Turk J Chem
24 (2000) , 371 – 376.

HPLC/Hydride Generation AAS Coupling for the Speciation of Sb(III) and Sb(V) in Wastewaters

Nuray SATIROĞLU, Sema BEKTAŞ and Ömer GENÇ*
Department of Chemistry, Hacettepe University,
Beytepe, 06532, Ankara-TURKEY
Haydar HAZER
Ministry Of Environment, Eskişehir Yolu 8. Km.,
06532, Ankara-TURKEY

Received 10.03.2000

A comparative study was made with two HPLC columns of different lengths (PRP-X 100, 250 mm × 4.1 mm id and PRP-X 100, 100 mm × 4.1 mm id) coupled to HGAAS for the speciation of inorganic Sb(III) and Sb(V) species. The effects of eluent concentration and pH on the retention times of Sb species in both columns were investigated. The separation of Sb species was realized by using 50 mmol/L citrate solution at pH 4.0 as the eluent. The retention times were 2.0 min and 10.0 min in the 250 mm column, and 1.4 min and 3.6 min in the 100 mm column for Sb(V) and Sb(III) respectively. The hydrides were produced by adding 1% $NaBH_4$ and 5.0 mol/L HCl solutions. The absorbance was linearly related to the Sb(V) concentration in the range 2.0-100 μg/L and to the Sb(III) concentration in the range 4.0-100 μg/L. The detection limits obtained for Sb(V) and Sb(III) were 1.0 and 0.8 μg/L respectively. Since certified standards for antimony in aqueous solutions are not currently available, the accuracy of the method was checked by the analysis of both species in several spiked water samples. The optimized experimental conditions were applied for the speciation and determination of the species in mining industry wastewaters.

Introduction

Antimony is used for various alloys with lead and other metals, for semiconductors and for thermoelectrical devices; antimony compounds are quite widely employed, especially as pigments. Occupational antimony exposures occur in the mining and refining of the metal and in the production of pewter, solder, storage battery plates and babbit metal. Exposure to antimony compounds has been reported from production of abrasives, textile dyeing, and handling of pigments and catalysts. Antimony-containing pharmaceuticals (antimony pentasulfide as cough medicine, and tartar emetic or stibophen against leishmaniasis and schistosomiasis) are still in wide use in certain parts of the world. The medical literature on antimony mainly deals with the use of organic compounds as therapeutic agents, and much less information is available on the significance of environmental and occupational exposures[1]. Several reports on health effects related to

*Corresponding author,

occupational antimony exposures are difficult to evaluate, because arsenic may have occurred as a contaminant and may have been responsible for some of the caustic and irritant effects. While cardiotoxicity has been documented to be a side effect of antimony pharmaceuticals, few reports of ECG (electrocardiogram) changes related to occupational exposures have been published. More commonly, antimony compounds have given rise to irritation of the mucous membranes, irritant eczema, and even chemical burns and perforation of the nasal septum. In particular, antimony trioxide frequently causes the so-called antimony spots, i.e., small, erythematous papules which develop with intense itching on exposed, moist skin areas in hot environments; they are fortunately short lasting. A simple benign pneumoconiosis is related to antimony exposures, but free silica may have been a partial cause in some of the more serious cases reported[2]. The carcinogenic potential of this metal is probably limited, but a relation to increased frequency of spontaneous abortions has been reported in one study. In the presence of strong acid, stibine (SbH_3) may be formed. Storage battery workers and metal etchers may be exposed to this hazard. This gas is very toxic and causes severe hemolysis, shock, central nervous system symptoms, and even death due to anuria. Most absorbed antimony is rather rapidly excreted, Sb(V) mostly in the urine and Sb(III) mostly via the gastrointestinal tract. A slow compartment seems to exist, and accumulation in the liver, kidneys, thyroid, and adrenals has been indicated.

Most of the efforts undertaken have been based on the determination of total antimony concentration[3–5]. However, as Sb(III) compounds are more toxic and produce a stronger irritative action than Sb(V) compounds, speciation of different forms of Sb species in environmental samples are necessary. Although many methods are available for the speciation of Sb, e.g., by the complexing ability of one of their oxidation states[6], by hydride generation or cold-trapping[7,8], or by chromatography[9], the methods are essentially based on the determination of total Sb, evaluating Sb(V) by difference. There is a very limited number of studies proposing analytical procedures which can simultaneously separate and measure Sb(III) and Sb(V) in one step.

Smichowsky et al.[10] proposed a method of high performance liquid chromatography (HPLC) coupled to hydride generation atomic absorption spectrometry (HGAAS) and inductively coupled plasma mass spectrometry (ICP-MS) for the speciation of Sb(III) and Sb(V) species in natural water samples. This method offers the advantage of on-line separation and determination of inorganic Sb(III) and Sb(V) species. Zhang et al.[11] used a miniaturized HPLC column coupled to HGAAS for the speciation of inorganic Sb(III) and Sb(V) species in spiked water samples. Although they obtained very short retention times, 0.5 and 2.8 minutes for Sb(V) and Sb(III) respectively, their detection limits were not sufficiently sensitive to measure real levels in natural waters.

The aim of the present study was to optimize the experimental conditions for speciation and determination of Sb(III) and Sb(V) in one step and to apply the optimized conditions for real wastewater samples, which have not appeared in the literature. The wastewater was obtained from Balya, a small town the Aegean region, where mining operations have been carried out since 1910.

Experimental

Reagents

All chemicals were of analytical grade or higher purity, and deionized water from a milli-Q system (Millipore) was used.

Standard Sb(III) solution: 1000 ng/mL was prepared by dissolving 0.2740 g of potassium antimonyl tartrate (Janssen Chimica, Beerse, Belgium) in deionized water and diluting to 100 mL. Working solutions were prepared daily.

Standard Sb(V) solution: 1000 ng/mL was prepared by dissolving 0.2160 g of potassium pyroantimonate (Aldrich, Milwaukee, WI, USA) in deionized water and diluting to 100 mL. Working solutions were prepared daily.

$NaBH_4$ 1% (w/v) solution was prepared by dissolving $NaBH_4$ powder (Aldrich) in deionized water and stabilizing in 1.0% (w/v) NaOH. Solutions were filtered before use to eliminate turbidity.

Citrate solution was prepared with sodium citrate (Janssen Chimica) at a concentration of 50 mmol/L.

Instrumentation

A Waters 510 HPLC system, consisting of two Waters 510 pumps and a Waters automatic injector, was used for chromatic separations. Two PRP-X 100 anion exchange columns (250 mm × 4.1 mm id and 100 mm × 4.1 mm id), with 10 mm particle size were used.

A Unicam 939 Atomic Absorption Spectrometer equipped with a VP-90 hydride generation system was used for all measurements. The HPLC column was connected to the HGAAS system by a polytetrafluoroethylene tube. A schematic diagram of the HPLC/HGAAS system is given in Figure 1 and the operating conditions are listed in Table 1.

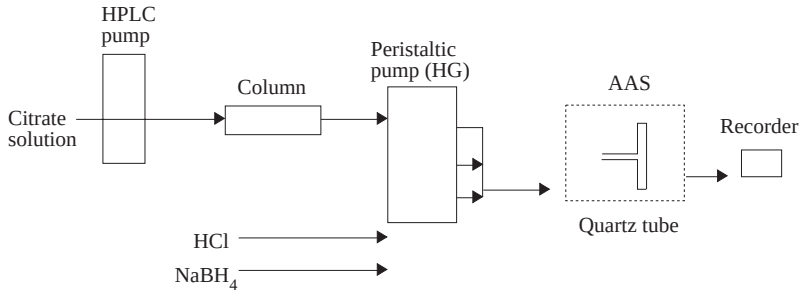

Figure 1. Schematic diagram of HPLC/HGAAS system for antimony speciation.

Table 1. Operating conditions for the hydride generation atomic absorption spectrometer.

Hydride generation		
$NaBH_4$ solution concentration	:	1.0% (w/v), stabilized with 1.0% (w/v) NaOH
$NaBH_4$ solution flow rate	:	2.0 mL/min
HCl solution concentration	:	5.0 mol/L
HCl solution flow rate	:	1.5 mL/min
N_2 flow rate	:	100 mL/min
Atomic absorption spectrometer		
Wavelength	:	217.6 nm
Bandpass	:	0.2 nm
Lamp current	:	12 mA
Quartz cell temperature	:	900°C

Results and Discussion

Hydride Generation

The criteria for the optimization of the hydride generation process are species selectivity, maximal yield, minimal blank, speed and convenience of manipulation. The efficiency of the hydride generation process depends strongly on the HCl concentration used. The effect of HCl concentration on the sensitivity was studied over the range 2-6 mol/L and the results are shown in Figure 2. The maximum sensitivity was achieved at 5 mol/L and this concentration of HCl was chosen for further experiments.

Figure 3 exemplifies the effect of $NaBH_4$ concentration on the absorbance values for Sb(III) and Sb(V). To choose the optimum $NaBH_4$ concentration, different concentrations in the range 1-5% (w/v) were tested. It was observed that concentrations higher than 1% (w/v) caused the absorbance to decrease.

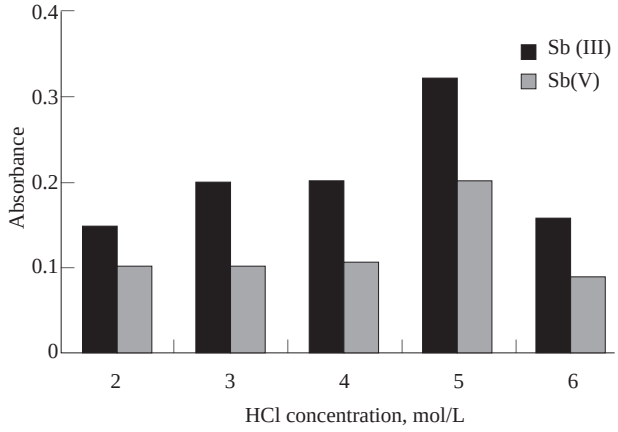

Figure 2. Optimization of HCl concentration for Sb(III) and Sb(V) species.

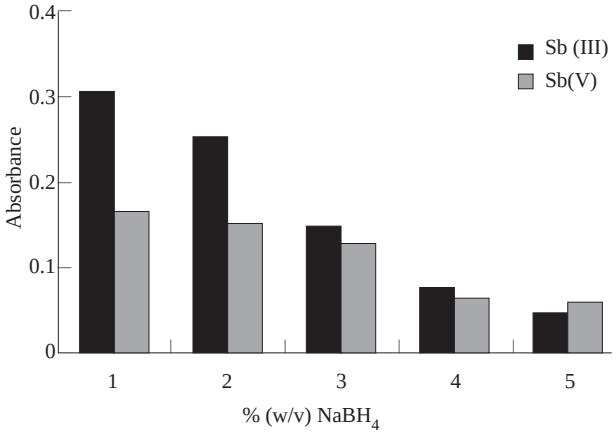

Figure 3. Effect of $NaBH_4$ concentration

Speciation Studies

The separation of Sb(III) and Sb(V) species was performed using two HPLC anion exchange columns with different lengths: 250 mm and 100 mm. For a satisfactory separation of the antimony species, two important parameters (eluent concentration and pH), were optimized. As the Sb(V) species was easily eluted from the column, a reasonable retention time for Sb(III) species was necessary.

Sodium citrate solution was chosen as the eluent and the effects of its concentration on the retention times were investigated in both columns. 20 μL of solutions containing 100 μg/L Sb(III) and Sb(V) at pH 4 were injected into the columns with varying citrate concentrations in the range 25-100 mmol/L at 2.0 mL/min flow rate. Figure 4 shows that a baseline separation of the two species was observed at a citrate concentration of 50 mmol/L. The retention of Sb(III) increased with decreasing citrate concentration, whereas no change in retention of Sb(V) was observed with changes in citrate concentration. The effect of pH on retention time in both columns was also optimized. As can be seen from Figure 5, the retention of Sb(III) increased with increasing pH, while there was no considerable change in retention of Sb(V). A baseline separation of the two species was observed at pH 4.0. A further increase in pH caused a longer retention time for Sb(III) and consequent peak broadening. The retention times obtained in this study were 2.0 min and 10.0 min in the

250 mm column, and 1.4 min and 3.6 min in the 100 mm column for Sb(III) and Sb(V) respectively. These retention times are longer than those obtained Zhang et al.[11]. It should be noted that their retention times were obtained by using a column 20 mm in length. A successful separation of the two species with shorter columns is possible at higher pH. Separation with a shorter column could not be investigated in this study as there was no shorter column available.

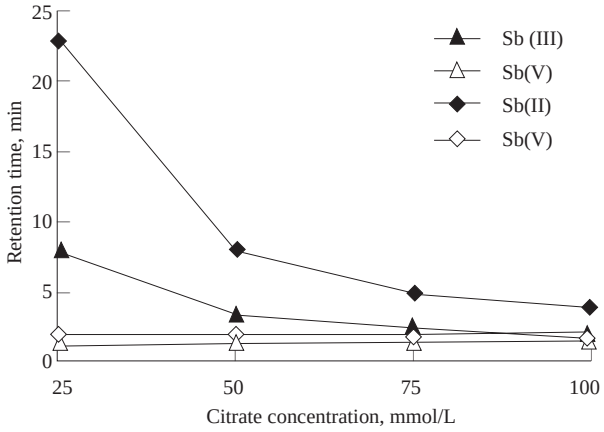

Figure 4. Effect of citrate concentration on the retention times of Sb(III) and Sb(V) species using 250 mm column (◊) and 100 mm column (Δ); pH: 4.0, flow rate: 2.0 mL/min.

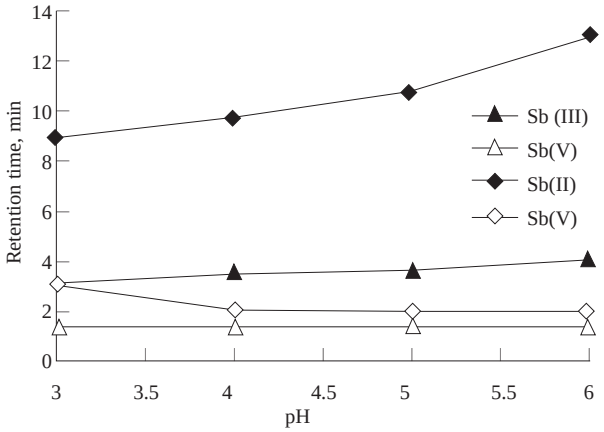

Figure 5. Effect of pH on the retention times of Sb(III) and Sb(V) species using 250 mm column (◊) and 100 mm column (Δ); citrate concentration: 50 mmol/L, flow rate: 2.0 mL/min.

Figure 6 shows the chromatograms obtained using optimum chromatographic and hydride generation conditions. The reason the differences in the height of the peaks is the difference the chromatographic retention. The efficiency of stibine generation and hence the peak areas for the two species are almost the same.

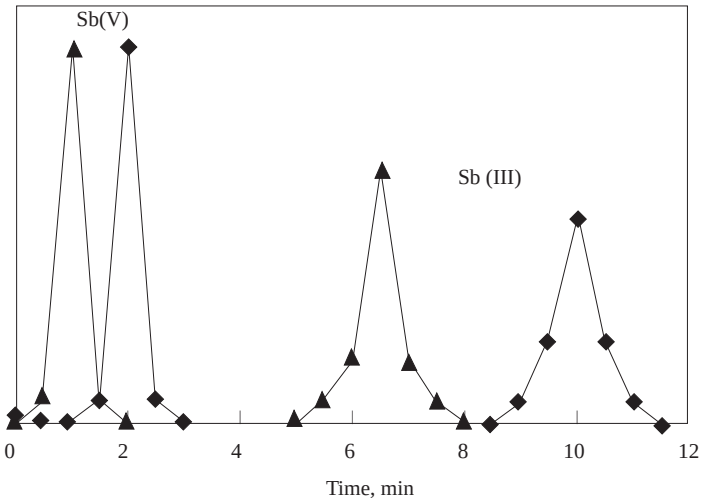

Figure 6. Chromatograms of a sample containing 100 μg/L of Sb(III) and Sb(V) species; 250 mm column (♦) and 100 mm column (▲). Chromatographic conditions: citrate concentration: 50 mmol/L; pH: 4.0; flow rate: 2.0 mL/min.

Analytical Figures of Merit

The analytical performance of the method is given in Table 2.

Table 2. Analytical Performance

	Sb(III)	Sb(V)
Linear range	4.0 - 100 μg/L	2.0 - 100 μg/L
Detection limit (3s)* 0.8 μg/L	1.0 μg/L	
RSD	4.7%	1.8%

*(n = 10)

Determination of Sb(III) and Sb(V) in Wastewater Samples

The optimized experimental conditions were applied for the speciation and optimization of antimony species in mining industry wastewaters. The results for the samples taken from Balya mining wastewater are given in Table 3. As the Sb concentrations in the samples may be below the detection limits, 10 μg/L of each species was added before determination.

Table 3. Determination of Sb(III) and Sb(V) in Waste Water Samples

Sample*	Added, μg/L		Found, μg/L	
	Sb(III)	Sb(V)	Sb(III)	Sb(V)
1	10.0	10.0	13.50.5	10.20.4
2	10.0	10.0	11.90.3	10.10.2
3	10.0	10.0	10.90.6	10.40.3
4	10.0	10.0	10.00.2	10.00.2

*Wastewater samples were collected from 4 different points of the area of interest, Balya Turkey.

References

1. National Institute for Occupational Safety and Health: Criteria for a recommended standard: Occupational exposure to antimony, ((DHEW) (NIOSH) Publication No. 78-216). Cincinnati, Ohio, (1978).
2. W. R Parkers, **Occupational Lung Disorders,** 2nd Ed., London: Butterworths, (1982).
3. B. Welz, **Atomic Absorption Spectrometry,** 2nd Ed.,VCH, Weinheim, (1985).
4. J. Bowman, B. Fairman, T. Catterick, **J. Anal. At. Spectrom., 12,** 313 (1997).
5. M. M. Smith, M. A. White, H. K. Wilson, **J. Anal. At. Spectrom., 10,** 349 (1995).
6. A. Menendez Garcia, M. C. Perez Rodriguez, J. E. Sanches Uria, A. Sanz Medel, **Fresenius J. Anal. Chem., 353,** 128 (1995).
7. M. B. De la Calle Guntinas, Y. Madrid, C. Camara, **Anal. Chim. Acta, 252,** 161 (1991).
8. M. O. Andreae, J. F. Asmode, P. Foster, L.Vant dack, **Anal. Chem., 53,** 1766 (1981).
9. M. Dodd, S. A. Pergantis, W. R. Cullen, H. Li, G. K. Eigendorf, K. J. Reimer, **Analyst, 121,** 223 (1996).
10. P. Smichowsky, Y. Madrid, M. B. De la Calle Guntinas, C. Camara, **J. Anal. At. Spectrom., 10,** 815 (1995).
11. X. Zhang, R. Cornelis, L. Mees,**J. Anal. At. Spectrom., 13,** 205 (1998).