Investigation on stability and preservation of antimonite in iron rich water samples

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HIGHLIGHTS

- The fast oxidation of antimonite is demonstrated when Fe^{2+} is in the water samples.
- We tested different agents to preserve both inorganic redox species of antimony.
- An easy to handle and effective procedure is suggested for species preservation.

GRAPHICAL ABSTRACT
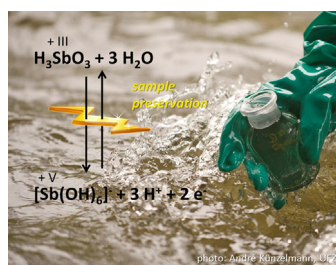
ABSTRACT

The stability of antimonite in iron rich water samples is rather poor. The aim of the study was to find a simple procedure by using preservation agents to keep the speciation information from sampling till analysis. Species analysis of antimony traces (lower $\mu g\,L^{-1}$ range) was done by HPLC–ICP-MS. Phosphoric acid, tartrate, and EDTA were tested as preservation agents in comparison to no addition. The use of EDTA as the preservation agent provided the best results. The suggested procedure is to add 20 mM EDTA as final concentration immediately during sampling and store them at dark and cool ($6\,^{\circ}C$) as usual. Using this procedure, the stability of Sb(III) as well as of Sb(V) was proven for at least 7 days, even for high iron concentrations.

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1. Introduction

In recent years the analysis of antimony species has become a main issue in environmental science [1,2]. Various analytical procedures have been suggested.

A special problem for the speciation analysis of Sb(III) and Sb(V) seems to be the instability Sb(III) in water samples which have been in contact with atmospheric oxygen and other oxidants. The oxidation rates in natural waters differ in the range between stable and 2.07 day^{-1} (pseudo first order kinetics) [3,4]. Factors influencing the oxidation kinetics seem to be microbial activity,

presence of oxidants, as well as organic substances which can form complexes with Sb(III).

The oxidation of Sb(III) by oxygen in the presence of Fe^{2+} has been investigated by Leuz et al. [5]. The oxidation rates increase with higher Fe:Sb ratios as well as with the pH value. Half-lives of Sb(III) were reported to be in the range of some minutes to hours.

Consequently, water samples which contain Fe^{2+} and Sb(III) coming into contact with oxygen during sampling will hardly get the right speciation result after several hours of transporting the samples to the lab or even days of storage in the fridge.

Dealing with the analysis of instable redox species, the stability of the species in the sample is of special concern. For arsenic species different preservation techniques have been published (see review [6]). The principles for the preservation of redox species are the addition of acids (e.g., phosphoric acid [8,9]) or chelating

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agents like EDTA [10]. The stability of antimony in environmental matrices was reviewed [11] where mainly solid phase extractions were applied. To our best knowledge, there has been no procedure published for water samples containing distinct amounts of iron, such as many contaminated seepage or groundwater samples.

The aim of this study was to develop a procedure to preserve traces of Sb(III) as well as Sb(V) in water samples additionally containing Fe^{2+}.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical grade or higher. All standard solutions were dissolved in de-ionized water (Direct-QTM 5 system; Millipore). Stock solutions of antimony were prepared from $K[Sb(OH)_6]$ (99%, Riedel de Häen) and $K_2[Sb_2(C_4H_2O_6)_2]\cdot 3H_2O$ (99%, Sigma–Aldrich) with a final concentration of $1\,g\,Sb\,L^{-1}$.

For every preservation experiments an amount of 2–4 mg Sb_2O_3 (p.a., MERCK) were freshly dissolved in 100 mL de-ionized water at room temperature. The resulting concentration of the supernatant liquor (saturated solution of about $4.5\,mg\,Sb\,L^{-1}$) was checked by measuring the total concentration (standard Certipur, MERCK) by ICP-MS (Agilent 7700), and diluted further to get the required concentration.

A stock solution of $100\,mg\,L^{-1}\,Fe^{2+}$ was freshly prepared for each experimental series using $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ (MERCK, Darmstadt, Germany).

The diammonium salt of EDTA (99.5%, Fluka) was used as eluent (20 mM) and as additive for samples (20 mM). The other chemicals used as a preservation agent were citric acid monohydrate, ammonium tartrate (both p.a. MERCK, Darmstadt, Germany) and phosphoric acid (diluted from concentrated H_3PO_4, 85%, MERCK, Darmstadt, Germany).

2.2. Analytical procedures

An anion exchange chromatography was coupled with ICP-MS using a Hamilton PRP-X100 column (150 mm × 2.1 mm, 10 μm; details see [7]) to analyze antimonite (Sb(III)) as well as antimonate (Sb(V)) in the samples. A solution of 20 mM EDTA with pH 4.5 was applied as eluent (with a flow rate of $0.4\,mL\,min^{-1}$). The chromatographic device (Agilent Technologies 1200 Series) equipped with an autosampler and a binary pump was coupled via MicroMist nebulizer (Agilent) with an ICP-MS (Agilent Technologies 7700 Series) for elemental selective detection. The following ICP-MS parameters were used: RF forward power: 1550 W, Ar plasma gas flow: $15\,L\,min^{-1}$, Ar nebulizer gas flow: $1\,L\,min^{-1}$, Ar auxiliary gas flow: $0.9\,L\,min^{-1}$, for detection $m/z = 121$.

The LOD's are $39\,ng\,L^{-1}$ for Sb(V) and $41\,ng\,L^{-1}$ for Sb(III) (mean of blank + 3σ) in a 20 mM EDTA solution [7]. A chromatogram of a standard with each $20\,\mu g\,L^{-1}$ Sb(V) and Sb(III) can be seen in Fig. 4.

All blanks, standards and samples (with the exception of the EDTA series) were spiked with EDTA to get a final concentration of 20 mM [7]. This ensures the complete formation of the Sb(III)–EDTA complex and better reproducibility.

The concentration of iron and antimony in the tailings materials was determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF). A X-LAB 2000 (SPECTRO A.I.) was calibrated with a set of geological standard materials (07309–07312, 07409 and 07411 – all GBW; LK SD-1 and LK SD-4 – both CCRMP-CANMET-MMSL; SRM2704 and SRM2710 – both NIST). The tailings material was dried at 105 °C for 1 h, afterwards ground by means of an agate ball mill (Retsch S 100). Sample preparation was

accomplished by mixing these materials with stearine wax (Hoechst wax for XRF-analysis) as binder in a ratio 80:20 w/w and after this by pressing the mixtures into pellets 32 mm in diameter.

2.3. Kinetics of Sb(III) oxidation by ferrous ions

Autosampler vials (1.8 mL dark glass vials, WICOM) were completely filled with a solution of $35\,\mu g\,L^{-1}$ Sb(III) (freshly prepared from Sb_2O_3) in de-ionized water. The fresh Fe(II) solution was added to get final concentrations of 0.5, 1.0, and $2.0\,mg\,L^{-1}$ Fe(II). The measurement of the species (see Section 2.2) was started immediately in the first vial followed after 8 min each (duration of the chromatographic run) with the next vial. Replicates from the same vial were not used to avoid effects on the oxidation reaction through the sampling procedure (contact with the stainless steel needle).

2.4. Preservation experiments with artificial samples

In a first set of experiments samples were prepared containing $20\,\mu g\,L^{-1}$ Sb(III) (freshly prepared from Sb_2O_3) and as preservation agents 20 mM EDTA, 20 mM tartrate or 10 mM phosphoric acid. The samples were prepared as triplicates and stored in the fridge in completely filled 30 mL HD-PE bottles. A set of 3 samples was stored without any preservation agents. The same set of samples was produced with additionally $2\,mg\,L^{-1}\,Fe^{2+}$ (freshly prepared). All samples were analyzed immediately after preparation, and after 1, 2, 4, 7, and 14 days of dark storage at 6 °C.

The next set of experiments was carried out using 20 mM EDTA as preservation agents for $40\,\mu g\,L^{-1}$ Sb(III) (freshly prepared from Sb_2O_3). Additionally, these samples contained 0.5, 1.0, and $2.0\,mg\,L^{-1}\,Fe^{2+}$. A volume of 100 mL was prepared from all mixtures and filled as duplicate in 50 mL PE bottles. The samples were stored in the fridge (6 °C) until analysis.

2.5. Change of Sb(V) in presence of tartrate

A solution with $40\,\mu g\,L^{-1}$ Sb(V) and 20 mM tartrate was filled into 15 auto sampler vials (1.8 mL dark glass vials, WICOM). The measurement of the species was started immediately in the first vial followed after 8 min each with the next vial. After 10 and 12 samples a blank was included to get a total reaction time of 2 h. To check the retention time of the generated peak a spike experiment with Sb(III) was carried out. A volume of 1 mL of a solution with $50\,\mu g\,L^{-1}$ Sb(V) in 20 mM tartrate was filled in an autosampler vial, analyzed after 1 h and then spiked with 200 μL of an $100\,\mu g\,L^{-1}$ Sb(III) and analyzed again.

2.6. Preservation experiment with tailings material

Due to difficulties in reproducibly preparing Sb(III) samples with higher Fe^{2+} concentration, extracts from two samples containing antimony from the mine tailings Davidschacht near Freiberg, Germany, were used. Sampling was done by digging a hole with an excavator down to about 3 m. The samples were taken by plastic spoons in the depths 80 cm and 105 cm, representing the partly oxidized zone of the tailings pond. The total concentrations of Sb are $44\,mg\,kg^{-1}$ and $39\,mg\,kg^{-1}$ as well as of Fe 5.7% (w/w) and 8.3% (w/w) for sample 1 and 2, respectively (XRF results). The extraction was carried out with 1 g of sample (triplicates of each sample) leached with 10 mL of 20 mM EDTA for 4 h at room temperature. The liquids were separated by centrifugation (10 min at 2500 rpm). The Fe concentrations were analyzed by ICP-OES (Arcos, Spectro A.I.). The extracts were stored in PE bottles at 6 °C in