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Antimony Speciation in Environmental Samples by Using High-Performance Liquid Chromatography Coupled to Inductively Coupled Plasma Mass Spectrometry

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An analytical method based on the hyphenation of liquid chromatography and inductively coupled plasma mass spectrometry was developed and used for the speciation of antimony in environmental samples. The baseline separation of inorganic Sb(III) and Sb(V) was achieved by using a mobile phase of 2 mmol/l phthalic acid–5 mmol/l EDTA at pH 4.5 on a silica-based anion-exchange column (Synchropak Q300, 100 × 4.6 mm i.d.). The retention times were 164 and 260 s for Sb(V) and Sb(III), respectively. The calibration curves were linear over the range of 1.0 – 100 µg/l for the investigated Sb species. The detection limits were 10 pg and 30 pg per 100 µl sample for Sb(V) and Sb(III), respectively. The precision, evaluated by using the relative standard deviation (RSD) with a 5 µg/l standard solution, was 2.4% and 4.3% (n=6) for Sb(V) and Sb(III), respectively. The detection limits achieved in the present work were sufficiently low to measure Sb species in environmental samples. The proposed method for the speciation of Sb was applied to the determination of Sb(V) and Sb(III) in tap-water and the aqueous extracts of airborne particulate matter. The results showed that for airborne particulate matter there are multiple Sb species.

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Antimony, a toxic element, is present in the environment as a result of its natural occurrence as well as human activities. The main pathways are atmospheric input and the water cycle. Around 3.8×10^{10} g per year of Sb is released into the environment as a consequence of human activities.[1] The concentration level of antimony in the earth's crust[2] is around 0.2 µg/g. Typical concentrations of Sb in unpolluted water samples are less than 1 µg/l; however, the concentrations can be substantially elevated to the 100 µg/l level in the vicinity of anthropogenic sources.[3,4] In the environment, antimony may exist in different forms. The inorganic species pentavalent Sb(V) is the predominant form in oxygenated water, while trivalent Sb(III) is important in reducing interstitial water.[5] In the ocean, methylantimony species account for about 10% of the total dissolved antimony with monomethyl species being predominant.[6] Dodd *et al*.[7] have reported the presence of organoantimony compounds in a fresh-water plant extract. Krupp *et al*.[8] have described the speciation of metals and metalloids in sediments. Besides inorganic Sb, three methylated forms were identified and in some samples the presence of triethylantimony compound was suggested.

It was reported that antimony is a non-essential element in plants, animals and humans; its toxicity is similar to that of arsenic, and is perhaps even more toxic.[9] Sb(III) is reported to be ten-times more toxic than Sb(V); generally, inorganic species are more toxic than organic ones.[10] The toxic effects of Sb result from irreversible binding to thiol-containing enzymes.[11] Sb(III) shows affinity for red cells and thiol groups of cell constituents, while red cells are almost impermeable to Sb(V). Inhalation exposure to Sb compounds can produce a series of diseases, such as pneumonitis, fibrosis, bone-marrow damage and carcinomas. Because the different toxicities and migration behaviors of the Sb species in the environment have been a public-health concern, strict control is required. The US Environmental Protection Agency (EPA) lists Sb and its compounds as priority pollutants. The European Union Standards set the maximum admissible level of Sb in drinking and surface water at 10 µg/l; less than 2 µg/l Sb in drinking water is recommended in Japan. To evaluate the toxicity and the biogeochemistry of Sb in the environment, speciation analysis of Sb species is required.

There are numerous different methods of Sb speciation reported in the literature. Smichowski *et al*.[11] classified the analytical methods applied to the selective determination of Sb species as follows: chemical methods based on extraction techniques, hydride generation and coprecipitation, methods based on chromatographic techniques, methods based on electrochemical techniques, and kinetic methods. Among these methods, much attention is focused on various kinds high-performance liquid chromatography (HPLC) methods with different separation mechanisms and different detection methods, because the coupling of chromatographic techniques with element specific detection allows the simultaneous separation and determination of Sb(III) and Sb(V), as well as organoantimony species, in one step, thus avoiding the risk of errors resulting from the approach of evaluating Sb(V) based on the difference between the total Sb and Sb(III), which was adopted by most hydride generation-atomic spectrometric analytical procedures.[4,12-14] Recently, several analytical methods based on the hyphenation of HPLC and element-specific detectors, such as atomic absorption spectrometry (AAS) and

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inductively coupled plasma mass spectrometry (ICP-MS), have been reported. Smichowski *et al.*[1] separated Sb(III) and Sb(V) on an anion-exchange column (PRP-X100) with 2 mmol/l phthalic acid (pH 5.0) as a mobile phase. This separation system was coupled with HG-AAS, ICP-MS and HG-ICP-MS, respectively. Ulrich[15] realized the separation of Sb(V), trimethylstiboxide (TMSbO) and Sb(III) using the same chromatographic conditions used by Smichowski *et al.*[1] Lintschinger *et al.*[16] presented a method for the fast and simultaneous determination of Sb(III) and Sb(V) on a PRP-X100 column by adding a complexing reagent in the mobile phase. The separation system was coupled to ICP-MS and applied to various environmental samples with anthropogenic and naturally elevated Sb concentrations. A more recent work presented by Lintschinger *et al.*[17] described the separation of Sb(V) and trimethylantimony dichloride ($TMSbCl_2$) on a PRP-X100 column using tetramethylammonium hydroxide as a mobile phase, however, Sb(III) could not be eluted under the used chromatographic conditions. Zhang *et al.*[18] explored the possibility of using a miniaturized HPLC column coupled to HG-AAS for the speciation of inorganic Sb(III) and Sb(V) species in spiked water samples. Guy *et al.*[19] described the separation of Sb species by reversed-phase and ion-exchange chromatography and their detection by ICP-MS. The methods developed have been applied to soluble extracts of plant and sediment samples.

Antimony exists primarily in two oxidation states, Sb(III) and Sb(V), in most environmental samples. Therefore, as a part of an ongoing research project on the identification of element species in airborne particulate matter (APM) in Tokyo, the purpose of the present study is to develop an analytical method for the speciation analysis of both Sb(III) and Sb(V) in environmental samples, such as water and airborne particulate matter. This work was stimulated by the fact that the total concentration of Sb in the airborne particulate matter collected in Tokyo, and in a Japanese quality control sample for airborne particulate matter (AS-1) was found to be twice higher than the concentration of As in the same materials during our monitoring of trace elements in airborne particulate matter. A polymer-based anion exchange column, for instance PRP-X 100, was widely used for the separation of Sb species in the past,[1,15-17] and a very long retention time of Sb(III) with serious broadening of the chromatographic peak was observed by using this polymer-based column.[1,15] So far, there has been no report on the speciation of Sb species by using a silica-based column. In this work, we explore the possibility of using a silica-based anion-exchange column (Synchropak Q 300) coupled to ICP-MS for the speciation of Sb in environmental samples.

Experimental

Chemical and reagents

All of the chemical and reagents used in this study were of analytical grade. The water used was Milli-Q purified water (18.3 MΩ cm) that was prepared by further purification of de-ionized water by a Milli-Q system (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan). Phthalic acid and ethylenediamine-tetraacetic acid (EDTA) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Working standard solutions of Sb(III) and Sb(V) were prepared by appropriate dilution from 1000 mg/l stock solutions with Milli-Q water. A stock solution of Sb(III) was made up from a commercially available concentrate, Spex plasma standard. A stock solution of Sb(V) 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. The used mobile phases for chromatography were freshly prepared by dissolving an appropriate amount of phthalic acid and EDTA to 1 liter Milli-Q water to obtain the required concentration. The pH of the mobile phase was adjusted by the dropwise addition of 20% NH_4OH and 1 mol/l HNO_3. The resulting solutions were filtered through a 0.45 µm membrane filter and degassed before use.

Table 1 Operating conditions for HPLC and ICP-MS instruments

HPLC	
Column	Synchropak Q300 (100 × 4.6 mm i.d.)
Mobile phase	2 mmol/l phthalic acid–5 mmol/l EDTA at pH 4.5
Flow rate	1.0 ml/min
Injection volume	100 µl
Column temperature	ambient
ICP-MS	
Forward rf power	1300 W
Plasma Ar flow	15.0 l/min
Auxiliary Ar flow	1.0 l/min
Nebulizer Ar flow	1.18 l/min
Data acquisition mode	time resolved analysis
Integration time	100 ms
Isotopes monitored	^{121}Sb and ^{123}Sb
Total analysis time	600 s

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 V-groove nebulizer. The chromatographic system consisted of a JASCO Tri-Rotar-V HPLC pump (Japan Spectroscopic Cooperation), a syringe-loading injector (Model 7125, Rheodyne six-port injection valve) with a 100 µl loop and a Synchropak Q300 anion-exchange column (Synchrom., Inc., USA, 100 × 4.6 mm i.d.), which was packed with a hydrophilic, silica-based strong anion-exchange support with quaternary ammonium exchange-sites; particle size 6.5 µm, stable between pH 2 and 8. The chromatographic system was interfaced with an ICP-MS instrument using a 300 mm PEEK (polyether ether ketone) capillary tubing (0.25 mm i.d.) to connect the column outlet to the inlet hole of the nebulizer. The chromatographic results were processed using Chromatosoftware (Yokogawa Analytical Systems, Tokyo, Japan). Quantifications were performed in the peak area mode. The operating conditions for HPLC-ICP-MS are summarized in Table 1. The ICP-MS measurement conditions, given in Table 1 were optimized daily using a standard built-in software procedure for the injection of a 10 µg/l solution containing Li, Y, Ce and Tl. Two antimony isotopes, ^{121}Sb and ^{123}Sb (with relative abundances of 57.21 and 42.79%),[20] were monitored.

Microwave digestion of airborne particulate matter samples

The total concentrations reported for airborne particulate matter were determined by an ICP-MS analysis after acid digestion. An MLS 1200 MEGA microwave digestion system from Milestone (Sorisole, Italy) equipped with a rotar for six teflon digestion vessels (high pressure) was used in this work. About a 100 mg airborne particulate matter sample was digested with 5 ml of concentrated HNO_3, 2 ml of 30% H_2O_2 and 3 ml of concentrated HF. The following microwave digestion program was used: 250 W, 6 min; 400 W, 6 min; 650 W, 6 min; 400 W, 100 min. The excess of HF in the digests was removed by

heating the digestion vessels on a hot plate at a temperature of 230˚C. Then, the obtained droplet digests were diluted to 50 ml with Milli-Q water.

Extraction of airborne particulate matter

For the extraction of trace-element species from airborne particulate matter, a procedure described by Caruso and co-workers[21] was employed with a slight modification. Briefly, airborne particulate matter of 0.3 g (0.5 g, in the case of a Japanese quality control sample for airborne particulate matter, AS-1) was weighed into screw-top polypropylene bottles (50 ml), and then 20 ml of Milli-Q water was added. The suspensions were stirred continuously with a magnetic stirring bar (1/2 in long × 1/8 in o.d.) at room temperature for 2 days. The extracts were then filtered (0.2 µm), and sub-samples of each extract were taken for the measurement of pH, ICP-MS total element analysis and HPLC-ICP-MS element speciation analysis.

Results and Discussion

Optimization of the chromatographic separation

The aqueous solution chemistry of inorganic Sb(V) and Sb(III) has been discussed in the literature.[16] In aqueous solutions of pH from 2.7 to 10.4, Sb(V) is mononegatively charged ($Sb(OH)_6^-$, pK_a 2.7) while Sb(III) may exist as meta-antimonious acid ($HSbO_2$) or antimony hydroxide ($Sb(OH)_3$), and as antimonite ions (SbO_2^- or $Sb(OH)_4^-$) in more alkaline solutions. Therefore, anion-exchange chromatography should be an ideal separation model for the simultaneous determination of Sb(V) and Sb(III). The Sb(III) should be eluted in the solvent front and Sb(V) should be retained on the column. In our preliminary experiment by using a Dionex AS4A anion-exchange column (250 × 4 mm, i.d.) with 10 mmol/l phthalic acid (pH 5.0) as a mobile phase, the elution order was reverse of that expected. Sb(V) was eluted rather early close to the solvent front, whereas Sb(III) was found to be strongly retained on the column, resulting in a broad and non symmetric peak. A possible reason for this chromatographic behavior might be that the used Sb(III) standard (potassium antimonyl tartrate) reacted with the phthalate in the mobile phase to form a negatively charged Sb(III)-phthalate complex, as proposed in the literature.[16] Based on this preliminary experiment, a shorter anion-exchange column, Synchropak Q300 (100 × 4.6 mm, particle size 6.5 µm, silica-based), was selected for a further investigation with phthalic acid as a mobile phase. The reason to choose phthalic acid as a mobile phase is due to the observation of similar chromatographic behavior of $SbCl_3$ and Sb(III) tartrate, which are most commonly used as Sb(III) standard, when phthalate was used as a mobile phase.[1]

Another approach adopted in our investigation to shorten the retention time of Sb(III) and to improve its peak shape was adding complexing reagents in the mobile phase. Ulrich[15] studied the influence of different complexing agents (tartrate, citrate and chloride) on the chromatographic behavior of antimony species. Sb(III) seems to form stable complexes with citrate. Sb(III) was eluted rather early when the Sb(III) standard was treated at lower excess of citrate prior to the chromatographic separation. However, our attempt to obtain the on-line formation of Sb(III) citrate complex by adding citrate into the used mobile phase, and thus to improve the separation of Sb(III), failed. With a mobile phase of 2 mmol/l phthalic acid–0.5 mmol/l citric acid at pH 4.5, Sb(III) was too strongly retained on the column, and could not be eluted within 30 min. Another investigated complexing agent was ethylene-diaminetetraacetic acid (EDTA). This is a well-known strong chelating reagent for di- and trivalent cations. Lintschinger *et al.*[16] demonstrated that EDTA will react with Sb(III) to form a soluble negatively charged complex that can be subsequently separated on a polymer-based anion-exchange column. The experimental results showed that the separation could be improved on our used silica-based anion exchange column, too, by varying of the EDTA concentration and pH when 2 mmol/l phthalic acid was used as a mobile phase. Table 2 summarized the effect of the EDTA concentrations on the separation of Sb(V) and Sb(III). It was found that the retention times of Sb(III) and Sb(V) increased with decreasing the EDTA concentration, and a retention time difference of 94 s between Sb(III) and Sb(V) was achieved at 5 mmol/l EDTA, which led to a baseline separation of Sb(V) and Sb(III). The influence of the mobile-phase pH on the separation was also investigated. The best pH range for the separation was found to be between 4.3 to 5.0. The peak of Sb(III) became less symmetrical, tailing and peak area decrease with increasing pH. After some optimization work, the optimal chromatographic conditions for the simultaneous separation of Sb(V) and Sb(III) on a silica-based anion-exchange column (Synchropak Q300) were obtained with a mobile phase containing 2 mmol/l phthalic acid and 5 mmol/l EDTA at pH 4.5 with a flow rate of 1.0 ml/min. A chromatogram of the separation of Sb(V) and Sb(III) standards is shown in Fig. 1. The concentration of the Sb species was 5 µg/l each as Sb. Under the optimal chromatographic conditions, a baseline separation of Sb(V) and Sb(III) was achieved within 600 s.

Table 2 Effect of EDTA concentrations on the separation of Sb(V) and Sb(III)*

EDTA conc./ mmol^{-1}	Retention time/s		Retention time difference/s
	Sb(V)	Sb(III)	
20	130±1	163±1	33
10	148±1	202±1	54
5	164±1	260±3	94

* Chromatographic conditions: Synchropak Q300 column; mobile phase, 2 mmol/l phthalic acid–*x* mmol/l EDTA, pH 4.5; flow rate, 1.0 ml/min.

Analytical characteristics

Under the optimal conditions described above, calibration curves and detection limits for Sb(V) and Sb(III) were determined. Peak integration was used for quantification. The linearity between the concentration and the peak area was found in the range between 1 µg/l and 100 µg/l with a correlation factor of 0.999. The detection limits were evaluated by making 6 repetitive injections of standards in the lower linear concentration range (5 µg/l each) and were calculated from the standard deviations of the peak areas (3σ). They were found to be 0.1 µg/l for Sb(V) and 0.3 µg/l for Sb(III), respectively. The detection limits could be further improved by using an inert PEEK-HPLC system to reduce the possible Sb contamination, as shown by Lintschinger *et al.*[17] The precision, evaluated by using the relative standard deviation (RSD) with a 5 µg/l standard solution, was 2.4% and 4.3% (n=6) for Sb(V) and Sb(III), respectively. The retention times were 164 and 260 s for Sb(V) and Sb(III), respectively. The time required for one analysis was within 600 s.

For the speciation of Sb, ICP-MS is an ideal detector, because the signal for antimony can be monitored at mass 121 (57.21%,

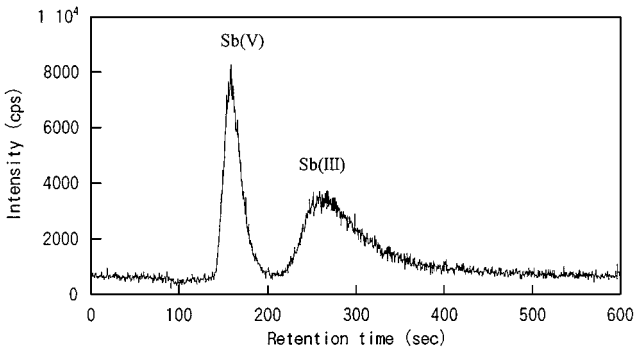

Fig. 1 Chromatogram of the separation of Sb(III) and Sb(V) (5 µg/l Sb, each) on Synchropak Q300 column. Mobile phase: 2 mmol/l phthalic acid–5 mmol/l EDTA, pH 4.5; Flow rate: 1.0 ml/min; Detection: ICP-MS at mass 121. The summation of integrated signals of Sb(V) and Sb(III) is 32000 counts and 34300 counts, respectively.

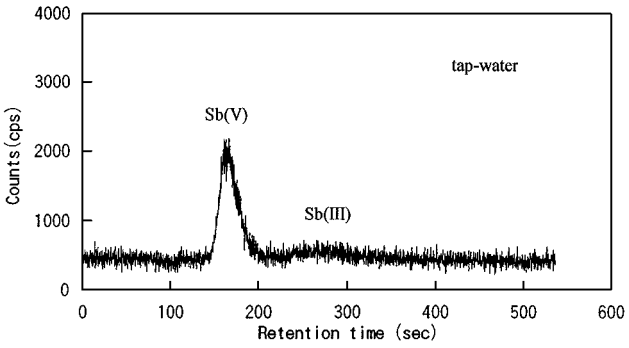

Fig. 2 Chromatogram for the determination of Sb species in a tap-water sample. Chromatographic conditions as in Fig. 1.

isotopic abundance) and mass 123 (42.79%, isotopic abundance) without any isobaric or polyatomic interference. In addition, the used mobile phase was found to be suitable for ICP-MS detection without any special precautions. There was no salt deposition and clogging of the sampling orifice of ICP-MS, even for measurements over a long period (>10 h). When potassium hydrogenphthalate (KHP) was used as a mobile phase, Lintschinger *et al.*[16] observed that a moderate negative peak appeared in the solvent front, which may interfere the determination of Sb(V). This negative peak was not observed in our analytical system by using phthalic acid instead of KHP.

Effect of the sample pH value on the separation of Sb species

The optimal pH value of the mobile phase is 4.5 in our separation system. Phthalic acid has a pK_{a1} value of 2.89 and pK_{a2} of 5.51; thus, a wide buffer range could be expected in our chromatographic separation system. The developed method will be applied to the speciation of Sb in a variety of environmental samples. The pH values of sample solutions obtained after suitable sample preparation steps may be distributed over a wide range; therefore, the effect of the sample pH on the separation of Sb species was investigated. Sb(V) and Sb(III) standards (50 µg/l) were prepared in pH-controlled Milli-Q water (pH 2, 4, 5.8, 7 and 9); the pH of the used Milli-Q water was controlled by adding HNO_3 and NH_4OH. The pH of the original Milli-Q water was 5.8 in our laboratory. These standard solutions were injected into the chromatographic system. It was found that for Sb(V) there was no change in the investigated pH range in terms of the retention time and the signal intensity. For Sb(III), the retention time remained constant in the pH range from 2 to 7, while a retention time shift of 90 s (from 260 s to 350 s) was observed at pH 9, and the oxidation of Sb(III) to Sb(V) (about 10%) was also observed at this pH which resulting in the decrease of peak area of Sb(III). Based on these experimental results, it was recommended that the pH value of the sample solution should be checked before it is injected into the chromatographic system. Direct injection of the sample solutions with a pH range of 2 to 7 can be performed, while the pH adjustment should be made prior to injection into the chromatographic separation system if the sample pH value is higher than 7.

Applications

In unpolluted water the typical concentration of antimony is in the low µg/l range, or even below. Less than 2 µg/l Sb in drinking water is recommended in Japan. Therefore, a sensitive analytical method for the determination of Sb species in natural water is required. The hyphenation of HPLC and ICP-MS combines the separation power of HPLC and the high sensitivity offered by ICP-MS, thus, leads to the determination of Sb(III) and Sb(V) simultaneously in natural water. Figure 2 shows the HPLC-ICP-MS chromatogram of Sb speciation in a tap-water sample collected in our laboratory. Sb(V) was found to be the predominant species (0.5 µg/l), and Sb(III) was less than the detection limit. The total Sb concentration in this tap-water sample was determined by a direct ICP-MS analysis; it was found to be 0.4 µg/l. Andreae *et al.*[4] reported that most natural water has Sb(V)/Sb(III) ratios on the order of 100 or more, which is in good agreement with our result.

The developed analytical method was applied to the speciation analysis of Sb in airborne particulate matter. One airborne particulate matter sample (APM sample) was collected from Tokyo, Japan, with a high-volume sampler (Model 120F, Kimoto, Osaka, Japan) in May 1999. To validate the developed HPLC-ICP-MS analytical method, a Japanese quality control sample for airborne particulate matter, AS-1 (Japan Environment Agency) and a standard reference material of urban particulate matter, NIST SRM 1648 (NIST, Gaithersburg, USA) were analyzed with respect to the antimony species. The certified Sb concentration in AS-1 is 92 µg/g, while no certified value of Sb is available in NIST 1648, except a non-certified value of 45 µg/g for information. Milli-Q water was used for the extraction of Sb species as described in "Experimental".

The total concentrations of Sb in airborne particulate matter, Milli-Q water-extractable concentrations, and the pH of the extracts are summarized in Table 3. The ranges of water-extractable Sb (expressed as % of the total) are found to be from 8.6% to 19.4%. The speciation results are given in Table 4. Although the concentrations of unknown species were quantified according to the calibration graph for Sb(V), mass balances were satisfactory. The sum of species concentrations always met the total Sb amount in the extracts. Representative HPLC-ICP-MS chromatograms based on ^{121}Sb signal for AS-1, NIST 1648 and APM sample are shown in Fig. 3. The peak identification was carried out by comparison of the retention times with standards and with standard spiking experiments. The predominant chemical form of Sb identified in airborne particulate matter was Sb(V), while Sb(III) was not detected. Three unknown peaks (U1, U2 and U3) were observed in aqueous extracts of AS-1 and NIST 1648. In aqueous extracts of an APM sample, an additional unknown peak U4 with a retention time about 1000 s was detected, besides the unknown

Table 3 Total and water-soluble Sb concentrations of airborne particulate matter: a Japanese quality control sample (AS-1), a standard reference material (NIST 1648), and a sample collected in Tokyo (APM sample)

Sample	Total digestion		Milli-Q water extraction		Water soluble, %
	Certified/μg g^{-1}	Found/μg g^{-1}	pH	Sb conc./μg g^{-1}	
AS-1	92	92.4±4.1	6.66	7.87±0.16	8.6
NIST 1648	45*	46.9±0.9	5.47	6.07±0.29	13.5
APM sample	—	195±13	4.52	37.9±0.8	19.4

* Non-certified value given for information only.

Table 4 Sb speciation results of airborne particulate matter with HPLC-ICP-MS Sb (μg/l): a Japanese quality control sample (AS-1), a standard reference material (NIST 1648), and a sample collected in Tokyo (APM sample)

Sample	Sb(V)	U1*	U2*	U3*	U4*	Sum	Conc. in extracts	Recovery, %
AS-1	170±6	2.50±0.10	6.88±1.69	5.66±1.26	—	185±4	199±4	93.0
NIST1648	75.0±1.2	4.00±0.50	5.71±1.87	1.36±1.10	—	86.0±0.8	93.3±4.4	92.2
APM sample	255±11	14.0±3.0	26.6±3.6	14.7±1.6	4.94±0.08	315±16	335±8	94.1

* Unknown species quantified with the calibration graph for Sb(V).

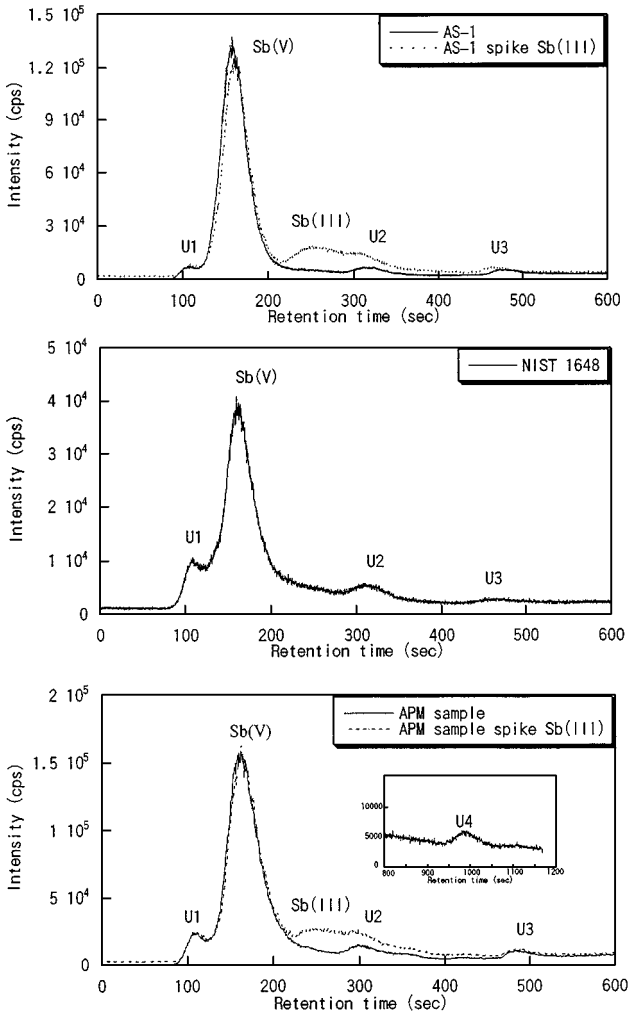

Fig. 3 Chromatograms resulting from the analysis of the aqueous extracts of airborne particulate matter: a Japanese quality control sample (AS-1), a standard reference material (NIST 1648), and a sample collected in Tokyo (APM sample). The chromatographic conditions are as in Fig. 1. The dotted lines indicate chromatograms obtained after spiking Sb(III) standard (50 μg/l) into the extracts of AS-1 and APM sample.

peaks (U1, U2 and U3) also found in AS-1 and NIST 1648 (U4 was not detected in AS-1 and NIST 1648). To check if one of the unknown peaks results from a shift of inorganic Sb(III) due to an increase in the ionic strength in the samples, Sb(III) was spiked in extracts of the AS-1 and APM samples. The obtained HPLC-ICP-MS chromatograms are also shown in Fig. 3 (dotted lines). It can be clearly seen that the observed unknown peaks are not due to a shift of the inorganic Sb(III). The Sb species in fly-ash samples, which were once combusted, was also investigated using the developed HPLC-ICP-MS method. In this case only inorganic Sb(V) and Sb(III) were observed, and no unknown peaks were detected. From the experimental results presented above, we can conclude that the unknown peaks observed in the airborne particulate matter are due to the presence of organic Sb species. To our best knowledge, this is the first report on the presence of organic Sb species in airborne particulate matter. Organic arsenic compounds have been found widely in the environment and biological systems.[22,23] Due to the extensive chemical similarity between arsenic and antimony, it was expected that organoantimony compounds may also be widely present in the environment. With the development of modern analytical techniques, studies of antimony in the environment have resulted in the discovery of some analogues of arsenic. Methylated antimony compounds have been found in a variety of environmental samples, such as seawater,[6] sediments,[8] sewage sludge,[24] and plants.[7] A pathway *via* bioalkylation of inorganic Sb species has been suggested,[25] resulting in organically bound Sb species. Our results presented in this paper provide further evidence of a wide presence of organic Sb compounds in the environment, although, unfortunately, we could not identify the observed unknown peaks in airborne particulate matter due to the lack of suitable Sb standards.

Conclusion

An analytical method for the speciation of antimony species is presented. A baseline separation of inorganic Sb(III) and Sb(V) was realized on a silica-based anion exchange column within 600 s by using EDTA as a complexing mobile phase. The combination of the developed HPLC system with ICP-MS

provides a technique to determine antimony species at real level concentrations (sub-µg/l) in environmental samples. The application of the developed method to the speciation of Sb in environmental samples indicates the presence of organic Sb species in airborne particulate matter. This result also shows the potential separation capacity for the separation of organic Sb species by the proposed anion-exchange chromatographic system and highlights the urgent need for organic Sb standards to develop more chromatographic separation systems for Sb speciation analysis.

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