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Investigating the electrospray mass spectra of inorganic and organic antimony compounds

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Positive- and negative ion electrospray mass spectra of commonly encountered organic antimony compounds, *i.e.*, trimethylantimony dichloride ($TMSbCl_2$) and trimethylantimony dihydroxide [$TMSb(OH)_2$], and inorganic antimony compounds, *i.e.*, potassium hexahydroxyantimonate [Sb(v)] and potassium antimonyl tartrate [Sb(III)] have been obtained using electrospray time-of-flight mass spectrometry (ES-TOF-MS). By operating the ES-TOF-MS instrument at high sample cone voltage (100 V), fragmentation information of $TMSbCl_2$ and $TMSb(OH)_2$ was obtained. Positive ion electrospray mass spectra have been found to be more useful for the identification of organic antimony compounds, $TMSbCl_2$ and $TMSb(OH)_2$, whereas negative ion electrospray mass spectra are more suitable for the identification of inorganic antimony compounds, Sb(v) and Sb(III). Based on the ES-MS results, a solution chemistry of $TMSbCl_2$ and $TMSb(OH)_2$ was proposed. Peaks at *m/z* 183 and 185 corresponding to $[(CH_3)_3SbOH]^+$ can be considered as a characteristic fingerprint for the identification of trimethylantimony species (TMSb) in an aqueous solution when using a positive ion ES-MS technique. The characteristic fingerprint was applied for the identification of $TMSbCl_2$, following its elution from a size-exclusion chromatography (SEC) column.

Introduction

The importance of speciation of antimony (Sb) has been recognized in recent years. This was evidenced by the fact that the US Environmental Protection Agency (EPA) and the German Research Council have listed Sb and its compounds as priority pollutants. The discovery of various Sb compounds in the environment, especially the confirmation of a biomethylation process of inorganic Sb compounds resulting in the presence of organic Sb compounds in the environment, has greatly promoted the study on Sb speciation analysis.[1–4] It has been recognized that the toxicity of Sb compounds and their environmental cycle are to a great extent dependent on their chemical forms. In Japan, due to the intense use of Sb in different industrial processes, a high concentration of Sb up to 240 $\mu g\ g^{-1}$ has been detected in airborne particulate matter (APM),[5,6] and some concern has been raised about the impact of a high Sb concentration in APM on human health.

Many analytical methods, from simple methods such as liquid–liquid extraction and hydride generation to hyphenated techniques such as HG-GC-AAS,[7] HPLC-HG-AAS,[8,9] HPLC-ICP-MS[5,6,10] and CE-ICP-MS,[11] have been developed for the speciation of Sb compounds. However, in principle, all of them provide only elemental information, and deliver no structural information. Identification can only be achieved when adequate standards are available. Therefore, as a supplementary technique, electrospray ionisation mass spectrometry (ES-MS), which delivers structural information about the analyte, has become popular for elemental speciation studies in recent years. Stewart[12] has provided an excellent review on the applications of ES-MS for elemental speciation. Nevertheless, the application of ES-MS in Sb speciation is very scarce. In the last decade, only two publications dealing with Sb speciation using ES-MS are available in the literature. Lintschinger *et al.*[13] investigated the chemical form of trimethylantimony dichloride ($TMSbCl_2$) in aqueous solutions. They concluded that $TMSbCl_2$ occurs most probably as $[TMSbOH]^+$ in aqueous solutions under neutral conditions. Guy *et al.*[14] demonstrated the association or complexation of three α-hydroxy acids with Sb(v) using ES-MS as well as HPLC-ICP-AES and NMR data.

Although the discovery of biomethylation of inorganic Sb compounds has led to an increasing interest in the determination of volatile Sb species,[2–4,15] in environmental solutions methylated Sb compounds, especially trimethylantimony, are expected to occur as oxidized species rather than the reduced trimethylstibine.[16] Therefore, analytical methods that are able to determine non-volatile Sb species in the environment are urgently required. Presently, two readily available organic Sb compounds, $TMSbCl_2$ and trimethylantimony dihydroxide ($TMSb(OH)_2$), are often used as standard compounds representing the oxidized form of the trimethylstibine for the identification of HPLC peaks of Sb compounds. Ulrich[17,18] also used a synthetic standard of trimethylstiboxide (TMSbO) for this kind of investigation. However, some concern has been raised about these standards,[13] because their solution chemistry is not well understood. This results in difficulties in the development of a chromatographic method for the simultaneous separation of trimethylantimony species and inorganic Sb compounds, Sb(v) and Sb(III). In this work, we investigated the ES-MS spectra of the Sb compounds most often used as chromatographic standards, namely, potassium hexahydroxyantimonate(v) [Sb(v)], potassium antimonyl tartrate [Sb(III)], $TMSbCl_2$ and $TMSb(OH)_2$. The objective of this investigation is to shed light on the solution chemistry of Sb compounds, in order to provide fundamental data for the development of a chromatographic method of Sb speciation and for the direct identification of Sb compounds in the environment by using ES-MS.

Experimental

Chemicals

All the chemicals and reagents used in this study were of analytical-reagent grade. The water used was Milli-Q purified water (18.3 MΩ cm) (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan). Tris was obtained from Sigma. A stock solution of

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Sb(III)tartrate 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 hexahydroxyantimonate(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,[19] was donated by Dr. Michael Krachler (Research Centre Juelich, Institute of Applied Physical Chemistry, Germany). Trimethylantimony dihydroxide ($TMSb(OH)_2$) was obtained from Tri Chemicals (Yamanashi, Japan). The mobile phase used for chromatography was freshly prepared, filtered through a 0.45 μm membrane filter and degassed before use.

Instrumentation and procedures

Experiments were performed using a Micromass LCT (Altrincham, UK) electrospray time-of-flight (TOF) mass spectrometer equipped with an atmospheric pressure ionization (API) source operated in a nebulizer-assisted electrospray mode. The nebulizer gas was N_2. The electrospray potential was set to 3.2 kV in both positive- and negative ion modes and the sample cone voltage was usually 15 V unless otherwise stated. The extraction cone voltage was set at 3 V. Samples were dissolved in MeOH–H_2O (v/v, 50 : 50) and introduced into the ion source using an infusion pump at a constant flow rate of 10 μl min^{-1} for 2 min. Mass spectral acquisition was usually performed from *m/z* 100 to 1000. Data were acquired by operating the data system in a total ion current (TIC) acquisition mode and several scans were summed to obtain the final spectrum. Mass calibration was performed using a solution of polyalanine (500 μg ml^{-1}) for the positive ion mode, and a solution of NaI (2000 μg ml^{-1}) for the negative ion mode.

For the SEC-ICP-MS system, the instrumentation used was the same as described in previous work.[6] Briefly, an HP-4500 bench-top ICP-MS instrument (Yokogawa Analytical Systems, Tokyo, Japan) was used as an element specific detector. The chromatographic system consisted of a JASCO Tri-Rotar-V HPLC pump (Japan Spectroscopic Cooperation), a Rheodyne injection valve (Model 7125) with a 100 μl loop, and an Asahipak GS520HG size-exclusion column (Showa Denko, Japan, 300 × 7.6 mm). The used mobile phase was 50 mmol l^{-1} Tris (pH 7.4) delivered at a flow rate of 1.0 ml min^{-1}.

Results and discussion

Electrospray mass spectra of $TMSbCl_2$ and $TMSb(OH)_2$

Compared with well-established arsenic speciation analysis, the speciation of Sb compounds is more difficult. This is not only due to the much lower concentration of Sb in the environment,[20] but also due to lack of suitable standard compounds. To date, the only available organic Sb compounds are $TMSb(OH)_2$ and $TMSbCl_2$, which can be synthesized on demand by various research groups. They have been successfully used as standards to produce the volatile antimony stibine by a hydride generation technique with sodium borohydride.[7,15,21] However, the chemical forms of these Sb compounds in aqueous solutions are not well understood.

In this work, we investigated the ES-MS spectra of $TMSbCl_2$ and $TMSb(OH)_2$ obtained in the positive ion mode. These two standard compounds were dissolved individually in a solution of water : methanol (v/v, 50 : 50) with a concentration of 1 μg Sb ml^{-1}. The methanol was added for better ionization during ES-MS analysis. For ES-MS determination, the sample cone voltage is a very important experimental parameter, since increasing the sample cone voltage increases ion fragmentation within the source. Therefore, this parameter was carefully optimized in this investigation from 7 to 100 V. It was found that best results in terms of sensitivity and non-fragmentation of inherent molecular ions could be obtained when the sample cone voltage was set at 15 V. For $TMSbCl_2$, the ES-MS spectrum [Fig. 1 (a)] seems to be characterized by intense peaks at *m/z* 183 and 185 originating from the positively charged trimethylantimony hydroxide, $[(CH_3)_3SbOH]^+$, and peaks at *m/z* 201, 203 and 205 resulting from the positively charged trimethylantimony chloride, $[(CH_3)_3SbCl]^+$, because the mass ratios correspond to the isotopic pattern of this species. Lintschinger *et al.*[13] reported a much more complex ES-MS spectrum for $TMSbCl_2$. Besides the base peaks of *m/z* 183 and 185, significant peaks at *m/z* 201 and 203 assigned as $[(CH_3)_3SbOH(H_2O)]^+$, at *m/z* 233, 235 and 237 corresponding to $[(CH_3)_3SbCl(MeOH)]^+$, and at *m/z* 215 and 217 attributed to $[(CH_3)_3SbOH(MeOH)]^+$, were also observed. The peaks at *m/z* 233, 235 and 237, and *m/z* 215 and 217 were not observed in our investigation. However, when the sample cone voltage increased to 40 V [Fig. 1 (b)], peaks at *m/z* 201 and 203, which were assigned as $[(CH_3)_3SbOH(H_2O)]^+$ by Lintschinger *et al.*,[13] were observed. Considering the increase in peak intensity at *m/z* 199, the whole peak group at *m/z* 199, 201, 203 and 205 may more likely result from the mixture of $[(CH_3)_3SbCl]^+$ (*m/z* 201, 203 and 205) and a trace of $[(CH_3)_2Sb(O)(CH_3OH)]^+$ (*m/z* 199 and 201) because of the mass ratio and the isotopic pattern. It should be noted that, under these conditions, fragment peaks at *m/z* 167 and 169 appeared in the spectrum. These peaks may be attributed to $[(CH_3)_2Sb{=}O]^+$, based on the mass ratio and the isotopic pattern. Due to the fragmentation, the relative intensity of the peaks at *m/z* 183 and 185 decreased, while the peaks of *m/z* 201 and 203 became the base peaks. When the sample cone voltage was further increased to 100 V, more fragments were observed (see Table 1 for the

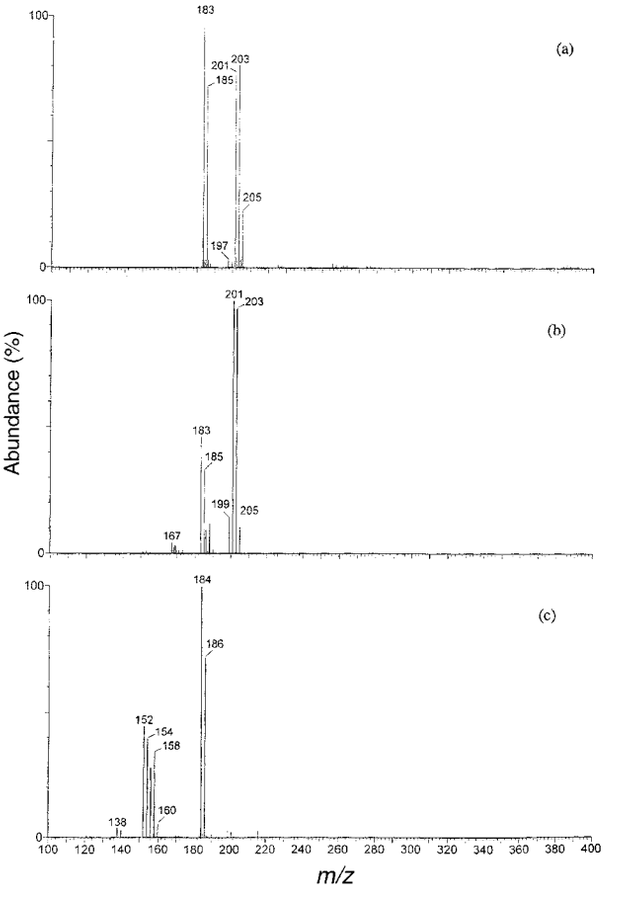

Fig. 1 Positive-ion ES-TOF mass spectra of $TMSbCl_2$ (1 μg Sb ml^{-1}) dissolved in H_2O–MeOH (v/v, 1 : 1) at different sample cone voltages: (a) 15 V, (b) 40 V, (c) 100 V. The intensities (counts) are normalized to the highest peak of the spectrum.

Table 1 Fragmentation of $TMSbCl_2$ and $TMSb(OH)_2$ obtained using a sample cone voltage of 100 V

		Compounds[a]	
m/z	Identity	$TMSbCl_2$	$TMSb(OH)_2$
121, 123	Sb^+	+	+
138, 140	$(SbOH)^+$	+	+
152, 154	$[CH_3Sb(O)]^+$	+	+
156, 158, 160	$(SbCl)^+$	+	−
183, 185	$[(CH_3)_3SbOH]^+$	−	+
184, 186	$[(CH_3)_2Sb(O)(OH)]^+$	+	+
199, 201	$[(CH_3)_2Sb(O)(CH_3OH)]^+$	+	+
216, 218	$[(CH_3)_2Sb(O)(OH)(CH_3OH)]^+$	+	+

[a] +, observed and −, not observed.

identification), while the base peaks became those at *m/z* 184 and 186 (see the discussion later); no peaks at *m/z* 183 and 185 were observed.

The ES-MS spectra of $TMSb(OH)_2$ is shown in Fig. 2. Similar to the spectra of $TMSbCl_2$, peaks at *m/z* 183 and 185, corresponding to $[(CH_3)_3SbOH]^+$, were the base peaks, while peaks accounting for *ca.* 17% relative intensity at *m/z* 365, 367 and 369 were also observed. According to the mass ratio and the isotopic pattern, these later peaks can be attributed to the protonated dimer of trimethylstibine oxide $[(CH_3)_3SbO_2Sb(CH_3)_3+H]^+$. This dimeric structure of trimethylstibine oxide has been reported by Morris *et al.*[22] No peaks at *m/z* 199–205 could be detected [Fig. 2(a)]; this result provides further evidence for the presence of $[(CH_3)_3SbCl]^+$, but not $[(CH_3)_3SbOH(H_2O)]^+$, in the ES-MS spectrum of $TMSbCl_2$ [Fig. 1 (a)]. When the sample cone voltage was set at 40 V, the intensity of the peaks at *m/z* 365, 367 and 369 decreased and new peaks at *m/z* 199 and 201 appeared in the spectrum. This is due to the fragmentation of the observed dimer of trimethylstibine oxide. Thus the peaks at *m/z* 199 and 201 can be assigned as the fragment, $[(CH_3)_2Sb(O)(CH_3OH)]^+$.

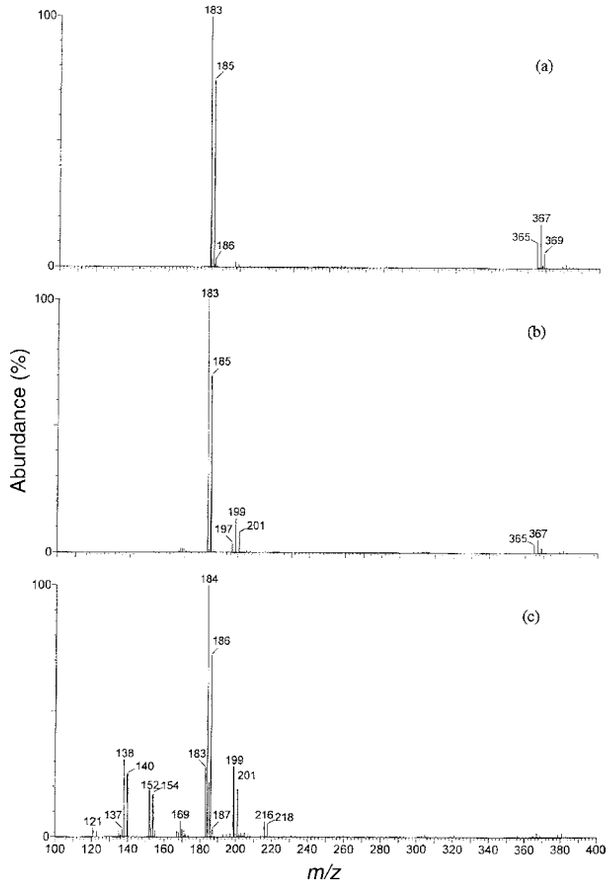

Fig. 2 Positive ion ES-TOF mass spectra of $TMSb(OH)_2$ (1 μg Sb ml^{-1}) dissolved in H_2O–MeOH (v/v, 1 : 1) at different sample cone voltages: (a) 15 V, (b) 40 V, (c) 100 V. The intensities (counts) are normalized to the highest peak of the spectrum.

When the sample cone voltage was set at 100 V, fragmentation of both $TMSbCl_2$ and $TMSb(OH)_2$ occurred. The observed significant fragments and their identifications are summarized in Table 1. It should be noted that the fragment of $(SbCl)^+$ (*m/z* 156, 158 and 160) was only detected in the case of $TMSbCl_2$. The main fragment was found at *m/z* 184 and 186 for both of $TMSbCl_2$ and $TMSb(OH)_2$, which can be attributed to the presence of $[(CH_3)_2Sb(O)OH]^+$. Peaks at *m/z* 183 and 185 with a relative intensity of *ca.* 30% could still be detected in the case of $TMSb(OH)_2$. A fragment of $[CH_3Sb(O)]^+$ (*m/z* 152 and 154) could be detected for both of the investigated compounds.

Based on the above findings we are inclined to believe that the following solution chemistry of $TMSb(OH)_2$ may exist under neutral conditions:

$$(CH_3)_3Sb(OH)_2 \rightleftharpoons [(CH_3)_3SbOH]^+OH^- \quad (1)$$

$$2(CH_3)_3Sb(OH)_2 \rightleftharpoons (CH_3)_3Sb\begin{matrix}O\\O\end{matrix}Sb(CH_3)_3 + 2H_2O \quad (2)$$

The dihydroxy compound could be present as a neutral molecule or as trimethylhydroxyantimony hydroxide, in which one OH-group serves as an anion [eqn. 1], and *ca.* 17% of the dihydroxy compound formed the dimeric structure [eqn. 2].

With respect to the dichloride compound ($TMSbCl_2$), it may be hydrolyzed to form $(CH_3)_3Sb(OH)(Cl)$ in an aqueous solution. This compound could be present either as a neutral molecule or in the ionic forms of $[(CH_3)_3SbOH]^+$ and/or $[(CH_3)_3SbCl]^+$ through the following equilibrium of eqns. 3 and 4.

$$(CH_3)_3SbCl_2 + H_2O \rightleftharpoons (CH_3)_3Sb\begin{matrix}OH\\Cl\end{matrix} + HCl \quad (3)$$

$$2(CH_3)_3Sb\begin{matrix}OH\\Cl\end{matrix} \rightleftharpoons [(CH_3)_3SbOH]^+Cl^- + [(CH)_3SbCl]^+OH^- \quad (4)$$

The proposed solution chemistry was further supported by the evidence obtained from the negative ion ES-MS spectra of $TMSbCl_2$ and $TMSb(OH)_2$ (Fig. 3). Peaks at *m/z* 253, 255 and 257 were observed in the spectrum of $TMSbCl_2$ [Fig. 3(a)], which could result from the $[(CH_3)_3Sb(Cl)(OH)]Cl^-$ molecular ion. In the case of $TMSb(OH)_2$, a complex spectrum was observed [Fig. 3(b)], where many peaks resulting from Sb species were present. Although some of them could not be assigned at this stage, we clearly observed the deprotonated $TMSb(OH)_2$, $[(CH_3)_3Sb(OH)(O)]^-$, at *m/z* 199 and 201; the species of $[(CH_3)_3Sb(OH)_2OCH_3]^-$ at *m/z* 231 and 233; and the dimer of trimethylstibine oxide combined with OH^-, $[(CH_3)_3SbO_2Sb(CH_3)_3OH]^-$, at *m/z* 381, 383 and 385. It should be mentioned that ions observed under ES-MS conditions may reflect not only the solution chemistry of species examined but also their gas phase chemistry. Therefore, further investigation is necessary to verify the proposed solution chemistry of $TMSbCl_2$ and $TMSb(OH)_2$.

Separation and determination of TMSb with SEC-ICP-MS and ES-MS

In the observed ES-MS spectra, the base peaks of both $TMSbCl_2$ and $TMSb(OH)_2$ appeared at *m/z* 183 and 185,

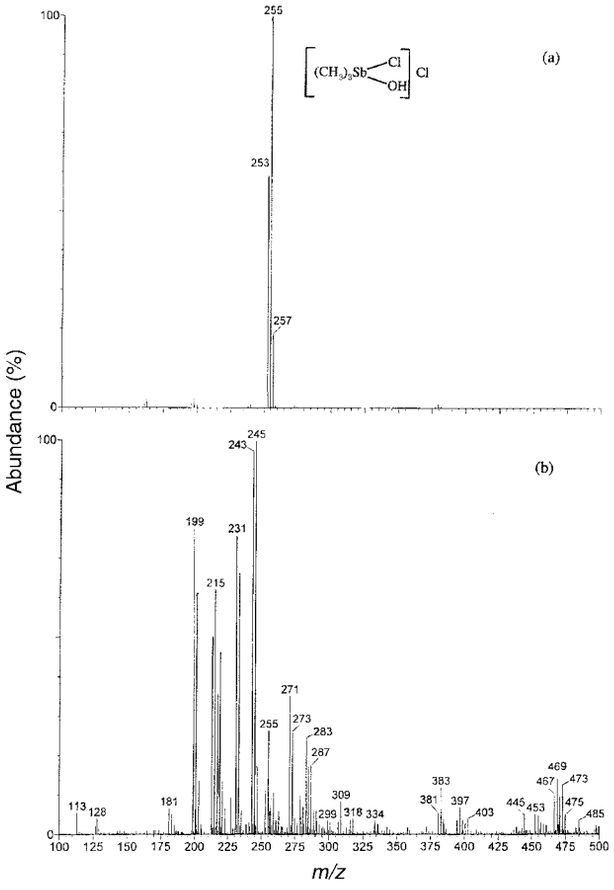

Fig. 3 Negative ion ES-TOF mass spectra of (a) $TMSbCl_2$ (5 μg Sb ml^{-1}) and (b) $TMSb(OH)_2$ (5 μg Sb ml^{-1}) dissolved in H_2O–MeOH (v/v, 1 : 1). Sample cone voltage was set to 15 V. The intensities (counts) are normalized to the highest peak of the spectrum.

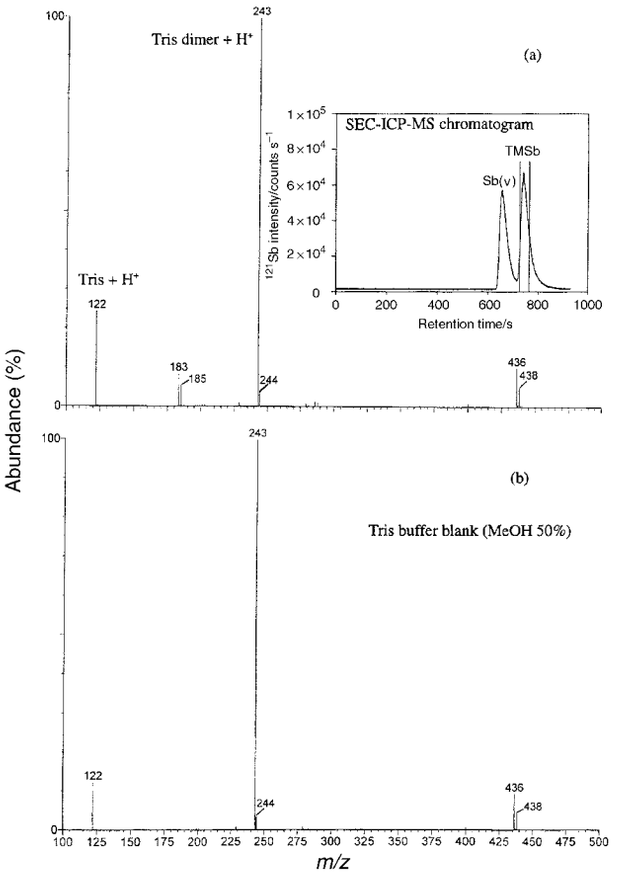

Fig. 4 Detection of trimethylantimony species in an aqueous solution. The SEC-ICP-MS chromatogram is inserted in Fig. 4(a). Due to the presence of Tris buffer, sample cone voltage was set to 40 V. (a) ES-TOF mass spectrum taken from the heart-cut fraction of a $TMSbCl_2$ standard separated by SE-HPLC. The vertical lines in the chromatogram shown in the inset indicate how the fraction was collected. (b) ES-TOF mass spectrum of Tris mobile phase used as a blank. Chromatographic separation conditions: Asahipak GS520HG column, 50 mmol l^{-1} Tris buffer with a flow rate of 1.0 ml min^{-1} at ambient temperature.

corresponding to $[(CH_3)_3SbOH]^+$ as discussed before. These peaks can be considered as a characteristic fingerprint of trimethylantimony species (TMSb).

As an analytical technique, the hyphenation of HPLC with ICP-MS is a very promising approach for elemental speciation analysis. Many difficulties, however, are encountered when this technique is applied to the speciation of inorganic Sb compounds and TMSb species. It has been reported that TMSb species are either irreversibly retained on the column or produce quite broad peaks;[8,23] an interaction between TMSb and the mobile phase used was also suggested in the literature.[17] In previous work,[6] we separated TMSb from inorganic Sb compounds with sufficient resolution and symmetric peak shape [see the insert in Fig. 4(a)] using a size-exclusion column (Asahipak GS520HG) with Tris buffer as a mobile phase. The retention time of TMSb species was found to be 740 s with a mobile phase flow rate of 1.0 ml min^{-1}, indicating an analyte with a molecular weight higher than 2000 Da, according to the mass calibration curve obtained with a series of proteins, namely, β-amylase, alcohol dehydrogenase, albumin, carbonic anhydrase and cytochrome C. This estimated molecular weight is almost 10 times higher than that of both $TMSbCl_2$ and $TMSb(OH)_2$. This chromatographic behavior could not be explained based on the size-exclusion mechanism unless there was an interaction between TMSb and the Tris buffer to form a big molecule. In order to further understand the observed chromatographic behavior, 100 μl of a $TMSbCl_2$ standard solution (100 μg Sb ml^{-1}) was injected into the SE-HPLC system. Fractions of TMSb peak were collected using a heart-cut technique[24] and diluted with methanol (1 : 1) prior to the ES-MS measurement [the vertical lines in the chromatogram shown in Fig. 4(a) indicate how the fractions were collected]. The used Tris buffer was also diluted with methanol (1 : 1), and analysed with ES-MS as a blank for comparison [Fig. 4(b)]. The obtained ES-MS spectra clearly showed the existence of $[(CH_3)_3SbOH]^+$ species (*m*/*z* 183 and 185) in the collected fractions, excluding the possibility of an interaction between TMSb and Tris buffer. Therefore, the separation of TMSb species in our SEC system may not be controlled by a size-exclusion mechanism, but probably by an ion-exchange or adsorption mechanism. However, it should be pointed out that an interaction between TMSb and the Tris buffer may exist in solution that does not survive the electrospray process, or be simply the result of the complex not existing as an ion in the gas phase. Thus, more investigation is needed to definitely elucidate the separation mechanism.

Electrospray mass spectra of inorganic Sb(v) and Sb(iii)

Potassium hexahydroxyantimonate(v) and potassium antimonyl tartrate were extensively used as standard compounds for Sb(v) and Sb(iii), respectively, for the speciation of inorganic Sb compounds. For identification purposes, their ES-MS spectra were also investigated in this work. With a positive ion mode, extended clusters of ions resulting from Sb species recognized by the *m*/*z* difference of 2 and the isotopic ratio were observed in the ES-MS spectrum (Fig. 5) of $KSb(OH)_6$. The major Sb species were observed in the *m*/*z* range from 301 to 331; clusters of Sb species could be also observed in the *m*/*z* range from 563 to 595. Their identifications are summarized in Table 2.

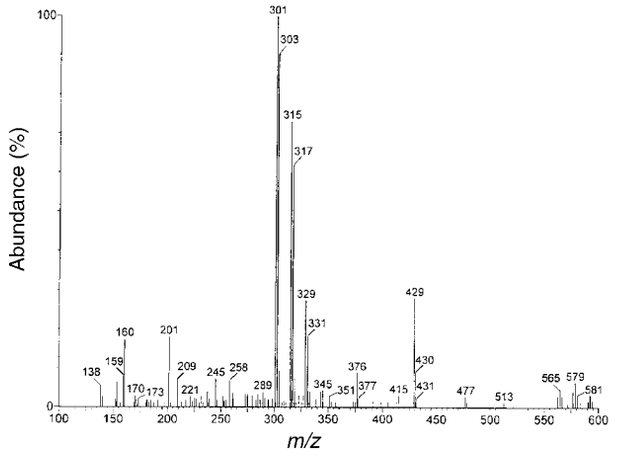

Fig. 5 Positive ion ES-TOF mass spectrum of potassium hexahydroxyantimonate [Sb(v)] (5 μg Sb ml^{-1}) dissolved in H_2O–MeOH (v/v, 1 : 1). The intensities (counts) are normalized to the highest peak of the spectrum.

Table 2 Hypothesised identification of the ES-MS spectrum of $KSb(OH)_6$ using a positive ion mode

No.	*m/z*	Formula
1	301, 303	$[KSb(OH)_6]\ K^+$
2	315, 317	$[KH_2SbO_4(CH_3OH)(H_2O)]\ K^+$
3	329, 331	$[KSbO_3(CH_3OH)_2(H_2O)]\ K^+$
4	563, 565, 567	$[(KSb(OH)_6)_2]\ K^+$
5	577, 579, 581	$[KSb(OH)_6KH_2SbO_4(CH_3OH)(H_2O)]\ K^+$
6	591, 593, 595	$[KH_2SbO_4(CH_3OH)(H_2O)]_2\ K^+$

Guy *et al.*[14] also obtained the ES-MS spectrum of $KSb(OH)_6$, but failed to identify the observed Sb species. With respect to Sb(III), no characteristic ES-MS spectrum could be produced using a positive ion mode.

Characteristic ES-MS spectra for both Sb(V) and Sb(III) obtained using a negative ion mode are shown in Fig. 6. Three Sb species could be detected in the ES-MS spectrum of Sb(V). Base peaks were found at *m/z* 223 and 225 originating from the $Sb(OH)_6^-$ ion, followed by peaks at *m/z* 237 and 239 corresponding to the $H_2SbO_4^-$ ion having water and methanol molecules associated $\{[H_2SbO_4(H_2O)(CH_3OH)]^-\}$. Peaks with a relative intensity of *ca.* 8% at *m/z* 251 and 253 were also observed. These peaks can be attributed to the SbO_3^- ion having water and methanol molecules associated $\{[SbO_3(H_2O)(CH_3OH)_2]^-\}$. These results suggest that three chemical species of $Sb(OH)_6^-$, $H_2SbO_4^-$ and SbO_3^- are present in the aqueous solution of potassium hexahydroxyantimonate under neutral condition, with $Sb(OH)_6^-$ as the predominant species. With respect to potassium antimonyl tartrate [Sb(III)], the ES-MS spectrum was characterized by abundant *m/z* 149 and 299 ions, as the base peaks, which correspond to the deprotonated tartrate and tartrate dimer. The Sb peaks at *m/z* 267, 268 and 269 indicate the presence of the $[Sb_2(C_4O_6H_2)_2]^{2-}$ ion in the solution. Trace peaks with a relative intensity of *ca.* 5% at *m/z* 417 and 419 resulting from $[Sb(C_4O_6H_4)_2]^-$ were also detected. The peak at *m/z* 316 may be attributed to the tartrate dimer having an OH^- anion associated.

Conclusion

The electrospray mass spectra of commonly used antimony compounds for speciation analysis were investigated. Electrospray mass spectrometry appears to be useful for the identification of trimethylantimony dichloride, trimethylantimony dihydroxide, potassium hexahydroxyantimonate [Sb(v)],

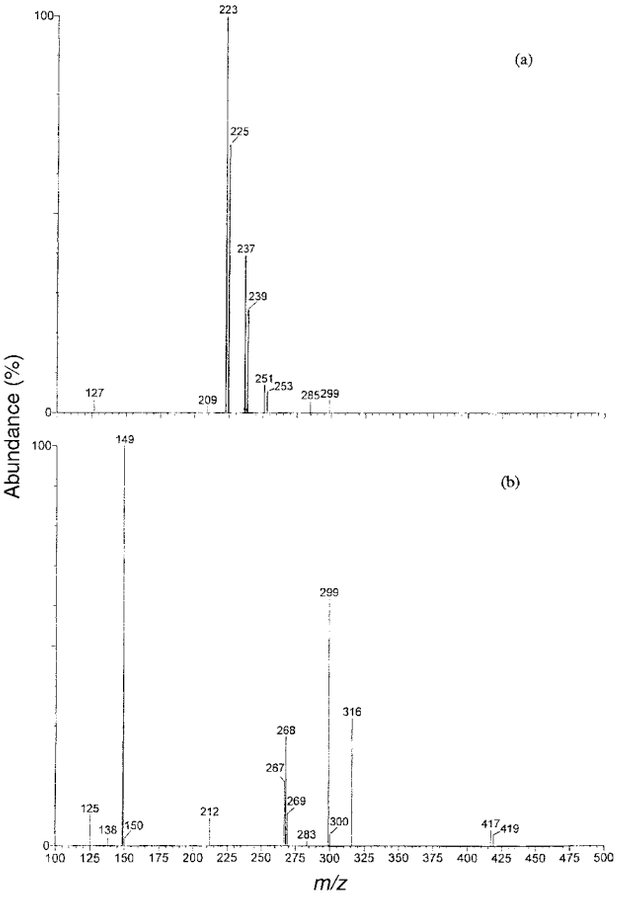

Fig. 6 Negative ion ES-TOF mass spectra of (a) potassium hexahydroxyantimonate [Sb(v)] (5 μg Sb ml^{-1}) and (b) Sb(III)tartrate (5 μg Sb ml^{-1}) dissolved in H_2O–MeOH (v/v, 1 : 1). The intensities (counts) are normalized to the highest peak of the spectrum.

and Sb(III)tartrate, since characteristic mass spectra of these compounds could be obtained when using this technique.

$TMSbCl_2$ and $TMSb(OH)_2$, which normally cannot be differentiated by HPLC-ICP-MS due to their similar chromatographic behavior,[6,13] have very different characteristic ES-MS spectra in both positive- and negative ion modes, and thus they can be readily speciated by the ES-MS technique. In positive ion mass spectra, they have the same characteristic *m/z* at 183 and 185 corresponding to $[(CH_3)_3SbOH]^+$, which can be considered as a characteristic fingerprint for the identification of trimethylantimony (TMSb) species in an HPLC-ICP-MS chromatogram of aqueous solution samples. Based on the obtained ES-MS spectra, a solution chemistry for $TMSbCl_2$ and $TMSb(OH)_2$ was proposed, which may provide useful information for the development of chromatographic separation methods for Sb speciation analysis.

Negative ion mass spectra were found to give more relevant information for the identification of inorganic Sb compounds, potassium hexahydroxyantimonate [Sb(v)] and Sb(III)tartrate. A complex positive ion mass spectrum of Sb(V) could be observed, whereas no Sb peaks could be detected for Sb(III)tartrate in a positive ion mode.

It is our conviction that the fundamental electrospray mass spectra of antimony compounds presented in this work will prove to be useful for the identification of antimony compounds in complex environmental samples.

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