Short communication

Selective determination of Sb(III) by gas chromatography–quartz furnace atomic absorption spectrometry after derivatization with triphenylmagnesium bromide

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Abstract

A method is described for the selective determination of Sb(III) in the presence of Sb(V) by capillary column gas chromatography–quartz furnace atomic absorption spectrometry. Sb(III) is complexed with pyrrolidinedithiocarbamate in a medium buffered with acetic acid–acetate at pH 4.5 and extracted into hexane; once extracted, Sb(III) is derivatized into a volatile gas chromatographable species, triphenylstibine, by Grignard reaction with phenylmagnesium bromide. A cool injection programmed-temperature vaporization injector (CTI) was used. Parameters affecting the extraction and derivatization reactions, as well as the atomization temperature in the quartz furnace and the maximum volume of organic phase that can be injected in the CTI, were optimized. The method was applied to the determination of Sb(III) in spiked tap water.

1. Introduction

Although the US Environmental Protection Agency (EPA) considers antimony and its compounds as pollutants of priority interest and the European Community Standards sets the maximum admissible level of antimony in surface and drinking water at 10 ng/ml, very few methods have been reported on the selective determination of antimony species. Speciation of antimony is of capital importance because its toxicity depends on the species in which antimony is present in the environment, Sb(III) being more toxic than Sb(V), and methylated

species of antimony being less toxic than the inorganic salts [1]. Per year, $3.8 \cdot 10^{10}$ g of antimony are released into the environment from industrial activities such as the manufacturing of semiconductor products [2] and the fabrication of glasses, dyestuffs, ceramics and fire retardants. Mining effluents, weathering of rocks and soil run-off also contribute to the total burden of antimony in the environment.

Sb(III), Sb(V), monomethylstibonic acid and dimethylstibinic acid are the four species that have been identified to date in natural waters [3]. Unfortunately, monomethylstibonic acid and dimethylstibinic acid are not commercially available and so, no quantitative or even qualitative determination can be done with certainty.

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Selective generation of antimony hydride by pH control is, so far, the most common method for Sb(III) and Sb(V) speciation at pH≥2 (citric acid medium) [4,5], at pH≥4 (tartaric acid medium) [4], in the pH range 6–7 [3], or even up to pH 8 (borate buffer) [6]. Campbell and Howard [7] suppressed the Sb(V) signal by generating the hydride at pH 5 (acetate buffer) and de la Calle-Guntiñas et al. [8] quantitatively suppressed the Sb(V) signal by adjusting the pH to 1.5–2 in H_3PO_4.

Mohammad et al. [9] indicate that speciation with citric acid and acetic acid is not related to a pH effect (which is a secondary factor) but to the formation of a complex with Sb(V). The list of complexant reagents was extended by de la Calle-Guntiñas et al. [10] to α-hydroxy acids other than citric acid, malic acid and lactic acid.

However, hydride generation is subject to serious interferences when real samples are analysed, due to transition metals and to other hydride-forming elements [11–15].

Liquid–liquid extraction of antimony complexes has also been used with speciation purposes [16,17]. The most widely applied system involves the formation of a complex with ammonium pyrrolidine-dithiocarbamate [18–21].

Metals and organometallic compounds can be determined using gas chromatographic (GC)-based methods coupled to very sensitive detection methods such as mass spectrometry, atomic adsorption spectrometry (AAS), atomic emission spectrometry and flame photometric detection. Derivatization reactions to transform the polar species in volatile gas chromatographable compounds are required. Derivatization with Grignard reagents, after complexation with tropolone [22] or sodium diethyldithiocarbamate [23], has been traditionally used in the field of organometallic compounds. More recently, sodium tetraethylborate has been introduced as a derivatizing agent and has been used in the determination of tin [24], lead [25], mercury [26] and selenium [27].

No GC combination methods have been reported specifically for antimony species. Although Talmi and Andren [28] determined inorganic antimony as triphenylstibine using a packed column, so far, capillary columns have not been used.

In this work, selective determination of Sb(III) is reported by complexation with pyrrolidine-dithiocarbamate at pH 4.5 and further extraction into hexane, Sb(III) being derivatized by phenylation with a Grignard reaction. A low detection limit is achieved by profiting from the advantage of using a sensitive detector (atomic absorption spectrometer) and a cool injection programmed-temperature vaporization injector (CTI), which allows the injection of 5–10 μl of the sample onto a capillary column.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water, obtained with a Milli-Q system (Millipore) was used.

A 1000 μg/ml standard solution of triphenylstibine was prepared by dissolving an appropriate amount of triphenylstibine (Aldrich) in hexane (Merck). Subsequent dilutions were also made in hexane. A 1000 μg/ml standard solution of Sb(III) was prepared by dissolving an appropriate amount of sodium antimonyl tartrate (Aldrich) in deionized water. A 1000 μg/ml standard solution of Sb(V) was prepared by dissolving an adequate amount of potassium pyroantimonate (Aldrich) in deionized water.

A 0.1 mol/l solution of acetic acetate buffer, pH 4.5, was prepared by dissolving an adequate amount of sodium acetate (Merck) in deionized water and adding, while magnetically stirring, a few drops of concentrated acetic acid (Merck).

Pyrrolidinedithiocarbamate (Aldrich), which was used as the complexing agent, was weighed and dissolved in the water sample after adjusting the pH to 4.5, as previously described. Phenylmagnesium bromide (Aldrich), which was used in the derivatization reaction, was diluted 1:4 in diethyl ether (Merck). The diethyl ether was kept in an erlenmeyer flask, to which several grams of sodium sulphate (Merck) has been added as a dessicant. The sodium sulphate had been dried overnight, at 110°C.

2.2. Apparatus

GC–AAS analyses were performed using a Hewlett-Packard HP Model 5890 Series II gas chromato-

graph on a capillary column (HP-1; 25 m×0.32 mm, 0.17 μm) coupled to an atomic absorption spectrometer (Perkin-Elmer 2380) equipped with a quartz cell atomizer that was electrically heated at 750°C. The GC–AAS interface consisted of a deactivated fused-silica capillary column placed in a nickel tube that was electrically heated at 270°C. The gas chromatograph was equipped with a temperature-cooled injector system (KAS 503; Gerstel, Mülheim, Germany). Injections were made manually using a Hamilton 701 RN syringe equipped with a needle (0.64 mm O.D.) with a polished finish to fit the septumless injection head. Smooth glass vaporization tubes (Gerstel) filled with 2 cm of Teenax (Hewlett-Packard) were used. Signals were registered by a Spectra-Physics SP4290 integrator. Analyses were performed using the experimental parameters indicated in Table 1.

2.3. Procedure

A 50-ml volume of sample is taken and the pH is adjusted to 4.5 with an acetic acid–acetate buffer. Pyrrolidinedithiocarbamate is added up to a final concentration of 0.1% (w/v) (for the study of interferences, the concentration of pyrrolidinedithiocarbamate in the solution was increased to 0.5%, w/v). A 1-ml volume of hexane is added and the Sb(III) complex is extracted by vigorous shaking for 5 min. The two phases are left to separate for another 5 min. The organic phase is taken and placed in an erlenmeyer flask and evaporated to dryness in a rotary evaporator. A 250-μl volume of hexane and 1 ml of a solution of phenylmagnesium bromide (diluted 1:4 in diethyl ether) are added in sequence and the mixture is vigorously shaken for approximately 1 min. A 10-ml volume of 1 mol/l sulphuric acid is added, to destroy the excess phenylmagnesium bromide. The content of the erlenmeyer flask is transferred to a separation funnel, shaken for 2.5 min and the two phases are left to separate for another 2.5 min. The aqueous phase is then discarded. The erlenmeyer flask is cleaned with 10 ml of deionized water, the water is

Table 1
GC–AAS operating conditions

Injector CTI	
Injection temperature	18°C
Solvent vent temperature	18°C (1 min)
Ramp	12°C/min
Desorption temperature	270°C (1 min)
Cool-down time	13 min (with CO_2)
GC parameters	
Carrier gas	Helium
Column	HP-1: 25×0.32 mm I.D., 0.17 μm
Column head preasure	130 kPa
Injector temperature	230°C
Oven programme	
Initial temperature	150°C (1 min)
Ramp	20°C/min
Final temperature	270°C (1 min)
GC detector temperature	270°C
Interface parameters	
Transfer line	capillary deactivated fused-silica tube
Temperature	270°C
AAS parameters	
Wavelength	196.0 nm
Light source	Se electrodeless discharge lamp (6 W)
Slit	0.7 nm
Hydrogen flow-rate	350 ml/min
Air flow-rate	45 ml/min

Complexation and extraction
50 ml of sample
(pH adjusted at 4.5 with acetic/acetate buffer)
+ pyrrolidinethiocarbamate (0.1% (w/v))
+ 1 ml of hexane
(extraction for 5 min)

Derivatization
Evaporation till dryness of the organic phase
+ 250 µl of hexane
+ 1 ml of phenylmagnesium bromide (diluted 1:4 in ethyl ether)
(Agitation for 1 min)
+ 10 ml of a solution 1 mol/l H_2SO_4 (shaked 2.5 min)
+ 10 ml of deionized water (shaked 2.5 min)

Determination
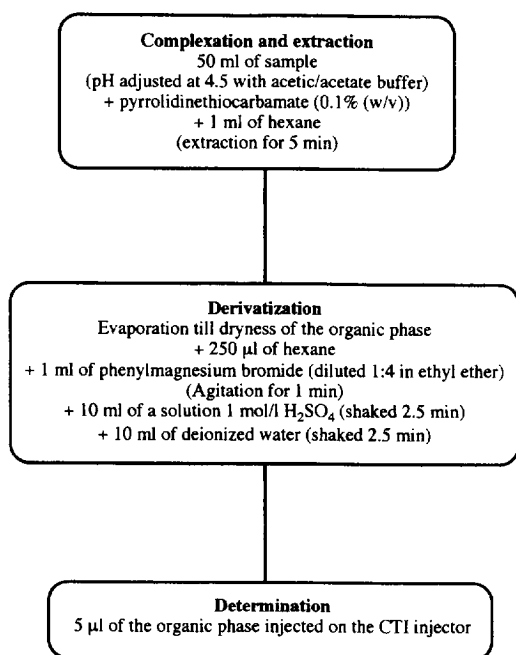5 µl of the organic phase injected on the CTI injector

Fig. 1. Scheme of the total procedure for the determination of Sb(III) by derivatization with phenylmagnesium bromide.

transferred to the separation funnel and the extraction step is repeated. Aliquots of 5 µl are injected into the gas chromatograph for the final determination. A scheme of the procedure is reported in Fig. 1.

3. Results and discussion

3.1. Optimization of the atomization temperature

This study was performed by injecting 5 µl (containing 5 ng of antimony) of a triphenylstibine solution. The temperature range of 600–900°C was studied. An increase in the peak height was observed by decreasing the temperature from 900 to 750°C, as shown in Fig. 2. A plateau is obtained between 750 and 700°C; at 650 and 600°C, no quantifiable signal was obtained. 750°C was chosen as the optimum temperature for further experiments.

3.2. Study of the maximum volume of sample that can be injected in the CTI
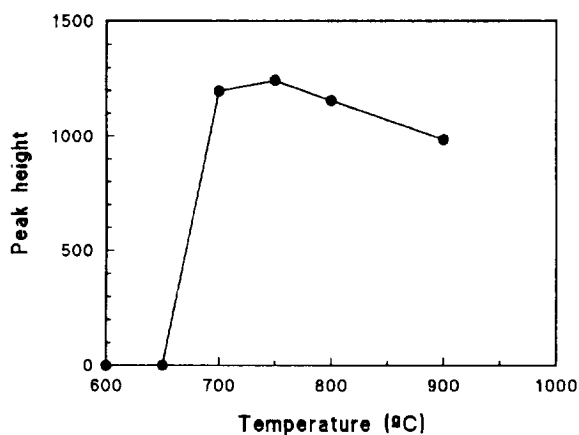
The CTI has the advantage of allowing volumes

Fig. 2. Optimization of the atomization temperature in the quartz cell.

greater than 1 µl to be injected into gas chromatographs equipped with capillary columns, thus achieving a considerable preconcentration factor. Nevertheless, a compromise situation must be found because impurities present in the sample are also preconcentrated, producing distorted signals.

A study of the maximum amount of sample that can be injected was done using both a triphenylstibine standard solution and a Sb(III) solution derivatized following the described method. Fig. 3 shows the maximum volume of standard solution that can be injected without a decrease in the peak height. As can be seen, the signal remains constant up to an injection volume of 10 µl. A decrease in the signal of 20–25% with respect to the maximum response obtained is observed when the volume of standard injected is increased up to 25 µl. A decrease of 35% is produced when 200 µl of standard is injected.

When samples of a solution of derivatized Sb(III) are injected, the maximum volume of sample that can be injected without any decrease in the absorbance signal is 10 µl, a decrease of 20% is obtained for an injection volume of 20 µl, and of 40% for 50 µl. Higher injection volumes were not tested because a distortion of the baseline was observed, probably due to a preconcentration of contaminants coming from the reagents used in the extraction and derivatization steps.

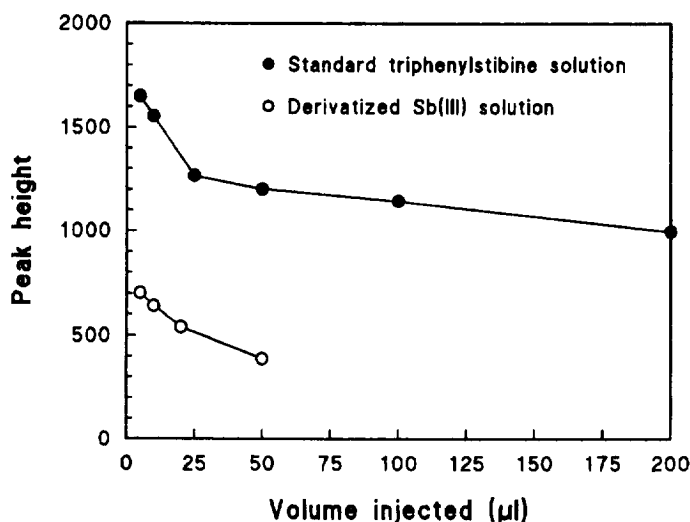For all further experiments, 5 µl of derivatized solution were injected.

Fig. 3. Study of the maximum volume of sample that can be injected in the CTI.

3.3. Optimization of the parameters affecting the complexation and extraction reactions

The parameters that could affect the efficiency of the reaction are the concentration of pyrrolidinedithiocarbamate used to complex the Sb(III), the pH at which the complexation and extraction is carried out, and the extraction time. All of these parameters were optimized. The recovery of Sb(III) increases by increasing the concentration of pyrrolidinedithiocarbamate up to 0.1% (w/v). When a concentration of 0.5% (w/v) was used, a decrease in the recovery was observed, probably because pyrrolidinedithiocarbamate is extracted into the organic phase and interferes with subsequent steps of the procedure, the derivatization with the Grignard reagent or more probably with the injection step, contaminating the Teenax of the liner and reducing the efficiency with which the derivatized compound is retained. Nevertheless, this parameter should be optimized for every new sample because there are a number of elements that form complexes with pyrrolidinedithiocarbamate and changes in the matrix to be analysed could result in variations in the amount of complexing agent that is available for the complexation of Sb(III).

Regarding the pH of the solution, a maximum signal is obtained in the range of 3.5–4.5. A pH of 4.5 was chosen for further experiments because the

lower the pH, the more difficult it becomes to dissolve the complexing agent.

A constant and maximum signal is obtained for reaction times equal to or higher than 5 min. The decrease in the signal when the formed complex was extracted for 10 min could be due to degradation produced during the long shaking time. A 5-min extraction time was chosen for further experiments.

Working under these conditions, the efficiency of the complete reaction was 80%.

3.4. Studies with different derivatizing agents

Derivatizing agents other than phenylmagnesium bromide were tested. First, different alkyl groups were checked, always using Grignard reagents. For ethylation, propylation and pentylation, the amount of Sb(III) derivatized was below the detection limit of the detector.

Phenylation was also tried, using sodium tetraphenylborate as the derivatizing agent, carrying out the derivatization reaction in an aqueous medium buffered at pH 5 with an acetic acid–acetate buffer. In this case also, the amount of Sb(III) that was derivatized was below the detection limit.

3.5. Analytical characteristics of the method

The analytical characteristics of the method were

calculated following the IUPAC recommendations on a calibration curve constructed by applying the described method to 50 ml of spiked tap water and the results are indicated in Table 2.

The interferences of Se, As, Pb, Sn, Bi, Ni, Fe, Co, Cu and Zn at a ratio of Sb–interferent of 1:10 were evaluated. Some authors indicate that the level of interference is not only dependent on the ratio of analyte to interferent, but is mostly dependent on the total amount of interferent. To cover this aspect, we have worked with concentrations of interferents that were higher that those likely to be found in drinking and surface waters, i.e., every interferent was present in the solution at a concentration of 100 μg/ml. Considering that some of the interferents can also form complexes with pyrrolidinedithiocarbamate, we increased the concentration of complexing agent in the solution up to 0.5% (w/v). Even when all the interferents were present in the solution, the signal obtained was 50% of that obtained with an Sb(III) standard solution in deionized water. Under the most unfavourable conditions, the use of the standard additions would enable the determination of Sb(III) to be performed.

3.6. Study of the interference of Sb(V) in the determination of Sb(III)

As mentioned previously, Sb(III) is more toxic than Sb(V); therefore, we wanted to develop a method that was capable of determining Sb(III) in the presence of Sb(V) at the ratio 20:80 for Sb(III)–Sb(V), i.e., the ratio at which they are normally present in the environment. To check this, the method was applied to a solution containing only Sb(III), and to a second solution containing Sb(III) and Sb(V), at the above-mentioned ratio. The results obtained indicated that Sb(V) does not interfere with

the determination of Sb(III), under the optimized conditions. Such a result makes the method applicable to the determination of the more toxic Sb(III) species.

3.7. Application of the method to the determination of Sb(III) in spiked tap water

Because of the lack of a certified reference material for Sb(III) and Sb(V), the method was applied to spiked tap water. The final concentration in solution was 20 ng/ml and the amount found was 16.97 ± 0.77 ng/ml ($n=4$). This slight decrease in the recovery is attributed to the fact that after the extraction of the complex Sb(III)-pyrrolidinedithiocarbamate into hexane from tap water, an emulsion was formed so that traces of hexane could not be recovered.

4. Conclusions

The method described in this work allows the selective determination of Sb(III) in the presence of Sb(V), representing an alternative to the more widely used hydride generation method. Even in the presence of transition metals and hydride-forming elements at very high concentrations, antimony can be determined by applying the standard addition method. The low absolute detection limit achieved, 0.26 ng, seems to be adequate for Sb(III) determinations for environmental purposes, when using the accessible AAS detector. The method would allow the easy introduction of antimony into a gas chromatograph, thus profiting from the use of some of the most sensitive detection methods, e.g., mass spectrometry, microwave-induced plasma atomic emission spectrometry, flame photometric detection and AAS, all of which can be coupled to GC.

Table 2
Analytical characteristics of the method

Detection limit	0.26 ng
Quantitation limit	0.87 ng
Precision	4% (for 1 ng)
	3% (for 2.5 ng)
Sensitivity	222 PHU/ng

$n=4$.

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