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Arsenic and antimony determination in non- and biodegradable materials by hydride generation capacitively coupled plasma microtorch optical emission spectrometry

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ABSTRACT

A sensitive method using a miniature analytical system with a capacitively coupled plasma microtorch (25 W, 13.56 MHz, 0.4 l min⁻¹ Ar) was developed and evaluated for the determination of As and Sb in recyclable plastics and biodegradable materials by hydride generation optical emission spectrometry. Given their toxicity, As and Sb should be subject to monitoring in such materials despite not being included within the scope of Restriction of Hazardous Substances Directive. The advantages of the proposed approach are better detection limits and lower analysis cost relative to conventional systems based on inductively coupled plasma optical emission and flame atomic absorption spectrometry with/without derivatization. Samples were subjected to acidic microwave-assisted digestion in a nitric-sulfuric acid mixture. Chemical hydride generation with 0.5% NaBH₄ after the prereduction of As(V) and Sb(V) with 0.3% L-cysteine in 0.01 mol l⁻¹ HCl (10 min contact time at 90 ± 5 °C) was used. Under the optimal hydride generation conditions and analytical system operation the detection limits (mg kg⁻¹) were 0.5 (As) and 0.1 (Sb), whereas the precision was 0.4–7.1% for 10.2–46.2 mg kg⁻¹ As and 0.4–3.2% for 7.1–156 mg kg⁻¹ Sb. Analysis of two polyethylene CRMs revealed recoveries of 101 ± 2% As and 100 ± 1% Sb.

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1. Introduction

Inorganic As compounds have been classified as Group I human carcinogens with variable toxicity depending on the As oxidation state [1]. Although there is no evidence that Sb compounds are carcinogenic, The International Agency for Research on Cancer has characterized antimony trioxide as carcinogenic based on animal testing [2]. For both elements the inorganic compounds of the +3 oxidation state (As(III) and Sb(III)) are more toxic than compounds in +5 oxidation state, As(V) and Sb(V). Antimony in its elemental state is more toxic than its salts. Many inorganic As compounds can be detoxified through methylation in mammals and excreted in urine, unlike Sb compounds. Antimony trioxide is used for its synergistic effect in brominated flame retardants formulations for plastics and is the most important catalyst in the manufacture of polyethylene terephthalate (PET) for water and other beverages

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bottles. Although As and Sb are not currently listed in the Directives 2002/95/CE and 94/62/CE (Restriction of Hazardous Substances—RoHS), their determination in plastics and biodegradable materials is necessary as they have been listed in the Green Procurement Guidelines by Joint Industry Guidelines. Antimony is also considered a priority pollutant by the U.S. Environmental Protection Agency and the German Research Community [3,4]. Although there are controversial views in the literature on the transfer of Sb compounds from PET in water [5], several studies confirmed the leaching and contamination increase of bottled water upon storage [6–8].

Analytical techniques for Sb determination in plastics include inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) [9,10], flame atomic absorption spectrometry (FAAS) [9,11], energy dispersive X-ray fluorescence (EDXRF) [9] and graphite furnace atomic absorption spectrometry (GFAAS) using slurry or direct solid sampling [12]. The corresponding techniques reported for As determination in plastics are EDXRF [9] and ICP-MS [10]. The development of methods for total content determination and speciation of As and Sb is of increasing interest, as highlighted in several reviews [13–17].

The hydride generation (HG), either chemical or electrochemical, with/without hydride preconcentration is widely used to increase the sensitivity of the determination of As and Sb by spectrometric techniques. Thus HG-AAS [18–20], HG-ICP-OES [21], HG-ICP-MS [22] and atomic fluorescence spectrometry (HG-AFS) [23–25] were mentioned as having improved performance. Recently, the determination of As and Sb has been achieved with good detection limits using HG and detection by miniaturized microwave microstrip plasma optical emission spectrometry (HG-MSP-OES) [26,27] or dielectric barrier discharge atomic absorption or atomic fluorescence spectrometry (HG-DBD-AAS, HG-DBD-AFS) [28–30]. Derivatization by chemical hydride generation involves two steps: prereduction of As(V) and Sb(V) to their species in the +3 oxidation state followed by hydride development in acidic medium with NaBH₄ stabilized in alkaline solution. Among agents used to prereduce As(V) and Sb(V) to As(III) and Sb(III), L-cysteine in diluted HCl (0.01–0.03 mol l⁻¹) has proved to be very suitable due to reduction of the contact time and removal of interference in liquid phase [22,31].

The aim of this work was to develop a sensitive method using a miniature analytical system with capacitively coupled plasma microtorch equipped with a microspectrometer to determine As and Sb by hydride generation optical emission spectrometry (HG-μCCP-OES). The possibility of As and Sb determination under similar conditions was investigated using prereduction with L-cysteine and hydride generation in diluted HCl. The optimized conditions for chemical derivatization and plasma operation, and the detection limits relative to other analytical systems are presented. The optimized methodology was applied to recyclable plastics from electronics and packaging containing non- and biodegradable materials and validated by analyzing two polyethylene certified reference samples. The study is of analytical importance given the current interest in the development of simple, low-cost and user-friendly miniature analytical systems for dedicated applications.

2. Experimental

2.1. Instrumentation

The μCCP-OES system had been previously used for the simultaneous multielemental analysis of environmental samples after mineralization and Hg determination in non- and biodegradable materials and water after cold vapor generation [32–34]. The HG-μCCP-OES experimental set-up (Fig. 1) consists of a capacitively coupled plasma microtorch (INCO-INOE 2000 Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania), free-running generator (13.56 MHz, 10–30 W, 15 × 17 × 24 cm³) (Technical University of Cluj-Napoca, Romania), HGX-200 hydride generation system (Omaha, Nebraska, USA) and HR 4000 microspectrometer (Ocean Optics, Dunedin, Florida, USA). The optical signal was collected via a QP fiber optic (600 μm diameter, 25 cm length) and processed by SpectraSuite software as the average of 10 measurements with a 5 s integration time. The viewing zone in plasma was selected by moving the fiber optic in 0.1 mm increments using an XYZ translator. The hydride generator was coupled with the plasma microtorch using a PTFE tube.

Plasma was developed within a quartz tube (25 mm length, 5 mm i.d. and 160 nm cut-off; H. Baumbach & Co, Ltd., Ipswich Suffolk, UK) on the tip of a 1-mm-diameter Mo microelectrode connected to an RF generator. Hydrides were carried into the plasma by a 0.3–0.5 l min⁻¹ Ar flow rate through four 0.75-mm-diameter channels crossing the Mo microelectrode support on a 3-mm-diameter rim.

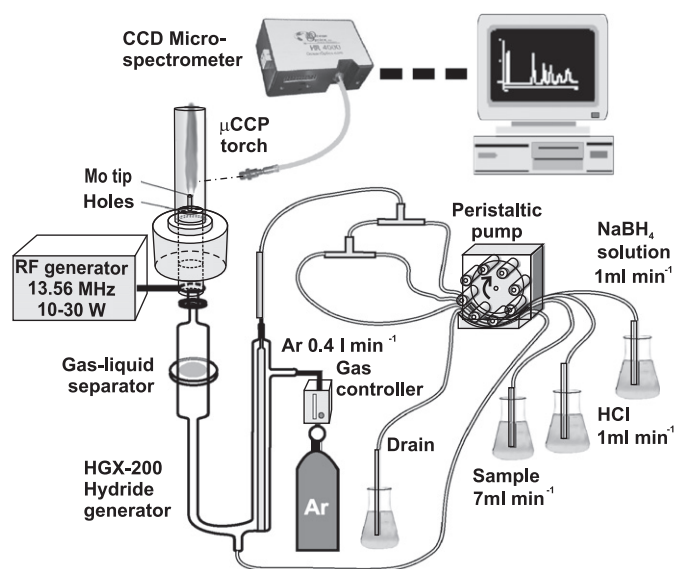


Fig. 1. Schematic of the HG-μCCP-OES set-up.

An MW3S+ Berghof model closed-vessel microwave digestion system (Berghof, Germany) at controlled temperature was used for sample mineralization. The pH of the samples was adjusted to 2.00 ± 0.01 prior to hydride generation using a 540 GLP pH-meter (WTW GmbH, Weilheim, Germany).

2.2. Reagents, standard solutions, CRMs and samples

Hydrochloric acid (10 mol l⁻¹) for As determination (< 5 ng l⁻¹ As), NaBH₄ (> 96%), NaOH ACS (> 99%) and L-cysteine BioChemika Mikroselect (> 99.5%) purchased from Fluka-Chemie (Buchs, Switzerland) were used. Nitric acid (65%), H₂SO₄ (97%) and stock solutions of 1000 μg ml⁻¹ As(V) and Sb(V) were procured from Merck (Darmstadt, Germany). Throughout the study, Milli-Q water obtained in laboratory (Millipore Corp., Bedford, USA) was used. The glassware was soaked in 5 mol l⁻¹ HNO₃ for at least 12 h and rinsed with Milli-Q water.

Stock solutions of 10% L-cysteine in 0.005–0.05 mol l⁻¹ HCl were prepared. Solutions of 50 ng ml⁻¹ As(V) and 10 ng ml⁻¹ Sb(V) in 0.005–0.05 mol l⁻¹ HCl in the presence of 0.02–0.7% L-cysteine and solutions of 0.005–0.05 mol l⁻¹ HCl as a carrier toward the hydride generator were prepared for optimizing the prereduction and derivatization processes. Solutions of 0.2–0.7% NaBH₄ stabilized in 0.5% NaOH and solutions containing 0.5% NaBH₄ stabilized in 0.2–0.7% NaOH were also prepared for optimizing the hydride generation. Standard solutions of 5–100 ng ml⁻¹ As and 1–100 ng ml⁻¹ Sb in 0.01 mol l⁻¹ HCl in the presence of 0.3% L-cysteine were used to calibrate the HG-μCCP-OES system.

Two polyethylene granule certified reference materials were employed for method validation: ERM-EC 680k and ERM-EC 681k (LGC, Promochem, Wesel, Germany).

The real samples were recyclable plastic based on acrylonitrile-butadiene-styrene copolymer (ABS) from electronic equipment, polyethylene (PE) shopping bags, materials containing oxo-biodegradable polyethylene (OPE) with 98% PE or corn starch for food packaging and polyethylene terephthalate (PET) bottles for still and mineral water.

2.3. Sample treatment

Samples were cut into pieces, washed, air-dried and ground to grain size < 2 mm using a cutting mill. Next, 150 mg samples were subjected to high-pressure (100 atm) microwave digestion

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