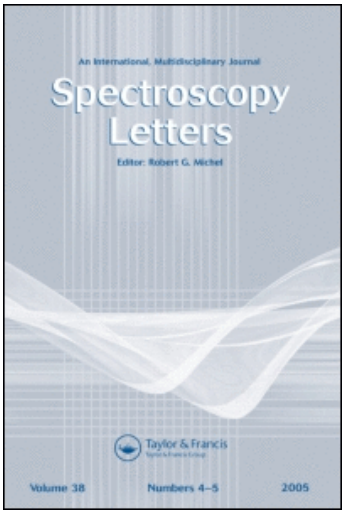

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Direct Speciation Analysis of Sb(III) and Sb(V) Based on Their Different Sensitivities for GFAAS

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ABSTRACT This paper presents a temptative work dealing with the possibilities of using GFAAS on speciation analysis purposes of antimony species—namely, Sb(III) and Sb(V)—in presence of three different complexing reagents (DDC, APDC and TTA). When using TTA, both antimony species can be analyzed setting 800 and 1700 to 1800°C as pyrolysis and atomization temperatures, respectively. However, the great differences detected between the values of the signals recorded for Sb(V) and for Sb(III) must be highlighted. Such differences suggest dissimilar sensitivities for both species, that are applied on speciation analysis purposes.

KEYWORDS antimony, atomic absorption, complex formation, sensitivity, speciation analysis

INTRODUCTION

Antimony has long been known as a non-essential, toxic element for man, chemically and toxicologically similar to arsenic and probably even more toxic. Because of this toxicity, maximum levels of antimony in different media have been published: For example, EPA[1] and the Council of the European Communities[2] have set maximum antimony levels for water intended for human consumption of 6 and 5.0 $\mu g\,L^{-1}$, respectively.

The toxicity of antimony is related to the specific form (chemical species) of the element[3]: Sb(III) is more toxic than Sb(V) and inorganic species are more toxic than the organic ones. Therefore, the increasing attention paid nowadays to speciation analysis of antimony needs no further explanation. However, speciation analysis requirements are not yet included in legal regulations.

Even when a variety of techniques have been proposed for antimony speciation analysis (as reviewed some years ago by Smichowski et al.[4] and by Krachler et al.[5]), this work is focused on graphite furnace atomic absorption spectrometry (GFAAS), because, nowadays, it is still a useful choice, even for speciation analysis. However, some other atomic techniques have also been proposed in the literature, such as hydride generation atomic absorption spectrometry (HGAAS),[6,7] flame atomic absorption spectrometry

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(FAAS),[8–10] or hydride generation-atomic fluorescence spectrometry (HG-AFS).[11]

Regarding the GFAAS methods published, the following is to be highlighted: Sb(III) is the species determined by all the authors (and sometimes it is the only species determined[12–14]), perhaps because it is more toxic than Sb(V). Moreover, most of the methods include the combination of the analyte, Sb(III), with a complexing agent, such as lactic acid-malachite green,[12] pyrocatechol violet,[14] pyrogallol,[15] or more usually, ammonium pyrrolidine dithiocarbamate (APDC).[6,8,13,16,17]

Some years ago, Cava-Montesinos et al.[11] developed a method to determine Sb(III) and Sb(V) based on the different sensitivity observed for both species by HG-AFS. The aim of the work presented here is to check if the same idea can be applied to GFAAS, in order to achieve the selective determination of Sb(III) and Sb(V), given that in the literature available to us, there are no references concerning the direct determination of antimony species by GFAAS. Accordingly, the temperatures for the pyrolysis and atomization steps are studied for both antimony species alone and in the presence of three different complexing reagents: diethyldithiocarbamate (DDC), APDC and 2-thenoyltrifluoroacetone.

EXPERIMENTAL

Instruments

A SpectrAA-600 atomic absorption spectrophotometer, equipped with a GTA 100 graphite furnace, a programmable sample dispenser and a longitudinal Zeeman-effect background corrector was used. Pyrolytic graphite coated graphite tubes with forked pyrolytic graphite platforms were used throughout (all by Varian Inc., Mulgrave, Victoria, Australia).

Reagents

Ammonium pyrrolidine dithiocarbamate (APDC) solution, 2.5%(m/v), prepared by dissolving 2.5223 g of APDC (p.a., Fluka Chemie, Steinheim, Germany) in ultrapure water and making up the solution to 100 mL. Antimony(III) stock standard solution, 925.6 $\mu g\,mL^{-1}$, prepared in 5 M hydrochloric acid by dissolving 0.1734 g of antimony trichloride (p.a., Merck, Darmstadt, Germany) and making up the solution to 100 mL. Antimony(V) stock standard solution, 1003.1 $\mu g\,mL^{-1}$, prepared by dissolving in ultrapure water 0.2166 g of potassium hexahydroxyantimonate (99.99%, p.a., Aldrich Chemical, Milwaukee, WI, USA) and diluting to 100 mL. Hydrochloric acid, 36.5–38.0%, for trace metal analysis, ACS grade (J.T. Baker, Phillipsburg, NJ, USA). Nitric acid solution, 5%(v/v), prepared by diluting 5 mL of nitric acid (69.8%, for trace metal analysis, ACS grade, J.T. Baker) to 100 mL with ultrapure water. Sodium diethyldithiocarbamate (NaDDC) solution, 2%(m/v), prepared by dissolving 1.3155 g of $NaDDC \cdot 3H_2O$ (AnalaR, BDH Chemicals, Poole, UK) in ultrapure water and making up the solution to 50 mL. 2-thenoyltrifluoroacetone (TTA) solution, 1.4%(m/v), prepared by dissolving 0.3485 g of TTA (99%, Panreac Síntesis-Avocado, Barcelona, Spain) in acetone and diluting to 25 mL with the same solvent. Ultrapure water, resistivity 18 $M\Omega \cdot cm$, obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Cleaning of Material, Personal Care and Waste Management

All material was washed and kept for 48 h in a 10%(v/v) HNO_3 solution. After that, it was carefully rinsed several times with ultrapure water and allowed to dry before use. Personal care devices were used, and waste solutions were collected for further treatment by the Service of Dangerous Waste Management of the University of Santiago de Compostela.

RESULTS AND DISCUSSION

Without Complexing Reagent

First, two standard solutions containing 38.8 $\mu g\,L^{-1}$ of Sb(III) and 24.1 $\mu g\,L^{-1}$ of Sb(V), respectively, and nitric acid (at a concentration of 0.5%(v/v)) as a chemical modifier, were prepared and subjected to GFAAS, to find out the best measurement conditions for each species. The results are shown in Fig. 1, in which two details can be emphasized: On the one hand, the pyrolysis temperature chosen was 300°C higher for Sb(III) than for Sb(V) (see Table 1). This difference was observed after repeating the experiments several times.

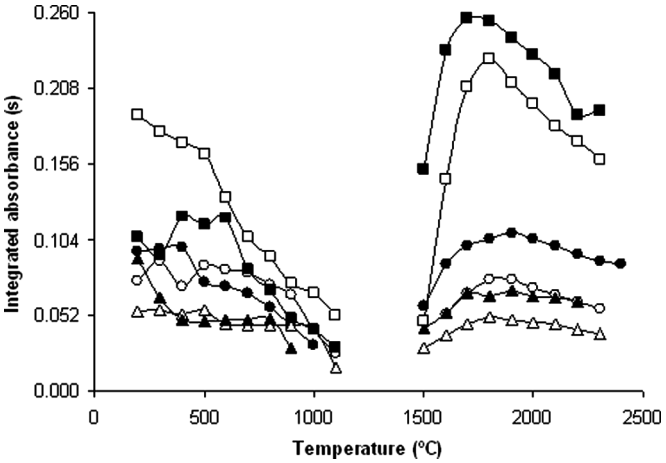

FIGURE 1 **Pyrolysis and atomization curves for standard solutions of Sb(III) and Sb(V). Lines with circles: 0.5%(v/v) HNO_3 as chemical modifier; lines with triangles: 0.5%(v/v) HNO_3 as a chemical modifier and 0.2%(m/v) DDC as complexing agent; lines with squares: 0.5%(m/v) APDC as complexing agent. Lines with white circles, triangles or squares: Sb(III); lines with black circles, triangles or squares: Sb(V).**

On the other hand, here, as well as throughout this work, the decision to select one temperature was made on the basis of both the value of the signal and the shape of the peaks recorded.

Effect of DDC

Two standard solutions, which contained 0.5% (v/v) of HNO_3, 0.2% (m/v) of NaDDC and 38.8 $\mu g\,L^{-1}$ of Sb(III) or 24.1 $\mu g\,L^{-1}$ of Sb(V) were used to investigate the influence of DDC. The amount of NaDDC represents a clear molar excess if compared with the amounts of the analyte species in each case, in order to ensure the total complexation of such species.

Figure 1 also shows the results achieved (see Table 1 for the exact pyrolysis and atomization temperatures chosen for each species) that led us to conclude that negligible differences existed between both antimony species. Therefore, no differences in the sensitivity of the technique for both species could be determined.

Effect of APDC

Before studying the influence of APDC, some experiments were made to confirm the necessity of using nitric acid as a chemical modifier, and it was concluded that, for both antimony species, that modifier was not essential. Therefore, no chemical modifier was used from then on.

Regarding the use of APDC as complexing agent, preliminary experiments led to set the APDC concentration in the solutions to be analyzed at 0.5% (m/v), for both Sb(III) and Sb(V), since that concentration assured the complexation of all the analyte present. Then, once more, the measurement conditions were separately investigated for Sb(III) and Sb(V), using two aqueous standard solutions, containing the following: APDC at 0.5% (m/v) (both solutions, as indicated above), 37.0 $\mu g\,L^{-1}$ of Sb(III) (one of the solutions) and 25.1 $\mu g\,L^{-1}$ of Sb(V) (the other solution). The results achieved (see again Fig. 1 and Table 1) showed again a very similar behaviour for both species, concerning the temperatures selected and the values of the signals recorded. Therefore, APDC was discarded for the aims of the work.

Effect of TTA

The proposal of using TTA as a complexing reagent for Sb(III) is based on the results obtained in a previous work,[18] where TTA was used to complex selectively Cr(III) in presence of Cr(VI). Thus, Cr(VI) could be determined by GFAAS as the Cr(III) complexed with TTA was volatilized at lower temperature than the pyrolysis temperature for Cr(VI). In that study, the following parameters were studied for the complex to be formed: Amount of TTA, heating time and temperature, time of formation of the complex and pH. The heating time and temperature (5 min at 40°C) proposed for the formation of the Cr(III)-TTA complex where selected to prepare the

TABLE 1 **Measurement Conditions Obtained for Sb(III) and Sb(V) Standard Solutions, Using 0.5% (v/v) HNO_3 as a Chemical Modifier and Different Complexing Agents**

	None[a]		DDC		APDC[b]		TTA[b]	
Variable	Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)
Pyrolysis	700	400	1000	800	500	500	800	800
Atomization	2100	2300	1900	1700	1700	1800	1700	1800

[a]Without any complexing agent.
[b]Without HNO_3 as a chemical modifier.

complex Sb(III)-TTA, and the amount of TTA, the time needed for the formation of the complex and the pH were the parameters studied.

Related to the amount of TTA, measurements on standard Sb(III) and Sb(V) solutions resulted in the selection of a TTA concentration of 0.3%(m/v) in the solutions analysed for both antimony species. This concentration is enough for all the analyte to be complexed.

Then, the time needed for the formation of the Sb(III)-TTA complex (this period runs after the heating time aforementioned) was then investigated, by measuring the absorbance of a standard solution containing $37.0\,\mu g\,L^{-1}$ of Sb(III) and 0.3%(m/v) TTA every 30 min during 3.5 h. The conclusion of this study was that 2.5 h was the time neccessary for the formation of the complex.

To evaluate the effect of pH on the formation of the complexes, two series of standard solutions were prepared, containing both series 0.3%(m/v) of TTA, one of the series $37.0\,\mu g\,L^{-1}$ of Sb(III) and the other series $25.1\,\mu g\,L^{-1}$ of Sb(V). In each series, pH was varied between 3.3 and 6.4, using an acetic-acetate buffer solution. Also, both solutions containing the indicated concentrations of TTA and Sb(III) or Sb(V) were also prepared without buffer solution. When all the solutions were analyzed by GFAAS using the conditions that had been obtained for each species in the absence of a chemical modifier (see first two columns in Table 1), the results shown in Fig. 2 were obtained. From that figure, it can be concluded that for both antimony species, as pH increases, absorbance signal decreases, whereas the background signal increases significantly (this latter increase is negligible at pH values below 4 also for both species). In addition, the signals recorded in absence of buffer are quite higher than the corresponding background absorption signals, both for Sb(III) and for Sb(V). Therefore, the use of a buffer for pH-controlling is not needed at all.

Finally, the best pyrolysis and atomization temperatures for each antimony species in presence of TTA were also investigated, working with a standard solution containing $37.0\,\mu g\,L^{-1}$ of Sb(III) and 0.3%(m/v) of TTA and another one containing $25.1\,\mu g\,L^{-1}$ of Sb(V) and 0.3%(m/v) of TTA. The respective pyrolysis and atomization curves are depicted in Fig. 3, and the temperatures selected as optimal within the intervals studied included in Table 1. In view of these results, it is clear that there is no difference between the temperatures for each species but, before this (as confirmed repeated measurements), Sb(V) signals are higher than the corresponding Sb(III) signals (actually the Sb(V) signals are about 2.3 times the corresponding Sb(III) signals). This fact can be interpreted as an indication that both species exhibit a different sensitivity for GFAAS in presence of TTA as complexing reagent, and therefore, the technique is likely to be applied to the selective determination of Sb(III) or Sb(V) in presence of the other species. This could be carried out following an analogous strategy as the one described by Cava-Montesinos et al.[11], i.e., making

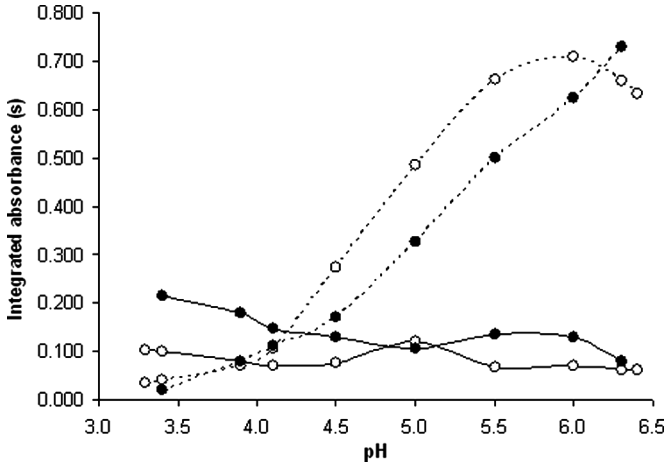

FIGURE 2 **Effect of pH on the complexation of Sb(III) and Sb(V) with TTA, for standard solutions. Lines with white circles: Sb(III); lines with black circles: Sb(V); solid lines: Atomic absorption; dotted lines: Background absorption.**

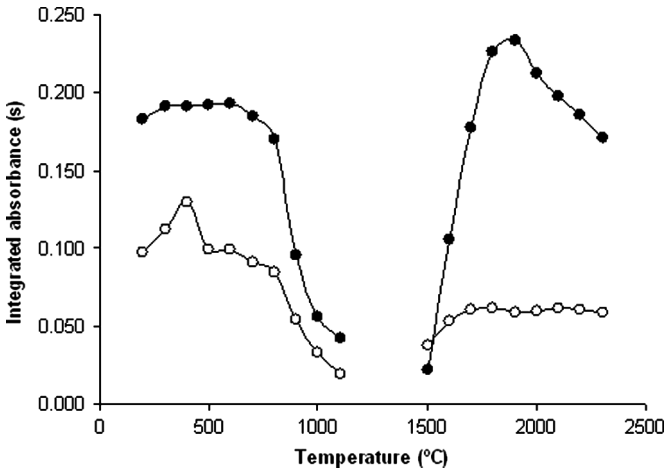

FIGURE 3 **Pyrolysis and atomization curves for standard solutions of Sb(III) or Sb(V) with 0.3%(m/v) TTA as complexing agent. Lines with white circles: Sb(III); lines with black circles: Sb(V).**

measurements on the same sample using two different atomization temperatures for both antimony species, and interpolating the two integrated absorbance values in proportional equations relating integrated absorbance with the concentrations of Sb(III) and Sb(V). The coefficients of these linearly independent equations can be calculated by measuring the absorbance for Sb(III) and Sb(V) standards in the presence of TTA and each sample should be, then, analyzed at both atomization conditions.

CONCLUSIONS

Given that both antimony species Sb(III) and Sb(V) do not exhibit different behaviours when determined by GFAAS in presence of DDC or APDC, these complexing reagents are not useful for speciation analysis. On the contrary, when using TTA, both species do exhibit different sensitivities, that indicates the possibility of determining selectively both Sb(III) and Sb(V) in aqueous solutions.

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