



Speciation of dissolved inorganic antimony in natural waters using liquid phase semi-microextraction combined with electrothermal atomic absorption spectrometry

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ABSTRACT

Liquid–liquid extraction preconcentration technique which allows the achievement of extremely high ratio between the aqueous and organic phase was specified as semi-microextraction. A modified highly effective liquid phase semi-microextraction (LSME) procedure was developed for preconcentration and determination of ultra trace levels of inorganic antimony species in environmental waters using electrothermal atomic absorption spectrometry (ETAAS) for quantification. Antimony(III) species were selectively extracted as dithiocarbamate complexes from 100 mL aqueous phase into 250 μ L xylene at pH range of 5–8. Total Sb was determined using the same extraction system over a sample acidity range of pH 0–1.2 without the need for pre-reduction of Sb(V) to Sb(III). The concentration of Sb(V) was obtained as the difference between that of total antimony and Sb(III). With an 8 min extraction an enrichment factor of 400 was achieved. The limit of detection (3 s) was 2 ng L^{-1} Sb. The method was not affected by the presence of up to 0.01% humic acid, 0.025 mol L^{-1} EDTA, 0.01 mol L^{-1} tartaric acid and 0.001 mol L^{-1} F^{-} . Recoveries of spiked Sb(III) and Sb(V) in river, tap, and sea water samples ranged from 93 to 108%. The results for total antimony concentration in the river water reference material SLRS-5 were in good agreement with the information value. The procedure was applied to the determination and quantification of dissolved antimony species in natural waters.

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1. Introduction

Antimony and its compounds are considered as pollutants of priority interest by the European Union [1] and by the Environmental Protection Agency of the United States [2]. The European Union established a maximum admissible concentration of antimony in drinking water of 5 $\mu\text{g L}^{-1}$ [3]. In unpolluted waters the total dissolved antimony was found to be less than 1 $\mu\text{g L}^{-1}$ [4]. It enters the aquatic environment as a result of the weathering of rocks, through wastes from mining and manufacturing, from municipal discharges and from soil runoff. Antimony in the environment is most often present as inorganic Sb(III) and Sb(V) species. Both states are strongly hydrolysed, Sb(V) occurring as $\text{Sb}(\text{OH})_6^-$ and Sb(III) as SbO_2^- [5]. Only few authors report the presence of methylstibonic acid, $\text{CH}_3\text{SbO}(\text{OH})_2$ (MSA) and dimethylstibinic acid ($\text{CH}_3)_2\text{SbO}(\text{OH})$ (DMSA) in river and sea waters [6,7]. Trivalent compounds of antimony are reported to be more toxic than pentavalent ones [8]. The most toxic compound is stibine (SbH_3). Organoantimony species are less toxic than the inorganic species. Speciation procedures applied for antimony include

selective hydride generation, liquid–liquid extraction, selective sorption, electrochemical and chromatographic methods [4,5,9]. But, the determination of antimony species still presents a challenging analytical problem due to extremely low concentration of Sb in natural waters, instability of Sb species during transportation and storage, absence of sophisticated instruments in common laboratories and necessity of new low cost, effective green analytical procedures. In the present paper a modified liquid phase semi-microextraction (LSME) was developed and used to differentiate between inorganic Sb(III) and Sb(V) species. The technique is based on the different extraction behavior of the Sb–ammonium pyrrolidine dithiocarbamate (APDC) complexes. In acidic medium (up to pH 1.2) both Sb(III) and Sb(V) form chelates with APDC that are quantitatively extracted into iso-butyl methyl ketone (IBMK) [10,11]. But, at a pH range of 5–8, only Sb(III) is extracted completely, Sb(V) is not extracted at all. The described liquid–liquid extraction procedures have the disadvantage of achieving low enrichment factors, which are insufficient to determine antimony species in the most aquatic systems. Liquid phase microextraction procedures were recently developed for determination of trace level of metals [12]. A single drop micro extraction (SDME) method combined with ETAAS was reported for determination of Sb(III) and total Sb in environmental water sample [13]. N-benzoyl-N-phenylhydroxylamine was applied as the

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complexing agent for Sb(III) in a chloroform drop (3 μL). Total Sb was determined after pre-reduction of Sb(V) to Sb(III) by L-cysteine. Our experiments showed the following main disadvantages of SDME–ETAAS procedures: i) the volume of the organic solvent is extremely low (3 μL) and it allows only one measurement replicate; ii) in natural waters a lot of metals form extractable complexes with the employed ligand and, in that case, a single drop of organic solvent cannot ensure quantitative extraction of all formed complexes; and iii) chloroform is not an appropriate solvent for ETAAS [14].

The purpose of this study was to optimize and to develop a green highly effective liquid phase semi-microextraction method for preconcentration/speciation and determination of ultra trace Sb(III) and Sb(V) in natural water systems, using the extraction system APDC–xylene and ETAAS for quantification. Investigations were performed also on the stability of antimony species during storage.

2. Experimental

2.1. Instrumentation

The ETAAS measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light source was an electrodeless discharge lamp for Sb. The selected wavelength was 217.6 nm, the spectral bandpass – 0.2 nm. Standard uncoated graphite tubes were used as atomizer. The injection of 20 μL organic phase was performed manually. Only peak areas were used for quantification. The graphite furnace operating parameters for ETAAS measurements of Sb are presented in Table 1. The extractant APDC used for preconcentration/speciation of Sb acts as a matrix modifier for the determination of this element [15].

2.2. Reagents and materials

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout. The stock standard solution of 1 g L⁻¹ Sb (V) was prepared by dissolving kaliumhexahydroxoantimonat (V) K [Sb(OH)₆] (p.a. Merck) in 2.5 mol L⁻¹ HCl (p.a. Merck). For Sb(III) a ready for use standard solution for AAS (Merck, Darmstadt, Germany) with a concentration of 1 g L⁻¹ Sb(III) in 20% HCl was used. Intermediate standard solutions with a concentration of 10 $\mu\text{g mL}^{-1}$ Sb(III) and Sb(V) were prepared weekly by appropriate dilution with 0.5 mol L⁻¹ HCl. The standard solutions at ng mL⁻¹ level were prepared daily. An organic standard solution of Sb was prepared by extraction of antimony–dithiocarbamate chelate from aqueous standard solution. A 1 mL volume of standard solution with a Sb concentration of 500 ng mL⁻¹ Sb(III) was mixed with 5 mL 0.5 mol L⁻¹ HCl, 0.5 mL of 2% ammonium pyrrolidinedithiocarbamate (APDC) and 5 mL xylene and extracted for 2 min. The organic layer obtained contained 100 ng mL⁻¹ Sb. This organic phase was further used for the preparation of the working organic standard solutions by appropriate dilution with xylene.

Humic acid was supplied by Fluka, Switzerland.

River water reference material for trace metal SLRS-5 (National Research Council Canada) with information value for antimony of

0.3 $\mu\text{g L}^{-1}$ was used after 5-fold dilution for checking the accuracy of the developed method.

2.3. Sample collection and preparation

River, lake and sea water samples were collected in high density polyethylene (PE) bottles and filtered through 0.45 μm membrane filters. Then to the filtrates solid EDTA (1 g L⁻¹ EDTA) was added and mixed. The filtrates were transferred to the laboratory and stored in a refrigerator at 4 °C. The separation/preconcentration procedure was finished within 72 h of sample collection. River and lake water samples were from various areas of Bulgaria and Macedonia. Sea water samples were from the Bulgarian Black sea coast. Tap water sample was from the local laboratory and was analyzed without filtration.

2.4. Procedure

The sample was placed in a 100.0 mL volumetric flask up to the mark. 1 mL conc. HCl (37%, mV⁻¹) was added and the sample was homogenized by shaking. Then 0.5 mL 2% APDC and 250 μL xylene were added. The extraction was performed by shaking the flask for 8 min. The organic phase remains as upper layer above the aqueous phase. Without any separation this xylene phase containing the dithiocarbamate complexes of both Sb(III) and Sb(V) species was directly introduced into the graphite furnace and the temperature program (Table 1) was started. The obtained absorbance signal corresponds to the concentration of total antimony. To a second aliquot of the sample placed in a 100.0 mL volumetric flask 1 mL 1 mol L⁻¹ acetate buffer solution (pH 5), 0.5 mL 2% APDC and 250 μL xylene were added. After 8 min extraction the concentration of Sb(III) was measured in the xylene phase by ETAAS.

3. Results and discussion

3.1. Optimization of the liquid phase semi-microextraction procedure

The aim of the optimization procedure was to obtain high extraction efficiency using microvolumes organic phase at 100 mL aqueous phase. As organic solvent xylene was preferred instead of the more common used isobutylmethylketone because of the lower solubility of xylene in water. Xylene is appropriate for the subsequent ETAAS determinations. The concentration of the ligand APDC was not found as substantial factor for optimization. In the range of 0.005–0.02% APDC (mV⁻¹) in the sample no difference in the extraction recoveries were observed. For all further experiments a concentration of 0.01% (mV⁻¹) APDC was chosen. Important factors for achieving quantitative separation and extraction preconcentration with high enrichment factor were a) the acidity (pH) of the sample; b) the volume of the organic phase, i.e. the ratio between the organic and the aqueous phase and c) the time for extraction.

The effect of pH on the extraction of antimony species as dithiocarbamate complexes into microvolumes of xylene was investigated separately. The pH values of distilled water samples were adjusted ranging from 0.3 to 2 and from 5 to 8.3 with diluted ammonia and hydrochloric acid. The results of the effect of pH on the extraction degrees of Sb(III) and Sb(V) are shown in Fig. 1. It can be seen that the extraction of Sb(III) is quantitative for the entire studied range from pH 0.3 to pH 2 and from pH 5 to pH 8.2. Antimony(V) is completely extracted in the pH range from pH 0.3 to pH 1.2. At pH range from pH 5 to pH 8.3 Sb(V) was not extracted at all. It means that at pH 5–8.3 the extraction system APDC–xylene is selective towards Sb(III) and that it is possible to separate quantitatively Sb(III) and Sb(V) by selecting the suitable pH.

The influence of the extraction time and of the volume of the organic phase (for 100 mL sample) was studied for distilled, tap and

Table 1
Electrothermal atomization program for determination of antimony as dithiocarbamate complex in xylene by ETAAS with Zeeman background correction.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Internal gas (Ar) flow rate (mL min ⁻¹)
Drying	120	10	10	300
Pretreatment	1100	10	10	300
Atomization	1700	0	3	0
Cleaning	2500	2	3	300

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