



Microwave extraction as an alternative to ultrasound probe for antimony speciation in airborne particulate matter



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ABSTRACT

An extraction method for Sb(V) and Sb(III) speciation in airborne particulate matter (PM) collected upon quartz filters has been developed, based on microwave extraction at 90 W with an 0.05 mol L⁻¹ hydroxylammonium chlorhydrate solution. The analysis of the extracts was performed by coupling high performance liquid chromatography (HPLC) with atomic fluorescence spectrometry (AFS). The parameters optimized were the volume of the extractant (5 or 10 mL, depending on the Sb concentration of the samples) and the time of extraction (6 min). The proposed microwave extraction method was compared to an existing one based on the use of ultrasound probe. Both extraction methodologies were applied to Sb spiked blanks (extracting solutions and quartz filters), and PM10 samples containing Sb collected at the city of Córdoba, an urban location of southern Spain. Similar and satisfactory results were obtained for spiked blanks with both methods. However, for PM10 samples quantitative results considering extraction efficiency (>95%) were obtained only by the proposed method based on microwave extraction, higher than with ultrasound probe extraction (<70%). Both Sb(V) and Sb(III) were found in the analyzed PM10 samples, Sb(V) being the main Sb species.

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1. Introduction

Sb is an element with no known biological role. It is considered an emerging contaminant in the environment [1–3]. It presents a chronic toxicity at very low concentration and many of its salts may be carcinogenic at long time exposure [4–6]. The toxicity and environmental risk of Sb depends on its oxidation state and the particular compound in which it can be found: inorganic Sb(III) and Sb(V) oxoanions, as well as an organic compound (trimethyl-antimony, Me₃SbCl₂) that can be present in some biological samples [7]. Trivalent Sb is considered more toxic than pentavalent form and both species are more toxic than trimethyl-antimony [8,9].

Sb has been widely used in industry and in the daily life since the 19th century [10]. Its most important use is as flame retardant in the production of electronics, textile and as a catalyst for plastic production [11,12]. It is also present in vehicles brake ware and tire ware [13,14].

Considering atmospheric emissions, about 58% of the Sb in the atmosphere originated from anthropogenic activities [2]. Fuel combustion is considered to be the most important one, followed by non-ferrous metals (e.g. lead and brass), pig iron and steel production, waste incineration and coal-fired power plants [15]. In addition to these

sources, Sb in urban air is considered a traffic-related element, along with Pb, Pd, Pt and Rh [13], as it has been reviewed by Smichowski et al. [16]. Brake pads contain Sb in the form of Sb₂S₃. It serves as lubricant, reducing vibrations and improving friction stability. There is evidence that Sb₂S₃ can be oxidized to Sb₂O₃ during the high temperatures that are reached during the braking process [17]. This causes dust emission, in which the mass distribution corresponds to particles with aerodynamic diameters comprised mainly between 3–6 μm [18].

Sb speciation has been studied in environmental samples like water [19] and soils [20], but there are few studies about Sb speciation in airborne particulate matter (PM) [21–25], in spite of the possible health effects caused by the high concentration of metals and metalloids in PM originated from anthropogenic sources [26]. There are several analytical techniques employed for Sb speciation, most of them based on the on-line coupling of high performance liquid chromatography (HPLC) with element specific detectors such as inductively coupled plasma-mass spectrometry (ICP-MS) [23,27–29] and atomic fluorescence spectroscopy (AFS) [19,20,22,30–32]. These instrumental couplings allow the determination of Sb species in solution in the μg L⁻¹ range.

For Sb speciation studies in solid samples, such as PM, an extraction procedure is required. It must fulfill the following requirements: quantitative extraction, no changes in the distribution of the Sb species, and the extractant must be compatible with the mobile phase of the subsequent chromatographic separation. A recent review of solid sample

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extraction procedures for Sb speciation has been published by Ferreira et al. [33]. In this sense, there are some extractant solutions described in the literature for PM samples: oxalic acid in 1% ascorbic acid, $\text{NH}_2\text{OH}\cdot\text{HCl}$, citrate or citric acid. The extraction procedure can be favored by mechanical shaking for several hours, or microwave extraction for 30 min [15,20,25,28]. Shorter extraction times can be achieved by ultrasound probe (3 min) [22], although the high frequency noise produced during its operation makes its use a potential health hazard for the operator, and obligates to take steps to reduce the impact of its noise.

The aim of the present work is to develop a new method for the extraction of Sb(V) and Sb(III) in airborne particulate matter, based on microwave extraction instead of ultrasound probe, with a similar extraction time in the minutes range, using $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution as extractant. After extraction, Sb speciation analysis was performed by HPLC-HG-AFS.

2. Experimental

2.1. Chemical and reagents

All of the chemicals and reagents used in this study were of analytical grade. Stock solutions of $1000 \text{ mg Sb(III) L}^{-1}$ and $1000 \text{ mg Sb(V) L}^{-1}$ were prepared from ClSb_3 and KSb(OH)_6 (Merck), respectively. For the chromatographic separation of the Sb species, the mobile phase was a 0.2 M solution of diammonium tartrate (Fluka). For hydride generation, two solutions were employed: i) sodium tetrahydroborate (Fluka) 1% (w/v), stabilized in 0.5% (w/v) NaOH (Panreac) and ii) 1.5 M HCl prepared from 37% (w/v) HCl (Sigma Aldrich). Hydroxylammonium chlorhydrate ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (Panreac) was used to prepare 0.05 M solutions for Sb extraction from the airborne particulate matter samples. For spiking experiments, Sb solutions in methanol (Sigma Aldrich) were used. Milli-Q water was obtained from an Elix Advantage system (Millipore).

2.2. Instrumentation for Sb speciation

Speciation of Sb(III) and Sb(V) in the extracts was achieved by HPLC-HG-AFS. This method uses ion-exchange liquid chromatography coupled on-line to atomic fluorescence spectrometry through continuous hydride generation [22].

The liquid chromatograph was a JASCO PU-2080 Plus HPLC quaternary pump with solvent degasser, equipped with a Rheodyne 7125 injector and a 200 μL loop for sample introduction. The isocratic separation of the Sb(V) and Sb(III) was accomplished in an PRP-X100 anion-exchange column (100 mm \times 4.1 mm, 10 μm particle size) (Hamilton). The optimized mobile phase was a 0.2 mol L^{-1} diammonium tartrate solution (pH 5, adjusted with HCl) at a flow rate of 0.8 mL min^{-1} .

Online hydride generation after chromatographic separation was performed by adding 1% (w/v) NaBH_4 (in 0.5% (w/v) NaOH) and 1.5 M HCl solutions by means of a peristaltic pump at a flow rate of 1.0 mL min^{-1} . Argon was used as a carrier gas to transport the Sb hydrides to a gas-liquid separator.

A Millennium Excalibur instrument (PS Analytical) was used for Atomic Fluorescence Spectrometry (AFS) detection, equipped with a Sb Boosted Discharge Hollow Cathode Lamp (Photron), and a hygroscopic membrane drying tube (Permapure). H_2 at a flow rate of 60 mL min^{-1} was added at the gas-liquid separator in order to maintain and stabilize the flame of the AFS detector.

HPLC-HG-AFS was calibrated with Sb solutions of Sb(V) and Sb(III) with concentrations between 2 and 20 $\mu\text{g L}^{-1}$, prepared in the same tartrate solution employed as mobile phase. Fig. 1 shows a typical chromatogram obtained for a 5 $\mu\text{g L}^{-1}$ standard.

For total Sb determination of the samples, a portion of the filters containing PM were placed in a Teflon vessel and acid digested

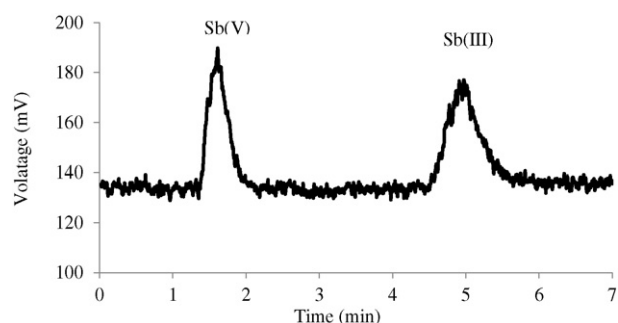


Fig. 1. Chromatogram of a 5 $\mu\text{g L}^{-1}$ Sb standard obtained by HPLC-HG-AFS.

(HNO_3 , HCl and HF) on a hot plate. The Sb determination was performed afterwards by ICP-MS (model 7700, Agilent).

2.3. PM10 sampling

Six PM10 (airborne particles with diameter < 10 μm) samples were collected in southern Spain during 2011–2013. They belong to Air Quality Monitoring Network (“Red de Vigilancia y Control de la Calidad del Aire”) of the Andalusian Autonomous Government. Two samples corresponded to rural or urban sites in which Sb was not detected, and were selected for Sb spiking experiments. Also, four samples collected at the city of Córdoba with either high or low Sb concentration were analyzed for Sb speciation. Three of them (filters 3, 4 and 6 of Table 2) corresponded to an urban background monitoring station influenced by traffic (Lepanto station), whereas the fourth one (filter 5 of Table 2) corresponded to an urban site with industrial influence (Parque Joyero station). The sampling campaign at Lepanto and Parque Joyero stations corresponded to 59 and 162 samples of PM10, respectively. Samples were collected by means of a Grasseby–Andersen high volume air sampler (68 $\text{m}^3 \text{h}^{-1}$) equipped with quartz glass microfiber filters (QF20S, Schleicher and Schuell) that retain the PM10 fraction.

2.4. Extraction procedure for Sb speciation in PM10

Circular portions of 1.2 cm^2 of quartz filter samples containing the airborne PM10 were cut using a stainless steel hollow cylinder and placed in 50 mL polyethylene centrifuge tubes. $\text{NH}_2\text{OH}\cdot\text{HCl}$ 0.05 M was used as extracting solution, trying volumes of 5 or 10 mL. The extraction was aided either by microwave radiation (microwave oven model NN-K105WB, Panasonic) operated at 90 W between 2–6 min, or the use of an ultrasound probe (model HD2200, Bandelin Sonopuls) with a 2 mm titanium tip, operated at 25–50 W between 30 s and 2 min. After the extraction, the solutions were filtered through 0.45 μm (Filter-lab) before injection onto the HPLC column.

2.5. Sample spiking procedure

Sample blanks and the extracting solution were spiked using an Sb solution prepared in methanol, in order to optimize the extraction methodology. Two spiking procedures were considered. A first procedure was conducted by adding 100 μL of 1 mg L^{-1} solution (containing both Sb(III) and Sb(V)) in methanol to a circular portion of 1.2 cm^2 of quartz filter blanks or quartz filter samples containing airborne PM10. The samples were extracted afterwards with 5 mL of the extracting solution, either with microwave radiation or ultrasound probe. For the second procedure, the concentration of the Sb(III) and Sb(V) of the methanol spiking solution was increased from 1 ppm to 2 ppm. In this second case, the volume of the extracting solution was increased from 5 to 10 mL. The final concentration in the extracts was 20 $\mu\text{g L}^{-1}$ for each Sb species.

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