{III} and Sb^{V}, while a NaBH$_4$ concentration higher than 5.0% (m/v) is needed for stibine hydride generation from Sb^{V}. These results demonstrate that the determination of Sb^{III} and Sb^{V} is possible under these conditions. The Sb^{III} was determined under conditions where there was no hydride generation from Sb^{V}. Thus, a NaBH$_4$ concentration of 0.4% (m/v) was selected in order to obtain the best analytical performance. The total antimony concentration was determined in the same flow system using a NaBH$_4$ concentration of 5.0% (m/v).

The effect of varying the HCl concentration on the analytical signal for Sb^{III} and Sb^{V} was investigated from 0.05 to 10.0% (v/v) HCl. The signals related to Sb^{III} and Sb^{V} increased up to a concentration of 6.0% (v/v) HCl. The sensitivity was not significantly different on comparing 6.0 and 10.0% (v/v) HCl and, thus, 6.0% (v/v) HCl was chosen for further measurements.

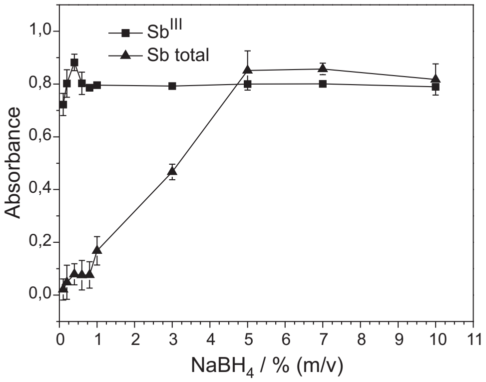

Figure 2. Behavior of the analytical signal for Sb^{III} and total Sb as a function of the total variation in the concentration of NaBH$_4$.

Comparative tests for efficiency of the reduction of Sb^{V}

Since the use of NaBH$_4$ at high concentrations proved to be effective in reducing Sb^{V} and the total antimony could be determined without a pre-reduction step, a study was conducted to evaluate the effectiveness of this reagent in comparison with L-cysteine. For this, two calibration curves with concentrations ranging from 0 to 10 µg L^{-1} Sb^{V} were constructed. The calibration curve obtained when the reduction was performed online using 5.0% (m/v) NaBH$_4$ was compared with that obtained for Sb^{V} solutions subjected to a pre-reduction step with L-cysteine. It was observed that the analytical signals obtained for the Sb^{V} determination using the proposed method are similar to those obtained when performing the pre-reduction step.

Studies of interfering ions

The effects of representative potential interferents that are known to affect the hydride process were determined, i.e., Sb^{V}, As^{III}, As^{V}, Ca^{II}, Na^{I}, Cl^{-} and PO_4^{3-}. To investigate the extent of their effect on the determination of antimony, 10 µg L^{-1} of Sb^{III} was spiked with increasing levels of these potential interferents and values for the interference factor were calculated for each experiment (data not shown). A considerable signal depression was observed for all interfering ions when present in a fifty-fold excess. Sb^{III} can be tolerated without interference up to a 25-fold excess.

Analytical figures of merit and application

The equations for the calibration curves obtained for aqueous standard solutions of Sb^{III} and Sb^{V} were: $A = 0.023 + 0.056[Sb^{III}]$ and $A = 0.001 + 0.050[Sb^{V}]$, where A is the absorbance and the Sb concentration is expressed as µg L^{-1}. The correlation coefficients for the calibration curves were 0.9984 and 0.9997, respectively. For the Sb^{III} determination, 0.4% (m/v) $NaBH_4$ was used and for the Sb^{V} determination, 5.0% (m/v) $NaBH_4$ was used. The calibration curves were linear up to a concentration range of 0.7-50.0 µg L^{-1} for Sb^{III} and 0.7-50.0 µg L^{-1} for Sb^{V}. The detection limits based on $3\sigma/m$, where σ is the standard deviation of 10 measurements of a blank and m the slope of the calibration curve, were 0.2 µg L^{-1} for Sb^{III} and 0.3 µg L^{-1} for total Sb. Based on ten measurements (n = 10), relative standard deviations of 0.1% for 10 µg L^{-1} Sb^{III} and 0.4% for 10 µg L^{-1} total antimony were obtained, demonstrating excellent repeatability. The analytical frequency was 30 samples *per* hour. The $NaBH_4$ consumption was around 300 mL and waste generation in the order of 960 mL h^{-1}. Thus, the determination of Sb in water samples by HG AAS represents an acceptable green analysis procedure. Its rank on the Eco-Scale (71) results from the minimal amounts of reagents used and waste generated.[28]

The proposed method was applied to the quantification of antimony in mineral, sea and river water samples (Table 1). Sb^{III} was not detected in these samples and Sb^{V} was detected in sea and river water samples. To validate the method for the analysis of water, two samples were spiked with Sb^{III} and Sb^{V} to give a final concentration of 10.0 µg L^{-1} of Sb^{III} and Sb^{V}. As can be seen in Table 1, recovery percentages of 98.8 to 103.7% were obtained. The results for sediment samples collected at Itaguá Beach (Ubatuba-SP) were in the range of 2.8 ± 0.5 µg L^{-1} to 3.8 ± 0.5 µg L^{-1} total Sb. Sb^{III} was not detected in these samples.

The accuracy of the method was evaluated by analyzing drinking water reference material APS 1075 with a certified inorganic antimony concentration of 10.0 ± 0.5 µg L^{-1}. The result obtained for total Sb was 9.7 ± 0.1 µg L^{-1} and Sb^{III} was not detected. These results are in good agreement with the certified values, confirming the reliability of the proposed method.

In this study, the proposed method was described and compared, according to the detection technique used. Important details related to previously published procedures for Sb^{III} and total Sb determination are given in Table 2. Most of these methods were applied to the analysis of antimony in environmental samples (water, sediment and particulate

Table 1. Experimental recovery of antimony in water samples spiked with 10.0 µg L^{-1} of Sb^{III} and Sb^{V} by HG AAS

Sample	Sb^{III} added / (µg L^{-1})	Sb^{III} found / (µg L^{-1})	Recovery / %	Sb^{V} added / (µg L^{-1})	Sb^{V} found / (µg L^{-1})	Recovery / %
A	–	N.D.	–	–	N.D.	–
	10	9.88	98.8	10	9.99	99.9
B	–	N.D.	–	–	N.D.	–
	10	9.98	99.8	10	10.37	103.7
C	–	N.D.	–	–	1.00	–
	10	9.99	99.9	10	9.82	88.2
D	–	N.D.	–	–	N.D	–
	10	9.78	97.8	10	10.18	101.8
E	–	N.D.	–	–	N.D	–
	10	8.86	88.6	10	8.95	89.5
F	–	N.D.	–	–	N.D	–
	10	8.56	85.6	10	10.47	104.7
G	–	N.D.	–	–	0.90	–
	10	9.42	94.2	10	9.98	90.8

A and B: mineral water samples; C, D and E: sea water samples from Itaguá Beach (Ubatuba, SP, Brazil), Lamberto Beach (Ubatuba, SP, Brazil) and Fortaleza Beach (Ubatuba, SP, Brazil), respectively. F and G: river water samples of two different locations along the Uberabinha River, which runs through an urban zone in the city of Uberlândia (Minas Gerais, Brazil). N.D.: not detectable.

Table 2. Comparison of methods for determination of Sb^{III} and Sb^{V} using hydride generation

Sample	Specie	Reduction step	Detection	LOD / (µg L^{-1})	Ref.
Soil, sediment	Sb^{III} Sb^{V}	L-cysteine	HG IAT F AAS	0.2	10
Particulate matter	Sb_{tot} Sb^{V}	–	HG QT AAS	0.3 0.2	16
Food packaging materials	Sb^{III}	L-cysteine	CPE ET AAS	0.02	27
Water	Sb^{III} Sb^{V}	Selective sorption	GF AAS	0.18 0.25	28
Water	Sb^{III}/ Sb^{V}	$NaBH_4$	HG F AAS	0.2 0.3	This study

HG IAT F AAS: hydride generation by integrated atom trap flame atomic absorption spectrometry, HG QT AAS: hydride generation quartz tube atomic absorption spectrometry, CPE ET AAS: cloud point extraction electrothermal atomic absorption spectrometry, GF AAS: graphite furnace atomic absorption spectrometry; LOD: limit of detection.

matter). To compare the method proposed herein, the limit of detection was taken into account. The lowest limit of detection reported for the previously published methods in Table 2 is 0.02 µg L^{-1}. However, these methods often require tedious sample pre-treatment procedures such as preconcentration and extraction steps.[29,30] It can be observed that the method described herein shows better or similar performance when compared with previously published procedures in terms of the limit of detection. Furthermore, the method does not require the use of a pre-reduction step and offers the advantage of selective determination.

Conclusions

The use of the HG AAS system described herein was found to be effective for the determination of Sb^{III} and Sb^{V}. The use of HG AAS provides adequate sensitivity and accuracy for the direct determination of antimony (Sb^{III} and Sb^{V}) in water samples using the same flow system, thereby avoiding the tedious reduction procedures required for the determination of Sb^{III} and Sb^{V} by previously published methods. Since the pre-reduction step is eliminated, the need for sample handling and therefore the risk of contamination are reduced. The number of samples that can be analyzed *per* hour is 30. $NaBH_4$ consumption is around 300 mL and waste generation is in the order of 960 mL h^{-1}, indicating that this can be considered as a green analysis procedure. As a result, this is an attractive technique for the routine determination of trace amounts of antimony in water samples.

Acknowledgments

The authors are grateful for financial support from the Brazilian Federal Governamental and State funding agencies: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

References

1. Amarasiriwardena, D.; Wu, F. C.; *Microchem. J.* **2011**, *97*, 1.
2. World Health Organization (WHO); *Guidelines for Drinking-Water Quality*, 4th ed., WHO Library Cataloguing-in-Publication Data: Geneva, 2011.
3. http://water.epa.gov/drink/contaminants/ accessed on March 11, 2015.
4. He, M. C.; Wang, X. Q.; Wu, F. C.; Fu, Z. Y.; *Sci. Total Environ.* **2012**, *421*, 41.
5. Santos, E. J.; Herrmann, A. B.; Prado, S. K.; Fantin, E. B.; Santos, V. W.; Oliveira, V. M.; Curtius, A. J.; *Microchem. J.* **2013**, *108*, 233.
6. Fujiwara, F.; Rebagliati, R. J.; Marrero, J.; Gomez, D.; Smichowski, P.; *Microchem. J.* **2011**, *97*, 62.
7. Nomngongo, P. N.; Ngila, J. C.; Kamau, J. N.; Msagati, T. A. M.; Moodley, B.; *Talanta* **2013**, *110*, 153.
8. Dessuy, M. B.; Kratzer, J.; Vale, M. G. R.; Welz, B.; Dedina, J.; *Talanta* **2011**, *87*, 255.
9. Sundar, S.; Chakravarty, J.; *Int. J. Environ. Res. Public Health* **2010**, *7*, 4267.
10. Matusiewicz, H.; Krawczyk, M.; *J. Anal. At. Spectrom.* **2008**, *23*, 43.
11. Hong, W.; Xuecui, W.; Bing, L.; Yueling, L.; Shanshan, L.; Jusheng, L.; Jiuying, T.; Wenfeng, Z.; Zonghui, Y.; *Spectrochim. Acta, Part B* **2011**, *66*, 74.
12. Kamlesh, S.; Kavita, A.; Neetu, H.; *J. Hazard. Mater.* **2008**, *155*, 173.
13. Mihaltan, A. I.; Frentiu, T.; Ponta, M.; Petreus, D.; Frentiu, M.; Darvasi, E.; Marutoiu, C.; *Talanta* **2013**, *109*, 84.

14. Gonzalvez, A.; Cervera, M. L.; Armenta, S.; De la Guardia, M.; *Anal. Chim. Acta* **2009**, *636*, 129.
15. Pitzalis, E.; Mascherpa, M. C.; Onor, M.; D'Ulivo, A.; *Spectrochim. Acta, Part B* **2009**, *64*, 309.
16. Ferreira, S. L. C.; Macedo, S. M.; Santos, D. C.; Jesus, R. M.; Santos, W. N. L.; Queiroz, A. F. S.; Andrade, J. B.; *J. Anal. At. Spectrom*. **2011**, *26*, 1887.
17. Lopez-Garcia, I.; Rivas, R. E.; Hernandez-Cordoba, M.; *Talanta* **2011**, *86*, 52.
18. Chen, Y. W.; Belzile, N.; *Anal. Chim. Acta* **2010**, *671*, 9.
19. Fornieles, A. C.; Torres, A. G.; Alonso, E. V.; Cordero, M. T. S.; Pavon, J. M. C.; *J. Anal. At. Spectrom.* **2011**, *26*, 1619.
20. Yousheng, Y.; Jianchi, S.; Hongbing, M.; Guanhong, T.; *Talanta* **2010**, *81*, 1502.
21. Semira, Y. U.; Şerife, Y.; *Anal. Chim. Acta* **2013**, *770*, 7.
22. Morgana, D. B.; Jan, K.; Maria, R. G. V.; Bernhard, W.; Jiří, D.; *Talanta* **2011**, *87*, 255.
23. Long, Z.; Chen, C.; Hou, X. D.; Zheng, C. B.; *Appl. Spectrosc. Rev*. **2012**, *47*, 495.
24. Ferreira, S. L. C.; Santos, W. N. L.; Santos, I. F.; Junior, M. M. S.; Silva, L. O. B.; Barbosa, U. A.; Santana, F. A.; Queiroz, A. F.; *Microchem. J*. **2014**, *114*, 22.
25. Ure, A. M.; Quevauviller, P. H.; Muntau, H.; Griepink, B.; *Int. J. Environ. Anal. Chem.* **1993**, *51*, 133.
26. Emur, H.; Yasemin, I.; Miray, K.; Nur, A.; Onur, Y.; Tülin, D. C.; Raif, I.; *Spectrochim. Acta, Part B* **2011**, *66*, 793.
27. Quiroz, W.; Ariasa, H.; Bravo, M.; Pinto, M.; Lobos, M. G.; Cortés, M.; *Microchem. J.* **2011**, *97*, 78.
28. Gałuszka, A.; Konieczka, P.; Migaszewski, Z. M.; Namiesnik, J.; *TrAC, Trends Anal. Chem.* **2012**, *37*, 61.
29. Jiang, X.; Wen, S.; Xiang, G.; *J. Hazard. Mater*. **2010**, *175*, 146.
30. Zih-Perényi, K.; Jankovics, P.; Sugár, É.; Lásztity, A.; *Spectrochim. Acta, Part B* **2008**, *63*, 445.

Submitted: November 25, 2014