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Studies on the speciation of inorganic and organic antimony compounds in airborne particulate matter by HPLC-ICP-MS

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There is a considerably increasing concern about the speciation of antimony because anthropogenic emission has resulted in an increasing concentration of antimony in the environment. Apart from inorganic Sb species, methylated Sb species have been detected in a variety of environmental samples. However, little is known about the distribution of Sb species in airborne particulate matter (APM). The speciation of Sb species in APM was performed using both anion-exchange and size-exclusion HPLC-ICP-MS detection. A Japanese quality control sample for APM (AS-1, 92 μg g^{-1} Sb) and an APM sample collected in Tokyo (APM sample, 56 μg g^{-1} Sb) were investigated. In aqueous extracts of APM sample and AS-1, apart from the major Sb(V) species (*ca*. 80%), trimethylantimony species (TMSb) and several hydride active unknown Sb species were for the first time detected.

Introduction

Over the years, anthropogenic emission of antimony has resulted in an increasing concentration of Sb in the environment. Antimony and its compounds have been listed as priority pollutants by the US Environmental Protection Agency (EPA). In Japan, about 20 000 tons of antimony were used in different industrial processes every year, while only 100 tons of arsenic, a well-known toxic element, was used for chemicals per year. The concentration ratio of Sb to As in the earth's crust is 1/10, however, due to the intensive use of Sb, the concentration ratio of Sb to As has been found to be reversed in the polluted environment. During our monitoring of toxic elements in airborne particulate matter (APM) in Tokyo, Japan, Sb concentration was found to be at least two times higher than that of As.[1] This fact has initiated a research project to investigate the speciation of Sb in APM specimens in our laboratory because it was recognized that the toxicity of Sb strongly depends on its chemical form and oxidation states, thus the total concentration of Sb is not sufficient for a better risk assessment.

In the environment, antimony may exist in different forms. Besides the two inorganic Sb species, Sb(III) and Sb(V), methylated forms were also detected in the environment. In sea water, methylantimony species account for *ca*. 10% of the total dissolved antimony with monomethyl species being predominant.[2] Dodd *et al*. have reported the presence of organoantimony compounds in a fresh-water plant extract.[3] In a recent work, Ulrich has found trimethylstiboxide (TMSbO) in several soil samples.[4] To date, information on Sb species in APM is not available because little work has been done on Sb speciation in such specimens.

For the speciation of Sb, many analytical methods have been reported in the literature. Among them, the hypenation of HPLC or capillary electrophoresis (CE)[5] with element-specific detectors, such as HG-AAS,[6,7] ICP-AES[4] and ICP-MS[4,8–10] has been increasingly employed. In our previous work using ion exchange HPLC-ICP-MS,[8] an analytical method for the speciation of Sb(III) and Sb(V) was developed and applied to environmental samples, such as tap-water and APM reference materials and an APM sample collected in Tokyo. Besides inorganic Sb(V), several unknown peaks were observed. However, we could not identify the observed unknown peaks due to the lack of organic Sb standards. Recently, two organic antimony standard compounds, trimethylantimony dichloride ($TMSbCl_2$) and trimethylantimony dihydroxide ($TMSb(OH)_2$) became available to us, thus analytical methods for the speciation of Sb(III), Sb(V) and trimethylantimony compound (TMSb) were established. In this paper, the speciation of inorganic and organic Sb compounds in APM samples was conducted by using HPLC-ICP-MS techniques. Considering that APM may migrate with rainfall in the environment, one objective of this study is to investigate Sb species in the aqueous extract of APM samples. Trimethylantimony species were detected in APM for the first time. Several unknown Sb species were observed and further experiments revealed that these unknown species were hydride active species, *i.e.*, Sb-containing species that form volatile hydrides that can be detected as gases using ICP-MS. The extraction of Sb with other solvents, such as phosphate and EDTA, was also performed to shed light on the Sb content in specific phases of APM samples.

Experimental

Chemical and samples

All the chemicals and reagents used in this study were of analytical grade. Water used was Milli-Q purified water (18.3 MΩ cm) (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan). Tetramethylammonium hydroxide (TMAH) was purchased from Merck. Tris was obtained from Sigma. A stock solution of Sb(III) was made up from a commercially available concentrate (1000 mg L^{-1}), Spex plasma standard. A stock solution of Sb(V) (1000 mg L^{-1}) was prepared from potassium hexahydroxoantimonate(V) (Kanto Chemical Co., Inc., Tokyo, Japan). All working standard solutions of Sb(V) and Sb(III) were prepared daily to prevent any possible species change. Trimethylantimony dichloride ($TMSbCl_2$), which was synthesized according to published methods,[11] was a donation of Dr Michael Krachler (Juelich Research Center, Institute for applied physics and chemistry, Germany). Trimethylantimony dihydroxide ($TMSb(OH)_2$) was obtained from Tri Chemicals (Yamanashi, Japan). The used mobile phases for chromatography were freshly prepared, filtered through a 0.45 μm membrane filter and degassed before use.

An airborne particulate matter sample (APM sample) was collected using a high volume sampler (Model 120 F, Kimoto, Osaka, Japan) with a Polyflon PF040 filter (Advantec, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) at Bunkyo-ku, Tokyo, in December 1999. The sampling time is one day with a flow rate of 1000 L min.$^{-1}$ To check the reproducibility of the developed analytical method, a Japanese quality control sample for

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airborne particulate matter (AS-1) with a certified Sb concentration of 92 μg g^{-1} issued by Japan Environment Agency, was used in this study.

Instrumentation

The ICP-MS instrument used was an HP 4500 (Yokogawa Analytical Systems, Tokyo, Japan). The sample introduction system used included a Scott-type spray chamber fitted with a concentric nebulizer. The chromatographic system consisted of a JASCO Tri-Rotar-V HPLC pump (Japan Spectroscopic Cooperation), a Rheodyne six-port injection valve (Model 7125) with a 100 μl loop and either a PEEK inert PRP-X 100 polymer-based anion exchange column (Hamilton, USA, 250 × 4.5 mm, particle size 10 μm, stable between pH 1 and 13), or an Asahipak GS520HG size-exclusion column (Showa Denko, Japan, 300 × 7.6 mm, stable between pH 2 and 12). The chromatographic system was interfaced with an ICP-MS instrument using a 150 mm PEEK capillary tubing (0.25 mm id) to connect the column outlet to the inlet hole of the nebulizer. The chromatographic results were processed using Chromato-software (Yokogawa Analytical Systems, Tokyo, Japan). The operating conditions for HPLC-ICP-MS were as follows: rf forward power, 1300 W; plasma Ar flow rate, 15.0 L min^{-1}; auxiliary Ar flow rate, 1.0 L min^{-1}; nebulizer Ar flow rate, 1.18 L min^{-1}; integration time, 100 ms; data acquisition mode, time resolved analysis; and isotope monitored, ^{121}Sb and ^{123}Sb. The used mobile phases were 10 m mol L^{-1} TMAH (pH 12) delivered at a flow rate of 1.5 mL min^{-1} and 50 mmol L^{-1} Tris (pH 7.4) delivered at a flow rate of 0.8 mL min^{-1}. For HPLC-HG-ICP-MS determination, a CETAC HGX-100 hydride generation system (CETAC Technologies Inc., USA) was used. The experimental conditions for hydride generation of Sb compounds were as follows: 0.2 mol^{-1} HCl (1 mL min^{-1}) and 0.3% $NaBH_4$ in 0.01 mol L^{-1} NaOH (1 mL min^{-1}).

Experimental procedure

The total concentrations reported for APM were determined by ICP-MS analysis after acid digestion. The weight of collected APM was obtained from the difference between the filter collected APM and the empty filter. An MLS 1200 MEGA microwave digestion system from Milestone (Sorisole, Italy) equipped with a rotar for six Teflon (R) digestion vessels (high pressure) was used in this work. Experimental detail has been described elsewhere.[8] For the extraction of airborne particulate matter, 0.3 g APM was weighed into screw-top polypropylene bottles (15 mL), and then 6 mL of extraction solvents (Milli-Q water, phosphate, and EDTA, respectively) was added. The extraction was performed using a horizontal shaker (Iuchi WCS-150, Osaka, Japan) for four hours (for APM sample, 2 days) at room temperature. The solution was then centrifuged in a centrifuge (Iuchi Pasolina, Osaka, Japan) for 25 min at 1500*g*. The supernatant was removed and filtered through a 0.45 μm membrane filter (Millipore, USA). Sub-samples of each extract were taken for the measurement of pH, ICP-MS total element analysis and HPLC-ICP-MS speciation analysis. For the determination of total Sb, the standard and sample solutions were spiked with 50 ng mL^{-1} Rh as internal standard and nitric acid was added to give a final concentration of 1% HNO_3 prior to analysis.

Results and discussion

Extraction of airborne particulate matter

Airborne particulate matter may consist of biological, organic and mineral phases and each of these phases has a different affinity for trace metals. Considering the migration of APM in the environment with rainfall, water was used for the extraction of Sb species. On the other hand, EDTA is assumed to extract carbonate-bound and organically-bound fractions of metals by formation of strong chelates, and the EDTA-extractable fraction of metals has been regarded as plant available fraction;[12] phosphate is thought to extract metal fraction which is adsorbed by anion exchange mechanism. Therefore, the extraction with EDTA (50 m mol L^{-1}, pH 7.0) and phosphate (250 mmol L^{-1} $NH_4H_2PO_4$, pH 4.2) was also investigated to shed light on Sb content in specific phases of APM samples. A Japanese quality control sample for APM (AS-1) was employed in this study as a control for reproducibility of the extraction and determination procedure and for comparison. The total Sb concentrations (μg g^{-1}) determined by ICP-MS were 92.4 ± 4.1 (certified value, 92) for AS-1, and 56.0 ± 4.1 for collected APM sample, respectively. Three digestions for each sample were performed.

Extraction experiments using three different extraction solvents for AS-1 were performed. For each solvent, four consecutive extractions (four hours for each extraction) were conducted. It was found that the extraction yields (average of three repetitions) obtained after four consecutive extractions were 10.7% with water, 16.1% with phosphate, and 26.9% with EDTA, respectively. Due to the limited sample weight of APM sample, only water extraction was performed. After two days extraction, the water-extractable percentage was determined to be 14.3%.

Speciation analysis

In our previous work,[8] a HPLC-ICP-MS analytical method was developed for the speciation of Sb(III) and Sb(V), which consisted of a silica-based anion-exchange column, Synchropak Q300 with 2 mmol L^{-1} phthalic acid–5 mmol L^{-1} EDTA as mobile phase (pH 4.5). It was found that both $TMSbCl_2$ and $TMSb(OH)_2$) were retained on the column, thus can not be eluted under the used separation condition. To separate trimethylantimony species (TMSb) and inorganic Sb species, another two chromatographic systems were developed: 1. Anion-exchange HPLC consisted of a PRP-X100 column with 10 mmol L^{-1} TMAH (pH 12) as a mobile phase. With this system, although Sb(III) was not eluted due to its strong retention on the column, TMSb species and Sb(V) can be separated; 2. Size-exclusion HPLC consisted of an Asahipak GS 520HG column with 50 mmol L^{-1} Tris (pH 7.4) as a mobile phase. With this system, Sb(III), Sb(V), and TMSb species can be separated. There is no difference in the chromatographic behavior between trimethylantimony species as $TMSbCl_2$ or $TMSb(OH)_2$. Representative HPLC-ICP-MS chromatograms for the standard solution of Sb species are shown in Fig. 1.

The aqueous extracts of AS-1 and APM sample were first injected into anion-exchange HPLC-ICP-MS system for the chemical speciation analysis. The obtained chromatograms are shown in Fig. 2. Based on the matching of retention time and the spiking with standards, Sb(V) was found to be the predominant species, and TMSb species was detected in both AS-1 and APM sample. Several unknown Sb species (indicated with arrows in Fig. 2), at least four unknown Sb species in AS-1 and three Sb species in APM sample, were also observed. Due to the lack of suitable organic Sb standards, we can not identify the observed unknown Sb species at this stage, however, AS-1 was further subjected to HPLC-HG-ICP-MS analysis to explore if the unknown Sb species are hydride active species. The obtained chromatogram (Fig. 2(c)) clearly showed that these unknown Sb species were hydride active species with different hydride generation efficiency. Since TMSb eluted in the solvent front, its determination may suffer from matrix interferences,[10] thus, for a clear identification, the aqueous extracts of AS-1 and APM were injected into SEC-ICP-MS detection system. For identification, a spiking experiment with 10 ng mL^{-1} $TMSbCl_2$ was performed. The obtained chromatograms (Fig. 3) clearly showed the existence of TMSb species in the investigated samples. Thus, by using anion-exchange and size-exclusion

HPLC-ICP-MS detection, TMSb was detected unambiguously in the aqueous extracts of airborne particulate matter.

Based on anion-exchange HPLC-ICP-MS detection, the percentage of detected Sb species (against the total Sb in extracts) in aqueous extracts was obtained by assuming the sensitivity of Sb compounds is the same as inorganic Sb(v): TMSb, 0.51%, Sb(v), 89.5%, unknown, 6.62%, for APM sample; TMSb, 0.21%, Sb(v), 85.4%, unknown, 7.71%, for AS-1. No detectable Sb(iii) was found in this investigation and in the previous work.[8] Prior to the aqueous extraction of AS-1, 300 ng trimethylantimony dichloride was spiked into 6 mL of water. However, HPLC-ICP-MS analysis only yielded a recovery of 43% for TMSb. Since no decomposition of TMSb during the extraction process was observed by HPLC-ICP-MS analysis (chromatograms not shown here), it was concluded that the low recovery resulted from the re-adsorption of TMSb species on the surface of airborne particulate matter.

The results reported here are very important in terms of risk assessment and the understanding of the biogeochemical cycle of Sb in the environment. Due to the extreme chemical similarity between As and Sb, the existence of a variety of organic Sb species in the environment is expected. Methylated Sb species, such as monomethylated, dimethylated and trimethylated Sb species have been detected in a variety of environmental samples, such as sea water,[2] plants,[3] soils,[4] and sewage sludge,[5] however, little was known about Sb species in

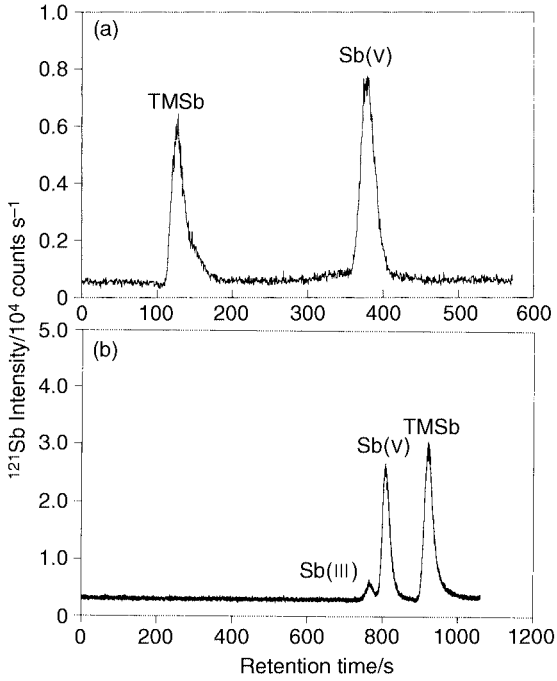

Fig. 1 HPLC-ICP-MS chromatograms obtained with Sb standard solution. (a) TMSb and Sb(v) (2 ng Sb mL^{-1} for each). Experimental conditions: column, PRP-X100; mobile phase, 10 mmol L^{-1} TMAH (pH 12); flow rate, 1.5 mL min^{-1}; column temperature, ambient. (b) Sb(iii) (50 ng mL^{-1}), Sb(v) (10 ng mL^{-1}) and TMSb (20 ng mL^{-1}). Experimental conditions: column, Asahipak GS 520HG; mobile phase, 50 mmol L^{-1} Tris (pH 7.4); flow rate, 0.8 mL min^{-1}; column temperature, ambient.

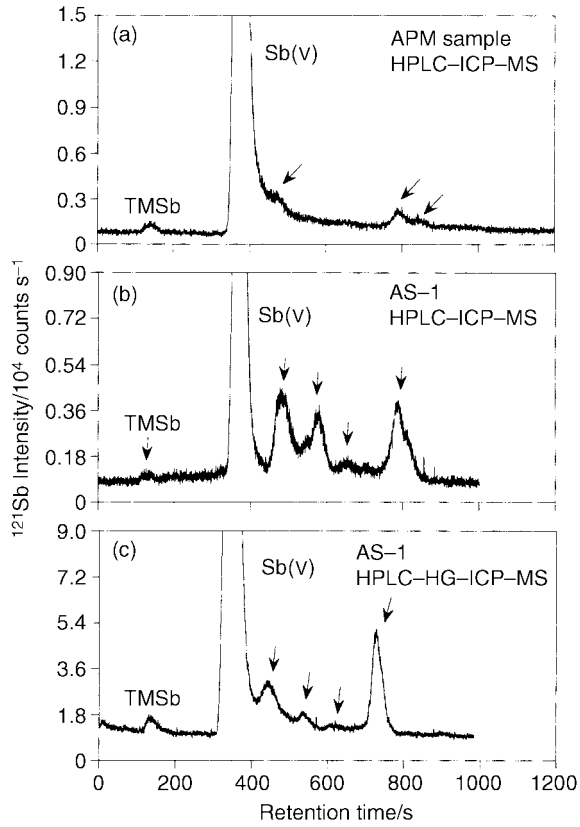

Fig. 2 HPLC-(HG)-ICP-MS chromatograms of aqueous extracts of AS-1 and APM sample. (a) HPLC-ICP-MS chromatogram of APM sample; (b) HPLC-ICP-MS chromatogram of AS-1; (c) HPLC-HG-ICP-MS chromatogram of AS-1. Chromatographic conditions see Fig. 1. For HPLC-HG-ICP-MS, 0.2 mol^{-1} HCl (1 mL min^{-1}) and 0.3% $NaBH_4$ in 0.01 mol L^{-1} NaOH (1 mL min^{-1}) were employed for hydride generation of Sb compounds.

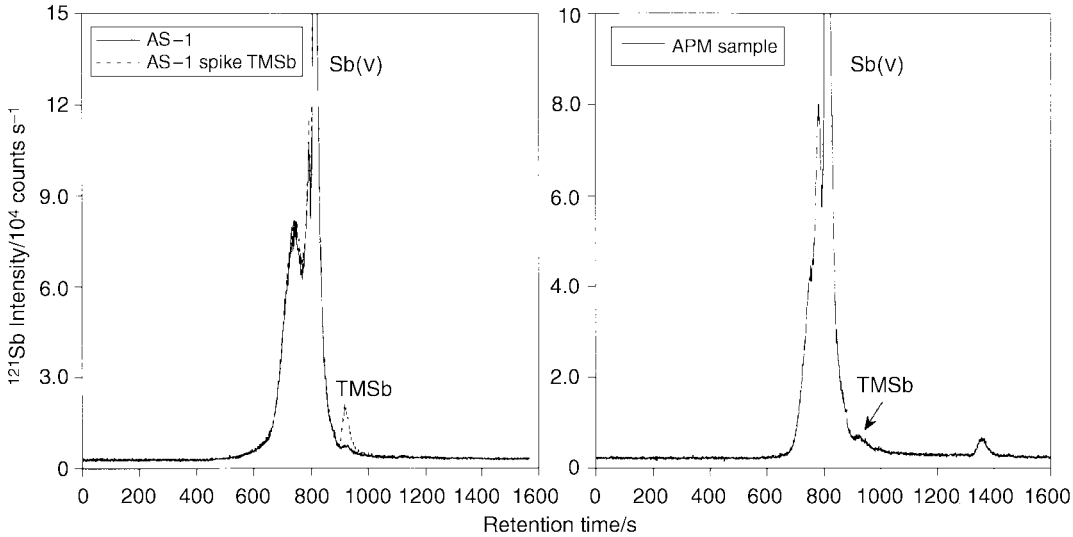

Fig. 3 SEC-ICP-MS chromatograms of aqueous extracts of AS-1 and APM. Chromatographic conditions see Fig. 1.

APM. The existence of TMSb and hydride active Sb species in APM provided further evidence of a wide presence of organic Sb species in the environment and indicated that caution must be taken when using hydride generation for the selective determination of Sb(III) and Sb(V) in environmental samples due to the existence of unknown hydride active Sb species in the environment. Future work will focus on the identification of the observed unknown Sb species using electrospray mass spectrometry (ES-MS).

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