Potential of high performance liquid chromatography coupled to flow injection hydride generation atomic absorption spectrometry for the speciation of inorganic and organic antimony compounds

JAAS

Full Paper

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Received 10th November 1999, Accepted 24th January 2000

This investigation was undertaken to elucidate the potential of high-performance liquid chromatography coupled to a hydride generation system connected to an atomic absorption spectrometer (HPLC-HG-AAS) as an element specific detector for the speciation of Sb(III), Sb(V) and trimethylantimony dichloride ($TMSbCl_2$). HG parameters were optimised specifically with regard to the Sb-species and yielded distinctly different optima for Sb(III) and Sb(V) as regards concentrations of $NaBH_4$ and HCl. HCl (0.5% w/v) and of $NaBH_4$ (0.6% w/v) proved to be a good compromise for optimum sensitivity for all Sb species. After optimisation, signals for Sb(V) were still two times lower than for Sb(III) and $TMSbCl_2$. Among the five anion exchange columns tested, the Dionex AS14 provided best results for the separation of Sb(V) and Sb(III) with 1.25 mM EDTA at pH 4.7. The ION-120 column was used to separate $TMSbCl_2$ and Sb(V) with 2 mM NH_4HCO_3 and 1 mM tartaric acid at pH 8.5. When separating the three Sb-species in a single chromatographic run, sharp peaks for Sb(V) and Sb(III), but a very broad peak for $TMSbCl_2$, were obtained. In all chromatographic separations the peaks could be baseline separated. Calibration curves were linear between 2 and at least 100 $\mu g\,l^{-1}$. Detection limits of 0.4, 0.7, and 1.0 $\mu g\,l^{-1}$ for $TMSbCl_2$, Sb(III), and Sb(V) were obtained.

Introduction

Antimony and its compounds are listed as priority pollutants by the US Environmental Protection Agency (EPA) and the German Research Community (DFG) underlining the increasing environmental concern about Sb.[1,2] Over the years, anthropogenic emission of Sb, mainly from traffic, production of storage batteries, semiconductors and fireproof textiles, has resulted in an increasing concentration of Sb in the environment. Moreover, Sb is present in the aquatic environment as a result of rock weathering, soil runoff and mining and smelting effluents,[3] and might be accumulated in biological matrices.[4,5] Inhalation of Sb compounds may lead to pneumonitis, fibrosis, bone marrow disease and carcinomas.[6]

In previous work, we established total Sb concentrations ranging from 2 ng g^{-1} in pigeon eggs to about 600 ng g^{-1} in elder leaves collected beside a motorway.[7–9] Concentrations of Sb in elder leaves of different origins could be closely related to car traffic. However, for a better risk assessment, total concentrations of Sb in these samples alone are not sufficient.

As with other elements, the toxicity of Sb and its compounds is strongly dependent on the chemical form and oxidation state. Generally, trivalent Sb compounds have greater toxicity than pentavalent compounds.[10] Therefore, reliable speciation procedures to determine the oxidation state and chemical binding sites of Sb in environmental and human specimens are required. Beside the two inorganic Sb species, methylated Sb compounds have also been found in environmental samples.[1,11–14]

Approaches for the simultaneous speciation of Sb have mainly used high-performance liquid chromatography coupled to hydride generation atomic absorption spectrometry (HPLC-HG-AAS),[15,16] HPLC connected to inductively coupled plasma atomic emission (ICP-AES),[11] or mass spectrometry (ICP-MS)[12,13,17] as element specific detectors. Very recently, capillary electrophoresis has been successfully coupled on-line to ICP-MS for the speciation of Sb compounds in environmental samples.[18] Apart from standards for Sb(III) and Sb(V), only standards for trimethyl antimony dichloride ($TMSbCl_2$)[12,13,19] and trimethyl antimony oxide (TMSbO)[11] have been synthesised. These three Sb standards have been used by several authors to identify and quantify Sb(III), Sb(V) and $TMSbCl_2$ by HPLC-ICP-AES or HPLC-ICP-MS in environmental samples.[1,11–13] However, analytical procedures for Sb speciation by HPLC-HG-AAS have considered, until now, only the two inorganic species Sb(III) and Sb(V).[15,16] One objective of this contribution was to elucidate the potential of HPLC-HG-AAS for the speciation of all three Sb compounds for which standards are available.

It is well known that molecular rearrangements occur during hydride generation of $TMSbCl_2$ causing demethylation of the generated trimethylstibine.[14,19] This demethylation leads to the formation of $(CH_3)_2SbH$, $(CH_3)SbH_2$, H_3Sb and $(CH_3)_3Sb$ when a standard of $TMSbCl_2$ or TMSbO is introduced into a HG system. The formation of these four Sb species may result in broad peaks in the chromatograms when a trimethylated Sb standard has to be analysed by HPLC-HG-AAS. It should be stressed that the formation of the different Sb species takes place after the HPLC separation. However, different kinetics of the hydride forming process and different chemical behaviour of the Sb compounds may lead to broad peaks.

Hydride generation properties of inorganic Sb are well known to be dependent on the oxidation state, a fact that is used for the "off-line" speciation of Sb(III) and Sb(V). However, in two recent papers dealing with speciation of Sb(III) and Sb(V) by HPLC-HG-AAS, the authors reported no significant difference in the efficiency of stibine generation for both inorganic Sb species.[15,16] The detection limits of 50 and 6 $\mu g\,l^{-1}$ for Sb(III) and Sb(V) given by Smichowski *et al.*[15] indicate unoptimised experimental conditions because the detection limit for Sb(III) should be superior (due to the kinetic of the hydride forming process) to that of Sb(V). The chromatogram published in ref. 15 shows a significant peak broadening for the Sb(III) signal leading to a higher limit of detection. Moreover,

DOI: 10.1039/a908939j

they measured larger peak areas for Sb(v) than for Sb(III). Obviously, the sensitivity for both Sb species was distinctly different in this study.[15] In a recent paper we established 10-times lower signal intensities for Sb(v) compared to that for Sb(III) when using HG-AAS for the determination of total antimony.[7] In the present work we want to shed more light into this discrepancy, performing a detailed optimisation of physical parameters influencing the signal intensities of both inorganic Sb species, Sb(III) and Sb(v), before applying HPLC to the HG-AAS system for the speciation of Sb compounds.

Experimental

Instrumentation

The HPLC system consisted of a metal-free pump (L-6220, Merck, Darmstadt, Germany), a Rheodyne metal-free six-port injector valve with a 100 µl sample loop made from polyether-ether-ketone (PEEK), and one of the five different anion exchange columns listed in Table 1. All tubings of the chromatographic device getting into contact with the mobile phase were from inert PEEK material. The hydride generation atomic absorption spectrometer set-up was a FIAS 400 flow injection system (Perkin-Elmer, Norwalk, CT, USA) with a commercial hydride generator (Perkin-Elmer) coupled to an atomic absorption spectrometer (4100, Perkin-Elmer) as described in detail previously.[7,8] The analogue signal of the spectrometer was acquired at a sampling rate of 1 Hz with a Nelson 950 interface (Perkin-Elmer) connected to a personal computer. Data were processed with chromatographic software (Turbochrom 4.12, Perkin Elmer). Detailed operating conditions of the HPLC-HG-AAS system are summarised in Table 1.

Reagents and standards

For the preparation of all solutions, MilliQ water (Millipore, Milford, MA, USA) was used. For the generation of volatile stibines, a carrier solution was prepared from hydrochloric acid (32%, *p.a.*, Riedel-de Haen, Seelze, Germany). $NaBH_4$ solutions were prepared daily by dissolving appropriate amounts of powdered $NaBH_4$ (analytical-reagent grade, Riedel-de Haen) in 0.04% (w/v) NaOH (30%, suprapur®, Merck, Darmstadt, Germany).

Mobiles phases for HPLC were prepared from ammonium hydrogen carbonate, ammonium tartrate, ethylenediaminetetraacetic acid, *p*-hydroxybenzoic acid, phthalic acid, potassium hydrogenphthalate, tartaric acid and tetramethylammonium hydroxide. All chemicals used were of analytical-reagent grade or higher purity. Adjustment of pH values was made with an ammonia solution (25%, suprapur, Merck) or concentrated nitric acid (analytical reagent grade, Merck).

Two 1000 mg l^{-1} stock solutions of Sb(III) and Sb(v) were prepared by dissolving appropriate amounts of potassium antimony tartrate (Sigma-Aldrich Chemie, Steinheim, Germany) and potassium hexahydroxyantimonate (Fluka, Neu-Ulm, Switzerland) in high-purity water. Trimethylantimony dichloride ($TMSbCl_2$) was synthesised at the University of Bremen according to published methods.[20] A 100 mg l^{-1} stock standard solution of this compound was prepared by dissolution in water. All stock standard solutions were stored in polyethylene bottles in a refrigerator held at 4 °C.

Results and discussion

Optimisation of HG-AAS parameters

Instrumental parameters from previous work, with the same HG-AAS used as a detector for trace determinations of total Sb in combination with a flow injection device, proved not to give optimal performance for HPLC-HG-AAS measurements.[7–9] Therefore, various physical and chemical parameters were investigated using a Dionex AS14 anion exchange column and 1.25 mM EDTA as mobile phase to yield optimum sensitivity. These investigations were carried out for Sb(III) and Sb(v) to consider the potentially different behaviour of both Sb species.

The influence of the temperature of the quartz tube atomiser on the peak area was tested between 760 and 1000 °C (Fig. 1). A temperature optimum of 820 °C, yielding highest peak areas for both species, could be established and was thus used for further experiments. Below 780 °C and above 900 °C the

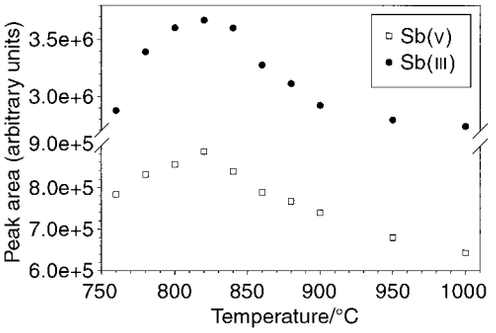

Fig. 1 Dependence of peak areas of Sb(III) and Sb(v) on the temperature of the quartz tube atomizer using the HPLC-HG-AAS setup. Column, Dionex AS 14; mobile phase, 1.25 mM EDTA at pH 4.7.

Table 1 Operating conditions for the HPLC-HG-AAS system

HPLC:—	
Anion exchange columns	ION-120, 120 × 4.6 mm, Cetac Technologies, Division of Transgenomics, Omaha, NE, USA Supelcosil SAX 1, 250 × 4.6 mm, Supelco, Bellefont, PA, USA Hamilton PRP-X100, 250 × 4 mm, Reno, NE, USA Dionex IonPak AS 14, 250 mm × 4 mm and IonPak AG 14, 50 × 4 mm (Dionex Corporation, Sunnyvale, CA, USA) Dionex IonPak AS 9, 250 mm × 4 mm and IonPak AG 14, 50 × 4 mm (Dionex Corporation)
Flow rate	1.5 ml min^{-1}
Injection volume	100 µl
Hydride generation:—	
$NaBH_4$ solution concentration	0.6% (w/v), stabilized with 0.04% (w/v) NaOH
$NaBH_4$ solution flow rate	4 ml min^{-1}
HCl solution concentration	0.5% (w/v)
HCl solution flow rate	6 ml min^{-1}
Carrier gas flow rate	Argon, 50 ml min^{-1}
Atomic absorption spectrometer:—	
Wavelength	217.6 nm
Slit	0.2 nm
Lamp current (HCL)	20 mA
Quartz tube atomizer temperature	820 °C

performance of the AAS became significantly worse resulting in very noisy baselines and worse peak shapes.

The dependence of the peak area on the concentration of hydrochloric acid was investigated between 0.2 and 10%. As summarised in Fig. 2, the responses of Sb(III) and Sb(V) are quite different. A distinct optimum for Sb(V) at a HCl concentration of 0.5% could be established, whereas the signal for Sb(III) was steadily increasing with increasing HCl concentration. Concentrations of 10% HCl yielded highest peak areas for Sb(III) and confirmed our previous findings.[7] After selective reduction of Sb(V) to Sb(III) by addition of a solution containing 30% KI and 5% ascorbic acid, a HCl concentration of 10% was found to produce best results for the quantification of total Sb in plant and lipid-rich materials.[7,8] For further experiments, a HCl concentration of 0.5% was used because the sensitivity for Sb(III) was always higher compared to that of Sb(V). Therefore, although the sensitivity for Sb(III) could still be increased by approximately 40%, a concentration of 0.5% HCl was chosen as a good compromise, giving highest signals for Sb(V).

As regards the concentration of the $NaBH_4$ solution, the behaviour of both Sb species was also quite different (Fig. 3). The response of Sb(III) and Sb(V) was tested with solutions containing between 0.05 and 0.8% $NaBH_4$. Highest peak areas were found at a $NaBH_4$ concentration of 0.25% for Sb(III), whereas the signals for Sb(V) increased linearly to its optimum concentration of 0.6% $NaBH_4$. Concentrations of $NaBH_4$ higher than 0.6% produced very rapidly decreasing signal intensities with increasing $NaBH_4$ concentrations (Fig. 3). At a $NaBH_4$ concentration of 0.8% almost no peaks were identifiable anymore. Between 0.05% and 0.6% $NaBH_4$, the influence of the reductant on the signals for Sb(V) was very strong, whereas for Sb(III) only a fluctuation of about 15% could be established. Because the sensitivity for Sb(V) was still lower when compared to that of Sb(III), a concentration of 0.6% $NaBH_4$ — the optimum for Sb(V) — was used for all further experiments.

These optimised HG-AAS parameters have also resulted in comparable signal intensities for other mobile phases tested as well as for $TMSbCl_2$.

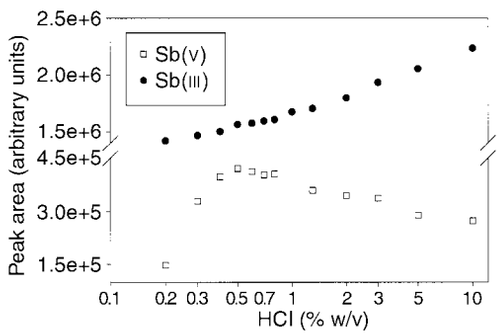

Fig. 2 Influence of the HCl concentration in the carrier solution on the signal intensities of Sb(III) and Sb(V) using the HPLC-HG-AAS setup. Temperature of the quartz tube atomizer $T = 820\,^{\circ}C$; column, Dionex AS 14; mobile phase, 1.25 mM EDTA at pH 4.7.

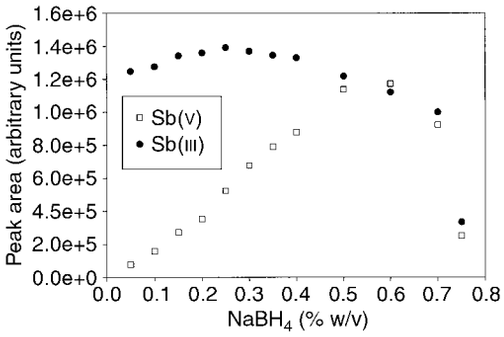

Fig. 3 Peak areas of Sb(III) and Sb(V) depending on the concentration of $NaBH_4$ as reductant determined with the HPLC-HG-AAS setup. Carrier solution, 0.5% HCl; temperature of the quartz tube atomizer $T = 820\,^{\circ}C$; column, Dionex AS 14; mobile phase, 1.25 mM EDTA at pH 4.7.

Investigation of chromatographic conditions

Initially, several screening experiments were carried out to elucidate the potential of the investigated mobile phases and different anion exchange columns for the separation of Sb(III), Sb(V) and $TMSbCl_2$. Chromatographic parameters have been optimised to achieve appropriate separation of the Sb species.

These preliminary experiments revealed two important issues: (a) elution of $TMSbCl_2$ from the column resulted in a broad peak or $TMSbCl_2$ eluted at the solvent front; and (b) the two anion exchange columns ION-120 and Dionex AS 14 produced best results with various mobile phases. The reason for the broad $TMSbCl_2$ peak and solutions to overcome this problem will be discussed in a subsequent paragraph.

Using the SAX 1 column, only Sb(V) was eluted and neither Sb(III) nor $TMSbCl_2$ could be detected with any mobile phase tested. When the AS9-SC column (mobile phase, 30 mM ammonium tartrate) was employed, Sb(V) and $TMSbCl_2$ co-eluted at the solvent front and Sb(III) was eluted after two to four min, depending on the pH of the mobile phase. The Hamilton PRP-X100 column gave only acceptable results when using EDTA with or without potassium hydrogenphthalate at pH 4 to 5. Thus Sb(V) and Sb(III) could be baseline separated. However, Sb(V) was eluted at the solvent front.

Separation of Sb(III) and Sb(V)

The two inorganic Sb species could be separated on the Dionex AS 14 column and on the Dionex guard column AG 14 using ammonium tartrate (40–50 mM) as eluent in a pH range of 5.0–7.1. Similarly to the Hamilton PRP-X100, Sb(V) was again eluted at the solvent front and Sb(III) was retained on the column. Under all the experimental conditions mentioned above, only Sb(III) and Sb(V) were eluted, whereas $TMSbCl_2$ remained on the column. Best results were obtained with the Dionex AS 14 column with EDTA as mobile phase. The chromatograms of the separation of Sb(III) and Sb(V) employing the Dionex AS 14 and Hamilton PRP-X100 columns are juxtaposed in Fig. 4. Although both Sb species could be baseline separated with both columns, Sb(V) could only be retained on the Dionex AS 14 column and thus did not elute with the solvent front.

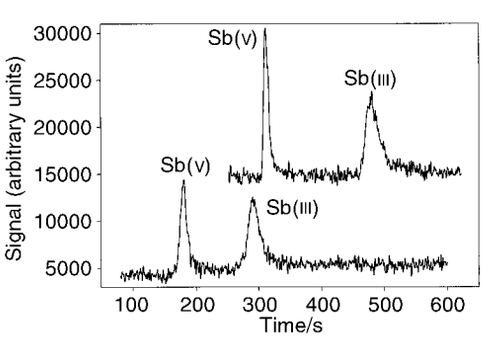

Fig. 4 Chromatograms of the separation of Sb(V) (10 $\mu g\,l^{-1}$) and Sb(III) (5 $\mu g\,l^{-1}$) using two different anion exchange columns and various mobile phases. (a) Hamilton PRP-X100; mobile phase, 20 mM EDTA + 1 mM potassium hydrogenphthalate, at pH 5.0; (b) Dionex AS 14; mobile phase, 1.25 mM EDTA at pH 4.7.

Separation of Sb(v) and $TMSbCl_2$

Initially no experiments were carried out with mobiles phases having alkaline pH values because acidic media are necessary for optimum generation of stibines. However, under neutral and weak acidic conditions $TMSbCl_2$ was always eluted — if not retained on the column — as a broad peak, the reason for which will be discussed later. Subsequent investigations revealed that also alkaline mobile phases provided the same sensitivity as neutral or weak acidic eluents. Among all anion exchange columns tested, the ION-120 using a mobile phase containing 2 mM ammonium hydrogencarbonate and 1 mM tartaric acid at a pH of 8.5 produced best results (Fig. 5). Antimony(III) was retained on the column, whereas $TMSbCl_2$ and Sb(v) were eluted. Thus the latter two Sb-species could be baseline separated (Fig. 5). Both Sb species gave sharp peaks, although $TMSbCl_2$ was eluted at the solvent front, which is generally not desirable for a selective identification of a species.

Separation of Sb(III), Sb(v), and $TMSbCl_2$

A separation of all three Sb species, for which standards are currently available, in one chromatographic run would be desirable. However, all approaches failed to produce satisfactory results. When the Dionex AS9-SC column with the mobile phase ammonium tartrate (30 mM, pH 4.7–7.3) was employed, Sb(v) and $TMSbCl_2$ co-eluted at the solvent front, whereas Sb(III) was retained for 2 to 4 min, depending on the composition of the mobile phase. The reduction of the ammonium tartrate concentration to as low as 2 mM did not improve the separation. Antimony(v) and $TMSbCl_2$ still co-eluted at the solvent front and the signal for Sb(III) was shifted to longer retention times. Other attempts to separate the three Sb species were performed with the ION-120 column using EDTA as mobile phase. A concentration of 20 mM EDTA and 1 mM potassium hydrogenphthalate yielded best results. Thus, the signals for Sb(v) and Sb(III) could be baseline separated, followed by a broad peak for $TMSbCl_2$ (Fig. 6). Reducing the amount of potassium hydrogenphthalate to 0.5 mM resulted in the co-elution of Sb(III) and $TMSbCl_2$. EDTA as mobile phase produced chromatograms with separated Sb(v) and Sb(III), but $TMSbCl_2$ in between overlapping with both inorganic Sb species. Molecular rearrangements of $TMSbCl_2$ as described in detail by Koch *et al.*[19] were initially considered as a reason for this broad TMSb peak. $TMSbCl_2$ is assumed to form the expected Me_3Sb, but $TMSbCl_2$ also demethylates during the hydride generation process giving SbH_3, $MeSbH_2$, Me_2SbH. The production of these four Sb hydrides could explain the broad peak for $TMSbCl_2$ in Fig. 6. However, our

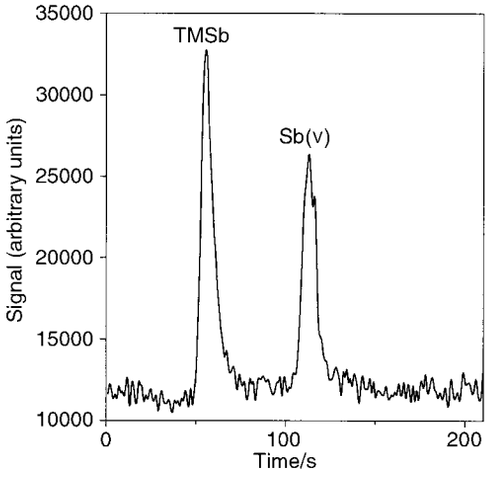

Fig. 5 Chromatogram of the separation of $TMSbCl_2$ ($5\ \mu g\ l^{-1}$) and Sb(v) ($10\ \mu g\ l^{-1}$) on the Ion-120; mobile phase, 2 mM $NH_4HCO_3 + 1$ mM tartaric acid at pH 8.5.

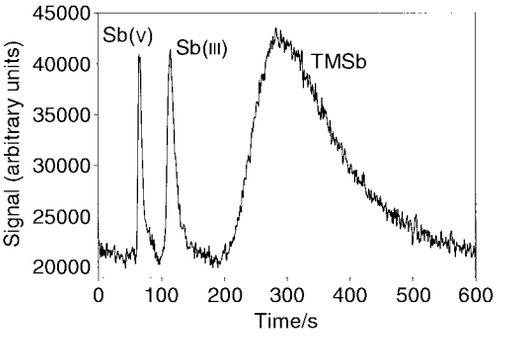

Fig. 6 Chromatogram of the separation of Sb(v) ($10\ \mu g\ l^{-1}$), Sb(III) ($5\ \mu g\ l^{-1}$) and $TMSbCl_2$ ($100\ \mu g\ l^{-1}$) with the ION-120 column and 20 mM EDTA and 1 mM potassium hydrogenphthalate as mobile phase.

HPLC-ICP-MS measurements confirmed that this broad peak is rather a "chromatographic problem" than caused by the demethylation of $TMSbCl_2$. Moreover, a very recent paper by Craig *et al.*[14] demonstrated that molecular rearrangements of $TMSbCl_2$ were not detectable after rigorous exclusion of oxygen during hydride generation. Consequently, no demethylation of $TMSbCl_2$ should occur in our HG system either, because this HPLC-HG-AAS set-up is continuously purged with argon.

Analytical characterisation

The optimum separations of the three Sb-species were tested for their analytical performances. These investigations included the determination of the reproducibility of retention times and of peak areas as well as the calculation of detection limits (LOD) of each Sb species. Detection limits were determined by performing at least 12 repetitive injections of standard solutions at low concentrations [$5\ \mu g\ l^{-1}$ Sb(III) or $TMSbCl_2$, $10\ \mu g\ l^{-1}$ Sb(v)]. From the slope of the calibration curve and three times the standard deviation of the peak areas, the LODs were calculated. Table 2 summarises the analytical characteristics for the three Sb species. The ION-120 column with ammonium hydrogencarbonate and tartaric acid resulted in detection limits of 0.4 and $1.0\ \mu g\ l^{-1}$ for $TMSbCl_2$ and Sb(v). The detection limit for Sb(III) using the Dionex AS14 column was $0.7\ \mu g\ l^{-1}$.

Conclusions

From the results of the optimisation of the HG parameters, it is evident that the production of stibines is species-dependent and has to be considered. With these optimised HG parameters, detection limits for Sb(III) and Sb(v) achieved with our method are distinctly lower than that reported previously by other authors.[15,16] Moreover, HPLC-ICP-MS detection limits of 7.5 and $0.9\ \mu g\ l^{-1}$ for Sb(III) and Sb(v), respectively, as reported by Smichowski *et al.*,[15] are comparable or even worse than the HPLC-HG-AAS detection limits of 0.7 and $1.0\ \mu g\ l^{-1}$ established in this study. Sb(III) and Sb(v) could be baseline separated employing the Dionex AS 14 column and 1.25 mM EDTA at pH 4.7 as mobile phase. The ION-120 column allowed baseline separation of $TMSbCl_2$ and Sb(v) using 2 mM $NH_4HCO_3 + 1$ mM tataric acid at pH 8.5. Applying appropriate extraction procedures, the developed analytical procedures are well suited for the speciation of Sb(III), Sb(v), and $TMSbCl_2$ in environmental specimens. Also speciation and monitoring of Sb in tap water can easily be performed with the developed speciation procedure, bearing in mind the EU drinking and surface water limits of $10\ \mu g\ l^{-1}$ for total Sb.

Table 2 Analytical characteristics of the developed chromatographic separations of Sb(III), Sb(V), and $TMSbCl_2$ using the HPLC-HG-AAS setup

		Retention times/min		Sensitivity[a]		Detection limits/μg l^{-1}	
Column	Mobile phase	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)
Dionex AS 14	1.25 mM EDTA, pH 4.7	3.00 ± 0.02 $TMSbCl_2$	4.85 ± 0.02 Sb(V)	9281 $TMSbCl_2$	35707 Sb(V)	1.8 $TMSbCl_2$	0.7 Sb(V)
Ion-120	2 mM NH_4HCO_3 + 1 mM tartaric acid, pH 8.5	0.93 ± 0.01	1.87 ± 0.01	37067	11929	0.4	1.0

[a]Peak area per μg Sb l^{-1} (μV s^{-1}).

Acknowledgement

M. Krachler is grateful to the European Community who financially supported this study through the Research Program TMR, EU contract No. FMBICT982889. The co-operation of H.J. Breunig, University of Bremen, in providing the $TMSbCl_2$ standard is gratefully acknowledged.

References

1 M. Dodd, S. A. Pergantis, W. R. Cullen, H. Li, G. K. Eigendorf and K. J. Reimer, *Analyst*, 1996, **121**, 223.
2 *MAK- und BAT-Werte-Liste 1996*, ed. Deutsche Forschungsgemeinschaft (DFG), VCH, Weinheim, 1996.
3 A. M. Garcia, M. C. P. Rodriguez, J. E. S. Uria and A. Sanz-Medel, *Fresenius' J. Anal. Chem.*, 1995, **353**, 128.
4 S. Maeda, H. Fukuyama, E. Yokoyama, T. Kuroiwa and K. Naka, *Appl. Organomet. Chem.*, 1997, **11**, 393.
5 M. Sadiq, A. A. Mian and A. P. Saji, *Chem. Speciation Bioavailability*, 1995, **7**, 101.
6 E. Steinnes, O. Hvatum and B. Bolviken, *Environ. Biogeochem. Ecol. Bull.*, 1983, **35**, 351.
7 M. Krachler, M. Burow and H. Emons, *Analyst*, 1999, **124**, 777.
8 M. Krachler, M. Burow and H. Emons, *Analyst*, 1999, **124**, 923.
9 M. Krachler, M. Burow and H. Emons, *J. Environ. Monit.*, 1999, **1**, 477.
10 *Analyses of Hazardous Substances in Biological Materials*, ed. Deutsche Forschungsgemeinschaft (DFG), VCH, Weinheim, 1996.
11 N. Ulrich, *Anal. Chim. Acta*, 1998, **359**, 245.
12 J. Lintschinger, O. Schramel and A. Kettrup, *Fresenius' J. Anal. Chem.*, 1998, **361**, 96.
13 J. Lintschinger, I. Koch, S. Serves, J. Feldmann and W. R. Cullen, *Fresenius' J. Anal. Chem.*, 1997, **359**, 484.
14 P. J. Craig, S. N. Forster, R. O. Jenkins and D. Miller, *Analyst*, 1999, **124**, 1243.
15 P. Smichowski, Y. Madrid, M. B. de la Calle Guntinas and C. Camara, *J. Anal. At. Spectrom.*, 1995, **10**, 815.
16 X. Zhang, R. Cornelis and L. Mees, *J. Anal. At. Spectrom.*, 1998, **13**, 205.
17 T. Lindemann, A. Prange, W. Dannecker and B. Neidhart, *Fresenius' J. Anal. Chem.*, 1999, **364**, 462.
18 B. Michalke and P. Schramel, *J. Chromatogr. A*, 1999, **834**, 341.
19 I. Koch, J. Feldmann, J. Lintschinger, S. V. Serves, W. R. Cullen and K. J. Reimer, *Appl. Organomet. Chem.*, 1998, **12**, 129.
20 G. O. Doak, G. G. Long and M. E. Key, *Inorg. Syn.*, 1967, **9**, 92.

Paper a908939j