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On-line photodecomposition for the determination of antimony species

R. Miravet, E. Bonilla, J. F. López-Sánchez* and R. Rubio

Departament de Química Analítica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028-Barcelona, Spain

Received 3 June 2005; Accepted 26 September 2005

On-line UV photooxidation by peroxodisulfate was coupled to ion chromatography hydride generation atomic fluorescence spectroscopy (IC-UV-HG-AFS) for the speciation of inorganic antimony [Sb(III) and Sb(V)] and methylated species. Several parameters (UV lamp, irradiation time and peroxodisulfate concentration) that greatly influence the sensitivity of these three antimony species were investigated in depth. Under optimized conditions, photodecomposition resulted in an improvement in methylantimony species sensitivity. Dilution in di-ammonium tartrate medium was necessary in order to ensure short-term stability of Sb(III) at the $\mu g\, l^{-1}$ concentration level. Furthermore, the efficiency of irradiation was strongly dependent on the chemical composition of the measured solution. Detection limits of 0.04 $\mu g\, l^{-1}$ for Sb(V), 0.03 $\mu g\, l^{-1}$ for Me_3SbCl_2 and 0.03 $\mu g\, l^{-1}$ for Sb(III) as well as repeatability and reproducibility better than 4 and 8% RSD, respectively, were obtained. The proposed methodology was applied for antimony speciation in terrestrial plant sample extracts. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: antimony photooxidation; speciation analysis; ion chromatography; hydride generation; atomic fluorescence spectrometry; antimony in plants

INTRODUCTION

The potentially harmful effects of antimony[1] has led it to be listed as a priority pollutant by the US Environmental Protection Agency (EPA),[2] so there is an increasing interest in the assessment of antimony concentrations in environmental, biological and geochemical samples. These samples may contain antimony in the (III) and (V) oxidation states and both inorganic and organic species can be formed.[3] Organoantimony species have been detected in a variety of environments in which methylantimony species are the most studied, since they are expected to be predominant. Mono- and dimethylantimony species have been found to be formed in both marine and fresh waters.[4,5] Moreover, Feldmann *et al*.[6] reported the volatilization of antimony from environmental sediments and municipal waste sites, suggesting antimony biomethylation under anaerobic conditions. Otherwise, the presence of organoantimony compounds in plants has rarely been addressed until now. Dodd *et al*.[7] reported the presence of $MeSbH_2$, Me_2SbH and Me_3Sb in extracts of pondweed samples collected from Yellowknife (British Columbia, Canada). Craig *et al*.[8] confirmed the presence of methylantimony species in some plant samples collected from sites adjacent to an antimony mine (Eskdale, Scotland). Levels of $MeSbH_2$ and Me_2SbH ranging from 100 to 200 ng g^{-1} were reported in liverwort and moss samples. Koch *et al*.[9] extracted Me_2Sb and Me_3Sb with concentration values ranging from 4 to 170 ng g^{-1} from several biota samples collected from streams and puddles receiving mine effluent.

Otherwise, organoantimony compound content in most matrices is very low, so speciation studies need specific and sensitive measuring techniques. Analytical methods for organoantimony compound speciation have scarcely been established. Only a few techniques have been described, the most popular involving separation by gas or liquid chromatography coupled with spectrometric techniques.[7–15]

On the other hand, the photodecomposition of some hydride-forming organometallic compounds by means of UV irradiation has been observed in previous studies, resulting in an increase in their sensitivity.[16–21] However, as far as we know, the photodecomposition of organic antimony species after UV irradiation has not been reported.

*Correspondence to: J. F. López-Sánchez, Departament de Química Analítica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028-Barcelona, Spain.
E-mail: fermin.lopez@ub.edu
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The present study describes an on-line coupling for organic and inorganic antimony speciation, consisting of ion chromatography–UV irradiation–hydride generation–atomic fluorescence spectrometry (IC-UV-HG-AFS). Several assays were conducted in order to choose the most appropriate conditions for the photoreaction of methylantimony species with the aim of increasing the measurement sensitivity. The introduction of a derivatization step consisting of UV irradiation after the addition of peroxodisulfate to the eluate was optimized and evaluated. The proposed methodology was applied to antimony speciation in several terrestrial plant samples collected from sites adjacent to abandoned antimony mines located in eastern Pyrenees (Catalonia, Spain).

EXPERIMENTAL

Apparatus

A Perkin-Elmer 250 LC quaternary pump (CT, USA) and a polystyrene-divinylbenzene-based anion-exchange column Hamilton PRP X-100 (Reno, NV, USA) with quaternary methyl-ammonium salt as ion-exchange groups, 10 μm particle size (250 × 4.1 mm), were used for the separation of antimony species. A gradient elution of 250 mmol l^{-1} diammonium tartrate pH = 5.5 and 20 mmol l^{-1} KOH pH = 12 was used for the chromatographic separation. A flow rate of 1.5 ml min^{-1} was used. More details are given elsewhere.[15] A Rheodyne 7125 injector (Cotati, CA, USA) with a 200 μl loop was used for sample introduction.

A Heraeus TNN 15/32 low-pressure mercury vapour lamp ($\lambda = 254$ nm, o.d. 2.5 cm, length 17 cm, 15 W) and a water-refrigerated 150 W high-pressure mercury vapour lamp (Heraeus TQ 150, Hanau, Germany) were combined with PTFE tubing (length from 3 to 8m i.d., 0.55 mm) for the photoreactor systems. More details are described elsewhere.[22] A computer-controlled microburette (MicroBU 2031, Crison, Parkland, FL, USA) was used to introduce the peroxodisulfate solution into the photoreactor.

Hydride generation was performed with a Millennium P.S. Analytical (Kent, UK), model 10.055. HCl 2 mol l^{-1} at 9.0 ml min^{-1} and $NaBH_4$ 0.7 (w/v) at 4.5 ml min^{-1} were added for stibine generation. After reaction in a coil, the generated stibine was driven by an argon flow (300 ml min^{-1}) to the AFS detector through the Type 'ME' gas–liquid separator. Before detection, the argon stream was passed through a Perma pure drying membrane (Perma Pure Products, Farmingdale, NJ, USA), which prevent droplets being transmitted into the transfer line. Air was used as drying gas at a flow rate of 2.5 l min^{-1}. Detection was carried out in a P.S. Analytical model Excalibur Atomic Florescence Spectrometer equipped with a diffusion flame and an Sb Boosted Hollow Cathode Lamp (Super Lamp, Photron, Teknokroma). Peak areas were calculated from custom-developed software running with the Matlab language.[23]

A Memmert oven model ULP 800 (Afora, Barcelona) was used for drying plant samples. Subsequently, they were pulverized to a fine powder using a tungsten carbide disc mill (Herzog). Plant sample digestion was performed in a Prolabo (Paris, France) microwave digester (model A301, 2.45 GHz). A Hettich (Tuttlingen, Germany) Universal 30F was used for the centrifugation of the extracts.

A Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer equipped with a 'cross-flow' nebulizer was also used for total antimony determination in the terrestrial plant samples. Data acquisition of the FIA peaks was carried out with a microcomputer using software (ELAN 2.3.1) from Perkin-Elmer. Antimony signal was monitored at mass 121 and 123 without any isobaric or polyatomic interference. Rh was used as internal standard.

Reagents, standards and certified reference materials

All of the chemicals and reagents used in this study were of analytical-reagent grade or higher purity and de-ionized water obtained from a MiliQ System (USF PURELAB Plus, Ransbach Baumbach, Germany, 18.2 MΩ cm^{-1}) was used throughout.

Two different 1000 mg l^{-1} stock standard solutions of Sb(III) were prepared by dissolving appropriate amounts of potassium antimonyl tartrate (Fluka, Neu-Ulm, Switzerland) and antimony(III) chloride (99.999%, Aldrich) in water and HCl 6 mol l^{-1}, respectively, and diluting to 100 ml. Aliquots of 1000 mg l^{-1} stock standard solutions of Me_3SbCl_2 and Sb(V) were prepared by dissolving trimethyl antimony dichloride (synthesized at the Research Centre Jülich, Institute of Applied Physical Chemistry, Jülich, Germany) and potassium hexahydroxyantimonate (Riedel de-Haën, Seelze, Germany), respectively, in water and diluting to 100 ml. All stock standard solutions were stored in polyethylene bottles in a refrigerator held at 4 °C. These solutions were standardized using a standard reference material (NIST 3102a, antimony standard solution) by ICP-AES measuring at three emission lines of antimony (206.8, 217.6 and 231.2 nm). Working solutions were prepared daily by diluting the stock standard solutions.

Sodium borohydride solutions were prepared daily from $NaBH_4$ 97% 'purum' (Fluka) and stabilized in $NaOH.H_2O$ 'suprapur' (Merck, Darmstadt, Germany) 0.1 mol l^{-1} aqueous solution. Solutions of HCl were prepared from fuming HCl Pro-analysi 37% (Merck).

Potassium hydroxide ('pellets' 99.99%, Aldrich) and diammonium tartrate (Fluka) were dissolved in water and filtered off through a 0.22 μm nylon membrane before using as mobile phases.

HNO_3 (J.T. Baker, Phillipsburg, NJ, USA) and H_2O_2 30% 'VLSI Selectipur' (Merck) were used for sample mineralization. Citric acid 99.5% (Fluka) was used for the extraction of antimony species.

Peroxodisulfate solution ($K_2S_2O_8$, Fluka, purity >99.5%) was prepared in sodium hydroxide ($NaOH.H_2O$ 'suprapur',

Merck) at several concentrations according to the optimization study.

The certified reference material, Virginia tobacco leaves (CRM-CTA-VTL-2; antimony certified value 0.312 ± 0.025 μg Sb g^{-1}) from the Institute of Nuclear Chemistry and Technology (Warsaw, Poland), was analysed in order to assess the efficiency of the acidic digestion tested.

Sampling

Plant samples were collected from sites adjacent to several abandoned antimony mines in the eastern Pyrenees (Catalonia, Spain) in October 2004. Samples were stored in polyethylene bags and transported to the laboratory where the specimens were washed carefully with double deionized water (Millipore system) to remove soil and other particles. The plants were then dried at 40 °C and pulverized to a fine powder before analysis.

Procedure for total antimony determination

A 0.2 g sample of dry solid sample was placed in an open reflux vessel of the focused microwaves system. Three independent digestions were carried out and the appropriate digestion program was applied (see Table 1). After cooling to room temperature, the digested samples were filtered through ash-free filter papers (Whatman no. 40) to remove silica residue, and diluted in water to 20 ml. The final solutions were stored at 4 °C until analysis. The total antimony content in plant samples was determined by measuring appropriate dilutions of the acid digests by ICP-MS. The accuracy of the procedure was assessed by analysing the certified reference material (found value 0.313 μg Sb g^{-1}, $n = 3$, 0.36% RSD).

Procedure for antimony speciation

A sample of plant (0.2 g of dry solid sample) was placed in a plastic tube with 10 ml of 0.1 mol l^{-1} citric acid.[24] The sample was agitated with an end-over-end shaker for 4 h at room temperature and later sonicated for 1 h. The mixture was then centrifuged for 20 min at 3500 rpm and filtered through a filter paper (Whatman no. 40). The final solution was diluted to 20 ml with water and filtered through a nylon membrane of 0.2 μm porosity. Finally, an adequate aliquot of the filtered extract was diluted in 250 mmol l^{-1} di-ammonium tartrate to a fixed volume and injected (200 μl) into the chromatographic system.

Table 1. Microwave program used for the digestion of terrestrial plants for total antimony determination

	Step			
	1	2	3	4
Reagent	HNO_3	H_2O_2		
Volume (ml)	3	3		
Power (W)	30	30	50	70
Time (min)	10	4	4	4

RESULTS AND DISCUSSION

On-line UV photooxidation of antimony species

UV lamp

A study was carried out in order to choose the most appropriate UV lamp for the photodecomposition of antimony species. First, molecular absorption spectra of three solutions containing 100 mg l^{-1} of antimony as Sb(III), Sb(V) and Me_3SbCl_2 were obtained. These spectra were contrasted with the emission spectra of two UV lamps: low-pressure (15 W) and water-refrigerated high-pressure mercury lamp (150 W). From the spectra, the 15 W UV lamp ($\lambda_{max} = 254$ nm) irradiates more effectively over the zone of maximum absorption of the antimony species [$\lambda_{max} = 201$, 218 and 202 nm for Sb(V), Sb(III) and Me_3SbCl_2 respectively].

Moreover, additional experiments were carried out in order to confirm that the 15 W UV lamp provided the highest Me_3SbCl_2 UV photodecomposition. Thus, 200 μl of a 100 μg l^{-1} Me_3SbCl_2 standard solution was injected in triplicate into the IC-UV-HG-AFS system and irradiated separately for 60 s with both UV lamps (15 and 150 W). From the results, only the 15 W UV lamp provided a 6% increase in the Me_3SbCl_2 signal with respect to that observed without UV irradiation. This lamp was adopted for further investigations.

Effect of the addition of peroxodisulfate

Peroxodisulfate in alkaline media has been used previously as an effective oxidant agent that favours the photodecomposition of organic arsenic species.[16,19–21] In the present study, the effect of adding an oxidant solution to the eluate prior to UV irradiation was also evaluated. For each assay, 200 μl of a 100 μg l^{-1} antimony standard solution as each one of the three antimony species were injected separately in the IC-UV-HG-AFS system. Sb(III) was assayed as both potassium antimonyl tartrate and antimony (III) chloride. Five alkaline peroxodisulfate solutions at different concentrations were added at the entrance of the photoreactor with a computer-controlled microburette at 0.2 ml min^{-1} using a T connection. The irradiation time was 60 s in all cases.

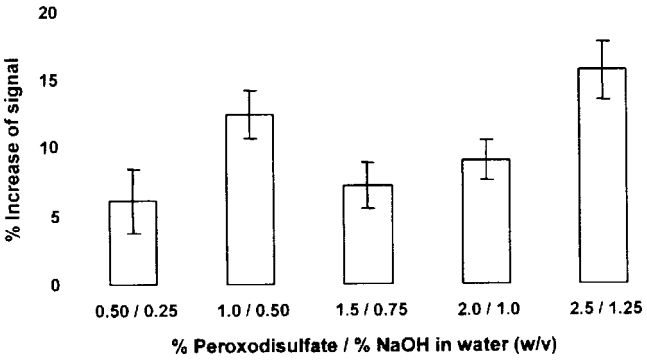

Figure 1. Influence of the peroxodisulfate concentration in the sensitivity of Me_3SbCl_2.

From the results, the introduction of peroxodisulfate in the IC-UV-HG-AFS system only affected the sensitivity of Me_3SbCl_2 and Sb(III). Figure 1 shows the results obtained for Me_3SbCl_2. The error bars represented one standard deviation from three independent results, calculated following the propagation of random errors law. The addition of $K_2S_2O_8$ 1% (w/v) and 2.5% (w/v) provided the highest increase in the Me_3SbCl_2 signal with respect to that observed for this species without photooxidation. In contrast, the signal of Sb(III) as both $SbCl_3$ and antimonyl tartrate decreased by around 15% for the same peroxodisulfate solutions. These signal decrements might have been due to a photooxidation of Sb(III) to Sb(V) since the latter presents lower hydride generation yield than the trivalent form.

Since the UV photooxidation resulted not only in the transformation of some analyte species but also in a substantial modification in sensitivity, the conditions adopted sacrificed the sensitivity of the inorganic species to allow for the best sensitivity of the methylated species, which are the most challenging to detect. For the present study, the UV photooxidation conditions that provided the highest increase in Me_3SbCl_2 signal were always given priority, since this species typically presents very low concentrations in most matrices. Therefore, addition of $K_2S_2O_8$ 2.5% (w/v) in 1.25% (w/v) NaOH was finally adopted.

Irradiation time

Several irradiation times were assayed in order to obtain the best yield in antimony compound photodecomposition. For each assay, the antimony species were tested separately by injecting in triplicate 200 µl of a solution containing 100 µg l^{-1} of antimony for each form. Irradiation times ranging from 34 to 90 s were tested. UV irradiation beyond 90 s was discarded since these conditions provided worse peak shapes for Me_3SbCl_2, whereas only a slight increase in sensitivity was observed for this species.

Figure 2 shows the influence of the irradiation time in the increase in the antimony species signal with respect to that observed for these species without UV irradiation or combined photooxidation. The error bars were calculated as in Fig. 1. The results obtained for Sb(V) are not shown since no significant differences in the signal of this species were observed. From the results, the sensitivity of Me_3SbCl_2 increased with increasing irradiation time in all cases, especially when $K_2S_2O_8$ was added to the system. Thus, UV irradiation for 90 s in the presence of $K_2S_2O_8$ 2.5% increased the Me_3SbCl_2 signal by as much as 33% with respect to that observed without photooxidation. On the other hand, under these conditions the Sb(III) signal both as antimony (III) chloride and potassium antimonyl tartrate decreased by 29 and 23%, respectively. These conditions were finally adopted since they provided the highest increase in Me_3SbCl_2 signal.

As an example, Fig. 3 shows the separation under optimized conditions [15 W UV lamp, 90 s irradiation time, $K_2S_2O_8$ 2.5% (w/v) in 1.25% (w/v) NaOH] by IC-UV-HG-AFS of a standard solution containing 50 µg l^{-1} of each one of the three antimony species.

Short-term stability of antimony (III) diluted standard solutions

The key requirement of speciation analysis consists of the preservation of the species integrity during the whole

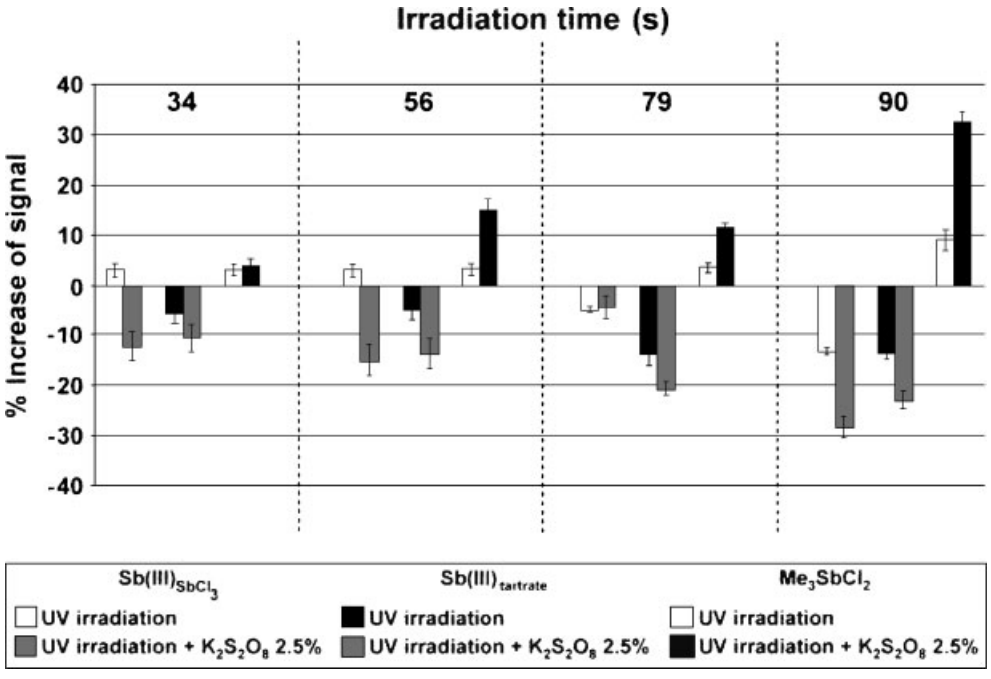

Figure 2. Influence of the UV irradiation time in the sensitivity of the antimony species.

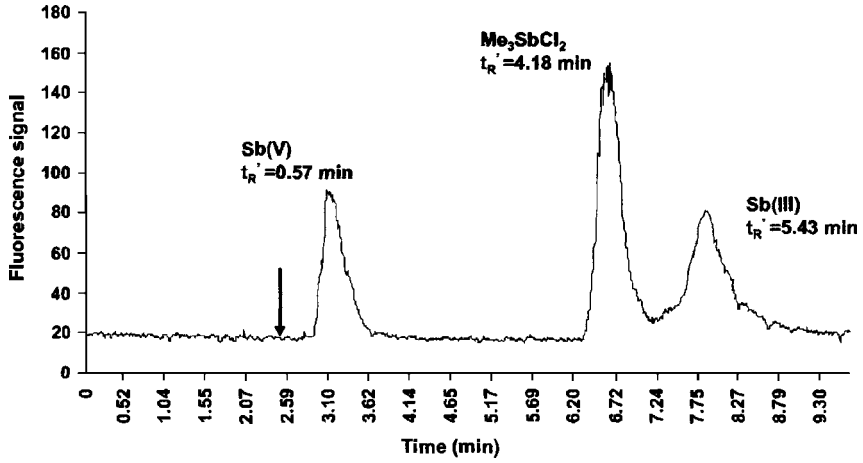

Figure 3. Chromatographic separation by IC-UV-HG-AFS of a standard solution containing 50 μg l^{-1} of Sb as Sb(V), Me_3SbCl_2 and Sb(III). Gradient elution used di-ammonium tartrate 250 mmol l^{-1} pH = 5.5 and KOH 20 mmol l^{-1} pH = 12.0. t_R' is the adjusted retention time. The arrow on the chromatogram indicates the dead time, t_m.

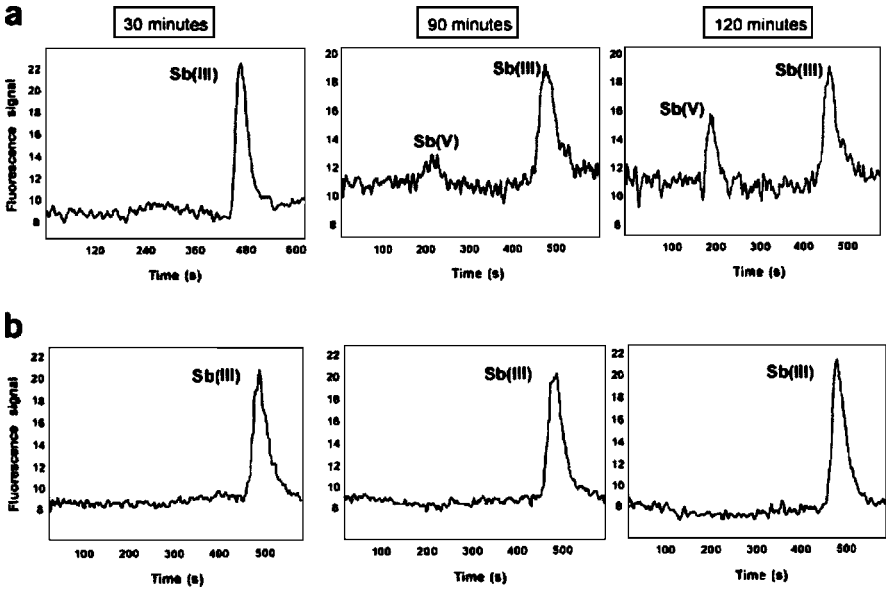

Figure 4. Short-term stability of diluted 100 μg l^{-1} Sb(III) standard solutions in (a) HCl 1% (v/v) and (b) di-ammonium tartrate 250 mmol l^{-1}. Chromatographic separation by IC-UV-HG-AFS used di-ammonium tartrate 250 mmol l^{-1} pH = 5.5 and KOH 20 mmol l^{-1} pH = 12.0 as mobile phases.

analytical process. Thus, the inalterability of the standard solutions is required to ensure the traceability. It is known that Sb(III) at low concentration level is easily oxidized to Sb(V) within a short time.[25] Moreover, previous studies reported that dilution of working standard solutions and fresh water samples in 250 mmol l^{-1} di-ammonium tartrate is recommended in order to ensure Sb(III) stability at the low μg l^{-1} level.[14] In the present study, a standard solution containing 100 μg l^{-1} of Sb as Sb(III) was injected consecutively into the chromatographic system and analysed with the overall coupling IC-UV-HG-AFS. From the results [see Fig. 4(a)], the signal of Sb(III) decreased with time, whereas an Sb(V) chromatographic peak appeared within 90 min when working standards were diluted in HCl 1% (v/v). These facts might have been due to a oxidation with time of Sb(III) to Sb(V) in that medium. On the other hand, stability of this species for at least 120 min was observed in 250 mmol l^{-1} di-ammonium tartrate solutions [see Fig. 4(b)].

Moreover, significant differences in the sensitivity of Sb(III) were also observed between standard solutions diluted in both described media. Although a lower signal for Sb(III) was obtained in 250 mmol l^{-1} di-ammonium tartrate, it was

finally adopted as the most suitable since Sb(III) stability was ensured in this medium.

Quality parameters

Linear range

The linear range was verified by using the corresponding peak area of the chromatograms obtained under the optimum conditions described above. Linearity was proved at least over three orders of magnitude for the three antimony species studied.

Detection and quantification limits

These parameters were calculated by analyzing four mixtures containing the three antimony species at increasing concentrations. The regression line for each compound was calculated from the mean values ($n = 3$) of the peak areas. The concentrations at the detection and quantification limits were calculated from the standard deviation of the background signal ($n = 12$) and then referred to those regression lines ($LOD = 3\sigma_b/m$, $LOQ = 10\sigma_b/m$). In Table 2 the detection limits obtained with the overall coupling IC-UV-HG-AFS, are compared with those assessed without UV irradiation. The results obtained are in agreement with the variations observed in the signal of these species during the optimization of the photodecomposition step. Thus, Me_3SbCl_2 LOD was improved, whereas a slight increase for that parameter was observed in the case of Sb(III).

Precision

Precision was established in terms of both repeatability and intermediate intra-laboratory reproducibility. Repeatability was calculated as the %RSD from 10 peak area measurements of two independent standard solutions containing the three antimony species at concentrations of 2.5 and 5 $\mu g\ l^{-1}$. From the results (see Table 2), repeatability was better than 4% for both couplings.

Reproducibility at three non-consecutive days was also assessed. This reproducibility corresponds to the intermediate intra-laboratory or within laboratory reproducibility and it was calculated from the data as the standard deviation (S) at each concentration.[26–28] The standard solutions described above for repeatability were measured 10 times each day. The intermediate intra-laboratory reproducibility was better than 8% RSD in all cases (see Table 2).

Table 2. Quality parameters for antimony determination by IC-(UV)-HG-AFS

	IC-HG-AFS			IC-UV-HG-AFS		
Quality parameter	Sb(V)	Sb(III)	Me_3SbCl_2	Sb(V)	Sb(III)	Me_3SbCl_2
Detection limit ($\mu g\ l^{-1}$)	0.04	0.02	0.07	0.04	0.03	0.03
Quantification limit ($\mu g\ l^{-1}$)	0.14	0.06	0.15	0.14	0.10	0.07
Repeatability[a] (%RSD)[b]	3.7	3.3	2.5	2.8	2.7	2.4
Reproducibility[c] (%RSD)[b]	4.7	5.3	4.2	6.8	6.9	7.9

[a] Calculated as the %RSD from 10 measurements.
[b] %RSD represents the highest value obtained for both concentration levels tested.
[c] Calculated as the %RSD from 30 measurements.

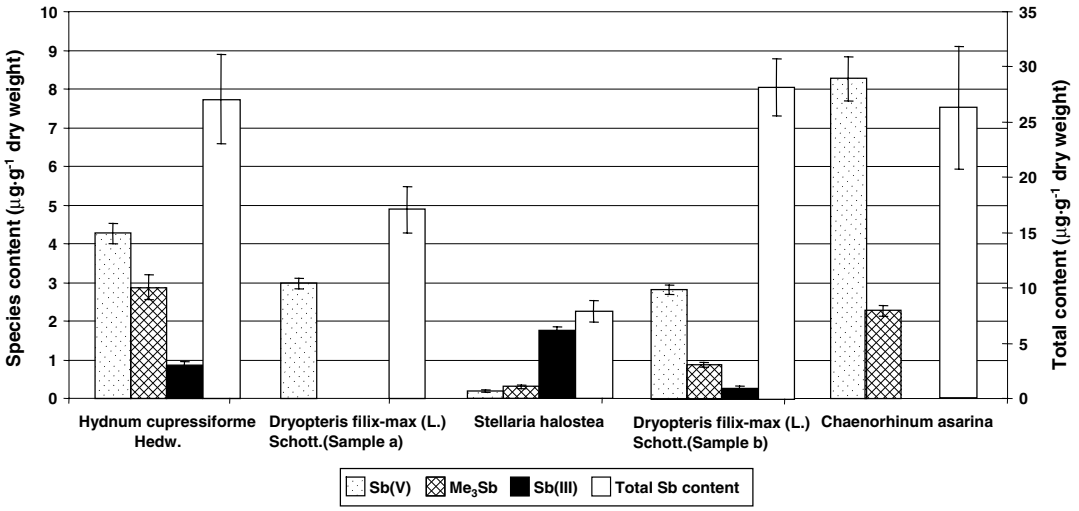

Figure 5. Sb species distribution (left y-axis) and total Sb content (right y-axis) in terrestrial plant extracts. Quantification of Sb species by standard addition.

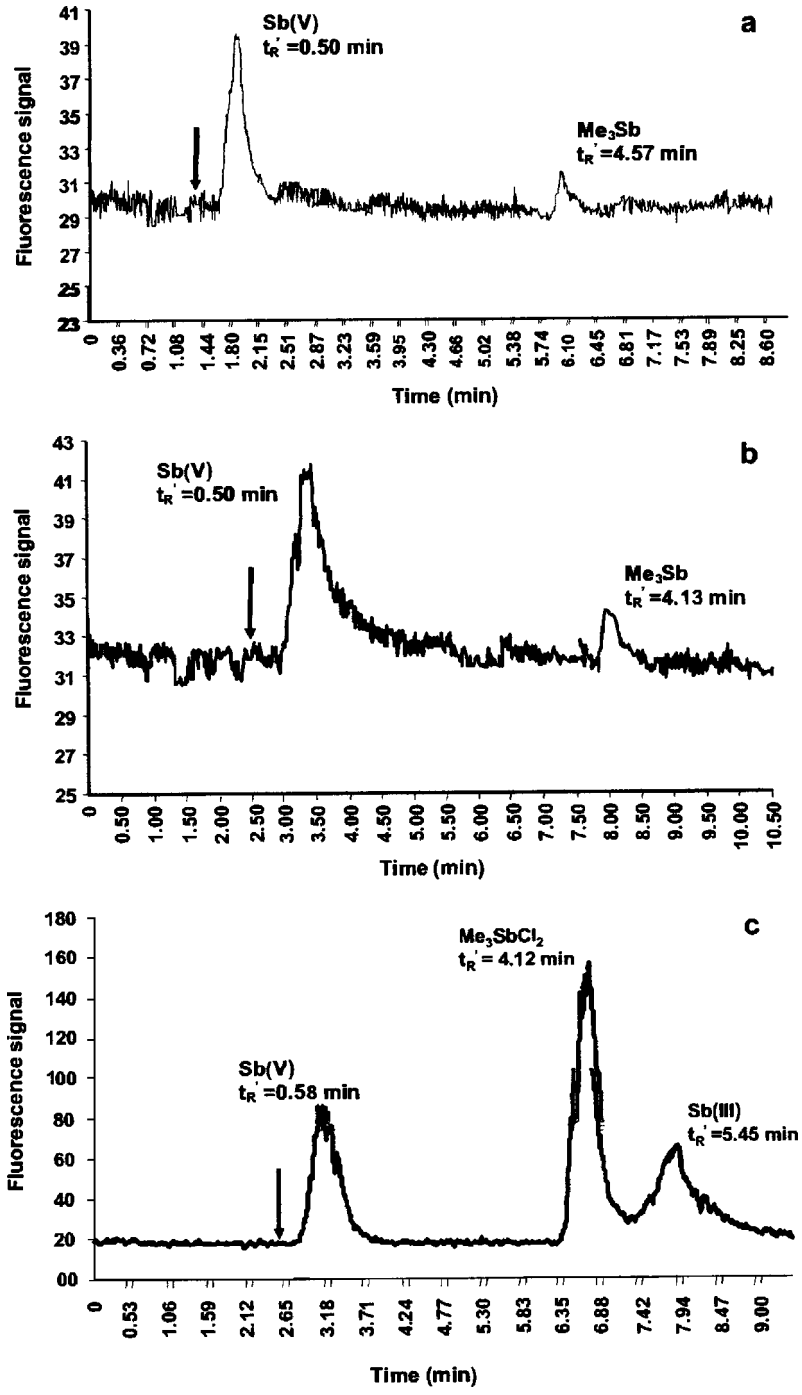

Figure 6. Chromatograms of a terrestrial plant extract (*Chaenorhinum asarina*) obtained by (a) IC-HG-AFS, (b) IC-UV-HG-AFS and (c) IC-UV-HG-AFS after standard addition of 10 μg l^{-1} of Sb as Sb(V), Me_3SbCl_2 and Sb(III). Chromatographic separation used a gradient elution of di-ammonium tartrate 250 mmol l^{-1} pH = 5.5 and KOH 20 mmol l^{-1} pH = 12.0. t_R' is the adjusted retention time. The arrow on the chromatogram indicates the dead time, t_m.

Speciation in terrestrial plant samples

The proposed methodology was applied to antimony speciation in several terrestrial plant samples. After applying the described extraction procedure (see the Experimental section), all the plant extracts were analysed in triplicate by both IC-HG-AFS and IC-UV-HG-AFS couplings under optimized conditions. Standard addition was used for the quantification of the antimony species. Figure 5 shows the total antimony content after acidic digestion as well as the quantification of the antimony species for all the plant samples analysed. Average concentrations (μg g^{-1} dry weight) and standard deviations ($n = 3$) are reported.

As an example, Fig. 6(a, b) shows the chromatograms obtained for *Chaenorhinum asarina* (figwort) without or with photooxidation. In this plant sample, Sb(V) is the major antimony species, also present is a methylantimony compound. Both peak shape and sensitivity (net peak area with and without UV irradiation 3.25×10^2 and 2.67×10^2, respectively) improved for the methylantimony compound with the introduction of UV irradiation. A chromatogram of the plant extract spiked with Sb(V), Me_3SbCl_2 and Sb(III) standards (10 μg Sb l^{-1} for each of the species) is also represented in Fig. 6(c). As shown, good agreement was obtained among the retention times of the chromatographic peaks for both plant sample and the spiked extract. Therefore, the methylantimony compound could be attributed to a trimethylantimony species. Sb(V) was the only antimony species found in *Dryopteris filix-max* (L.) Schott. (sample a) (fern), whereas *Hydnum cupressiforme* Hedw. (moss) and *Dryopteris filix-max* (L.) Schott. (sample b) presented Sb(V) as the major species, although quantifiable amounts of trimethylantimony species and Sb(III) were also found. On the other hand, *Stellaria halostea* (stitchwort) shows Sb(III) as the major antimony species, while trimethylantimony species and Sb(V) represented a minor fraction.

CONCLUSIONS

The introduction of on-line UV photooxidation by peroxodisulfate coupled to ion chromatography hydride generation atomic fluorescence spectroscopy is a suitable method for the separation and determination of antimony species. Several parameters, such as the UV lamp, the irradiation time and the peroxodisulfate concentration greatly influenced the photodecomposition efficiency. Under optimized conditions, photodecomposition resulted in higher sensitivity for the methylantimony species. This is a significant improvement for these compounds, since organoantimony content in most matrices is very low.

Otherwise, dilution of working standards and samples in di-ammonium tartrate medium ensured the stability of antimony species, since Sb(III) oxidation to Sb(V) was observed in other media. The developed methodology was successfully applied to antimony speciation in several terrestrial plants grown in polluted soils.

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