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Determination of antimony by atomic absorption spectrometry with flow injection hydride generation by a tetrahydroborate-form anion-exchanger

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A quartz tube atomic absorption spectrometric method for the determination of antimony by FI-HG was developed in which stibine (SbH_3) was generated from the reaction between antimony in the injected solution and tetrahydroborate immobilized on a strong anion-exchange resin (Amberlite IRA-400). Several samples could be injected before the column was reloaded. The LOD ($3s$) in 4 mol l^{-1} HCl and 10% cysteine, and 4 mol l^{-1} HCl and 10% thiourea, were 0.55 and $0.54 \mu\text{g l}^{-1}$, respectively. The precision, expressed as %RSD ($n = 5$), was 5.9, 4.9, 3.8, 2.6 and 1.0 for 5.0, 10.0, 20.0, 40.0 and $60.0 \mu\text{g l}^{-1}$, respectively, in 4 mol l^{-1} HCl and 10% (m/v) L-cysteine; and 8.1, 5.0, 1.5, 1.2 and 1.4 for the same concentrations in 4 mol l^{-1} HCl and 10% (m/v) thiourea. The throughput was 60 h^{-1} . Interferences from transition metals and hydride-forming elements, and signal suppression due to high ionic strength, were eliminated by the addition L-cysteine or thiourea to the samples, which also allowed the acid concentration to be decreased to 0.61 mol l^{-1} . The method was evaluated by the analysis of spiked sea and well waters, for which no matrix effects were observed: the recoveries for 3.0 and $5.0 \mu\text{g l}^{-1}$ were 102% and 110–114%, respectively.

Introduction

Antimony is a toxic element, which exists mainly as Sb(III) and Sb(V) in environmental, biological and geochemical samples.^{1–4} The toxicity and biological behavior of antimony depends on the oxidation state, the presence of binding partners and potential ligands, and the solubility of the compounds.^{3–7} Inorganic species of antimony are more toxic than the organic ones, and antimonite, Sb(III), is ten times more toxic than antimonate, Sb(V). Thus, relevant biological⁸ and environmental⁹ studies need the support of suitable analytical procedures, many of which involve FI and HG with AAS,¹⁰ though several more recently developed procedures involve other atomic spectrometric techniques.¹¹

Sodium tetrahydroborate(III) (also known as borohydride) is the most common hydride generation reagent.¹² However, due to the instability of aqueous solutions and the large volume required for both conventional batch and flow techniques, there is interest in the generation of hydrides from solid reagents.^{13–19} Such procedures may also have decreased matrix interferences as the effective concentration of the borohydride is increased. Tian *et al.*^{13,14} developed a movable reduction bed hydride generator (MRBHG) for the determination of arsenic, antimony and selenium by coating a mixture of potassium borohydride and solid organic acid powders onto the surface of an adhesive tape. The procedure worked with microlitre sample volumes, did not need a gas–liquid

separator, eliminated interferences among hydride-forming elements, and had low detection limits. Maleki *et al.*¹⁵ generated plumbane from solid sodium borohydride and solid tartaric acid. Tesfalidet and Irgum¹⁶ generated arsine with a column packed with an anion-exchange resin in the tetrahydroborate form. Interferences from transition elements were minimized and single digit $\mu\text{g l}^{-1}$ detection limits were obtained. Carrero and Tyson^{17,18} generated hydrogen selenide by retaining selenium(IV) and tetrahydroborate(III) simultaneously on a strong anion-exchange resin, thereby preconcentrating and separating the analyte from cation interferences. Chuachud and Tyson devised procedures for the determination of lead¹⁹ and cadmium²⁰ in which the volatile derivative was formed by reaction of the acidified sample with a borohydride-form anion-exchanger. They pointed out the advantages of decreased interferences and reagent consumption, and noted that during the passage of an acidified sample through the column, the decomposition of borohydride was incomplete.²⁰

We have developed a method for the generation of stibine (SbH_3) from the reaction between antimony and tetrahydroborate immobilized on a strong-anion exchange resin. In contrast to the previously reported procedures of this sort, several measurements could be made without reloading the column with borohydride. The procedure thus has potential as an interface between a solution-phase separation stage and measurement by HG atomic spectrometry. Interferences from transition and hydride-forming elements, and signal suppressions due to high ionic strengths, were eliminated by adding L-cysteine or thiourea to the samples. Reagent consumption was significantly decreased compared with other forms of hydride generation.

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Experimental

Reagents

All chemicals were of analytical reagent grade and all dilutions were made with deionized water. A standard solution of 1000 mg l⁻¹ of antimony(III) (Fisher Scientific) was used to prepare a stock solution of 1000 µg l⁻¹, from which working standard solutions were prepared daily. Sodium borohydride solution, 1% (m/v) in 0.05% (m/v) sodium hydroxide, was prepared by dissolving 1 g of sodium borohydride (98% purity, Alfa) in 100 ml of sodium hydroxide 0.05% (m/v) (original solid from Mallinckrodt). Hydrochloric acid, 4 mol l⁻¹, was prepared by diluting 82 ml of concentrated hydrochloric acid (Fisher Scientific) to 250 ml with deionized water. Solutions containing potentially interfering species were prepared by adding the appropriate amount of the interferent to standard solutions containing 10 µg l⁻¹ of Sb(III) in 0.61 and 4 mol l⁻¹ hydrochloric acid. L-Cysteine was added to all working standard solutions at a final concentration of 10% (w/v). The resins were Amberlyst A-26, Amberlite IRA-400 and Amberlite 410, which are strongly basic anion-exchangers containing quaternary ammonium functional groups on a styrene-divinylbenzene structure.²¹

Instrumentation

The detection unit used was a PerkinElmer Model 1100B atomic absorption spectrometer with deuterium background correction and a flame-heated, T-shaped, quartz tube atomizer. The operating conditions are given in Table 1.

The flow injection manifold, shown schematically in Fig. 1, was constructed from 0.8 mm id PTFE tubing. The gas-liquid separator used was the glass device with glass beads (Perkin-Elmer, part No. B019-3772). The column consisted of a glass tube of 50 mm length and 3.3 mm id. Two six-port rotary valves connected the column and the sample loop to the manifold. Three peristaltic pumps, equipped with Tygon pump tubing of different internal diameters, controlled the

Table 1 Optimum operation conditions for the determination of antimony by FI-HG-QTAAS

<i>Atomic absorption spectrometer</i>	
Wavelength	217.6 nm
Slit width	0.2 nm
Lamp	Electrodeless discharge lamp
Lamp current	290 mA
Background correction	On
<i>Hydride generation</i>	
HCl concentration	4 mol l ⁻¹
L-Cysteine concentration	10% m/v
Carrier flow rate	14 ml min ⁻¹
NaBH ₄ concentration	1.0% m/v
NaBH ₄ flow rate	6 ml min ⁻¹
NaBH ₄ loading time	40 s
Argon flow rate	540 ml min ⁻¹
Column size	50 × 3.3 mm
Resin	Amberlite IRA-400
Sample volume	300 µl
Number of injections without reloading	3 ^a

^a At lower acid concentration (0.61 mol l⁻¹) up to 6 injections may be made.

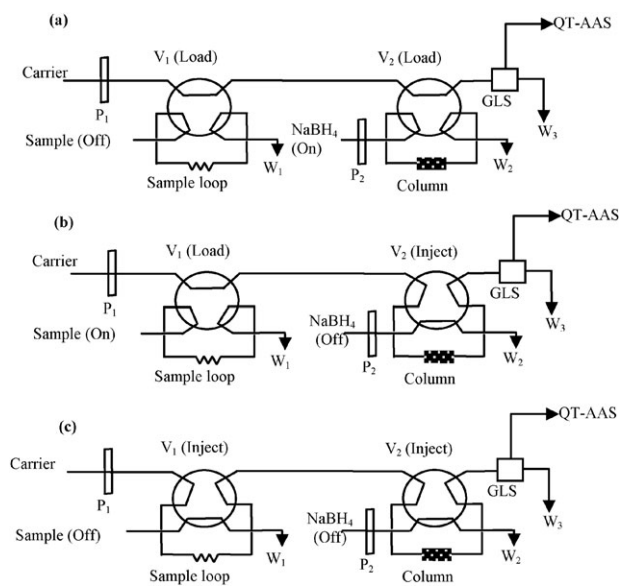


Fig. 1 Manifold for the determination of antimony by FI-HG-QTAAS with immobilized tetrahydroborate. (a) Load position, (b) V1 (load) and V2 (inject) and (c) inject position: V1, V2, 6-port valve; GLS, gas-liquid separator; W1, W2, W3, waste lines; P1, P2, P3, peristaltic pumps.

flows of carrier and borohydride through the system and the waste from the gas-liquid separator. Preliminary studies made with the manifold in Fig. 1 led to a three-step procedure. In the load position, Fig. 1(a), the borohydride solution was pumped through the column for a period of 40 s, resulting in the retention of BH₄⁻. At the same time, the carrier solution (deionized water) was pumped constantly through the system. Valve 2 was then switched to the inject position, Fig. 1(b), and the column was washed with the carrier solution while the sampling loop of valve 1 was filled with the sample solution. Valve 1 was then switched to the inject position, Fig. 1(c), and the acidified sample was carried through the column to generate the stibine (SbH₃). Several injections were made before reloading borohydride onto the column. The optimum operating conditions selected after the preliminary experiments are given in Table 1.

Method development

Column dimensions and type of resin

Three strong anion-exchange resins were studied: Amberlyst A-26, Amberlite IRA-400 and Amberlite 410. Columns of three different lengths (150, 100 and 50 mm) and the same internal diameter (3.3 mm) were packed with Amberlite 400. The resulting columns were tested for stibine generation at concentrations of 10 and 20 µg l⁻¹ antimony(III). The effect of column length was investigated for standards also containing L-cysteine.

Optimization

The multi-cycle alternating variable search method^{22,23} was used for the optimization of the following parameters: the borohydride concentration, the time the borohydride solution

was passed through the column, the flow rate of the borohydride and carrier solution, the sample acidity and the stripping gas flow rate. The figure of merit was maximum net peak height sensitivity, though conditions that did not permit multiple injections without reloading the column were considered sub-optimal. Parameters were optimized for a sample solution of $10 \mu\text{g l}^{-1}$ of Sb(III) and a column size of 50×3.3 mm id packed with Amberlite IRA-400 anion-exchange resin. The effect of the borohydride concentration and sample acidity were studied by varying these parameters within the ranges 0.1–2% m/v NaBH_4 in 0.05% m/v NaOH , and 0.05–4 mol l^{-1} HCl . The length of time that the borohydride was passed through the column was varied from 30 to 120 s and the effect of three different concentrations of this reagent was studied. The borohydride and carrier flow rates were varied from 2.3 to 8.2 ml min^{-1} , and from 8.6 to 25 ml min^{-1} , respectively. The argon stripping gas flow rates were varied between 113 and 600 ml min^{-1} . Preliminary experiments with gas–liquid separators confirmed that the glass device containing beads performed satisfactorily.

Analytical performance

Under optimized conditions, calibration curves for 300 μl of 0.0, 1.0, 5.0, 10.0, 20.0, 40.0 and 60.0 $\mu\text{g l}^{-1}$ of antimony solutions in 4 mol l^{-1} HCl and 10% (m/v) L-cysteine and 4 mol l^{-1} HCl and 10% (m/v) thiourea were constructed. Detection limits were calculated as the concentrations that gave signals equal to three times the standard deviations of the blank signals. The RSD of five replicate signals for solutions containing 5.0, 10.0, 20.0, 40.0 and 60.0 $\mu\text{g l}^{-1}$ of antimony was calculated. The effect of sample volume (50–500 μl) on detection limit was investigated for standards containing L-cysteine. The response for antimony(v) was measured.

Interference studies

The tolerance of the system to interferences was evaluated by investigating the effect of some transition metals and hydride active elements that are expected to affect the antimony signal for HG with quartz tube atomization. The following ions were studied: Cu(II), Co(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II), Pb(II), As(III) and Se(IV). Additionally, the effect of the sample ionic strength was evaluated. The interferents were added individually to 10 $\mu\text{g l}^{-1}$ of antimony standard solution in 0.6 mol l^{-1} HCl , and 10 $\mu\text{g l}^{-1}$ of antimony standard solution in 4 mol l^{-1} HCl and 10% (m/v) of L-cysteine or thiourea. The ionic strength of the sample was adjusted to 1, 2, 3 and 4 mol l^{-1} by adding different amounts of chloride salts to 20 $\mu\text{g l}^{-1}$ of antimony standard solutions in 0.6 mol l^{-1} HCl . All signals were compared with those obtained when no interfering elements or chloride salts were added. For these experiments the sample volume was 200 μl . Interferences in 0.61 mol l^{-1} HCl were investigated for the 100 and 150 mm columns. Interferences from all elements studied were evaluated at the optimum conditions (see Table 1).

Analysis of water samples

Natural water matrices (ground water and sea-water) were analyzed, spiked with either 3.0 or 5.0 $\mu\text{g l}^{-1}$ of Sb(III), and re-

analyzed to investigate possible interferences from these matrices. The samples came from a domestic well (Pelham, MA) and Chesapeake Bay (MD) and were analyzed with no pre-treatment other than the addition of hydrochloric acid and either L-cysteine or thiourea, to give concentrations of 4.0 mol l^{-1} and 10%, respectively. A sample volume of 300 μl was injected.

Results and discussion

Column dimensions and type of resin

The Amberlite IRA-400 gel type resin, which contains the $-\text{N}^+(\text{CH}_3)_3$ functional group, produced higher peak height sensitivity than did the macroreticular resin Amberlyst A-26 carrying the same functional group and the Amberlite IRA-410 gel type resin with the $-\text{N}^+(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ functional group. Although the results obtained for Amberlite IRA-410 and Amberlyst A-26 were similar, the sensitivity for Amberlyst A-26 resin was lower. The best peak height absorbance values were obtained with the shorter columns packed with Amberlite IRA-400 for solutions containing L-cysteine. This is in contrast to the effect observed when solution do not contain L-cysteine: longer columns give higher signals. In addition, the number of replicate measurements obtained without reloading the column with borohydride was higher for the shorter columns. The number of replicate measurements increased as the time for which the borohydride solution was passing through the column was increased.

Parameter optimization

The optimum conditions are given in Table 1. The studies of the concentration of borohydride and the time for which it was passed through the column showed that the signal was almost constant in the range 0.1–2% (m/v). In contrast, the number of replicate measurements did depend on both the borohydride concentration and the time it was passed through the column. This dependence possibly arises because of the amount of borohydride required during the generation of stibine. In general, no drift was observed in the signal from replicate injections until the final, much decreased, signal was obtained. No variation of the signal was observed as the flow rate of the borohydride solution was increased from 2.3 to 8.2 ml min^{-1} . However, the signal for the last replicate measurement increased as the borohydride flow rate increased. A concentration of 1% (m/v), at a flow rate of 4.0 ml min^{-1} , and a time of 30 s were chosen as optimal for further experiments. Studies on the effect of the carrier flow rate showed an increase in the signal, as the carrier flow rate varied from 8.6 to 25 ml min^{-1} . The number of replicate measurements was also affected by the carrier flow rate, this being higher at a flow rate of 25 ml min^{-1} . However, larger standard deviations were obtained at flow rates between 16.8 and 25 ml min^{-1} and so a flow rate of 14 ml min^{-1} was chosen as optimal.

Studies of the effect of argon flow rate showed that even in the absence of argon, the hydrogen by-product of the hydride generation reaction was sufficient to strip and transport the stibine to the quartz tube. However, when the argon flow rate was set to a value below 400 ml min^{-1} two peaks were often

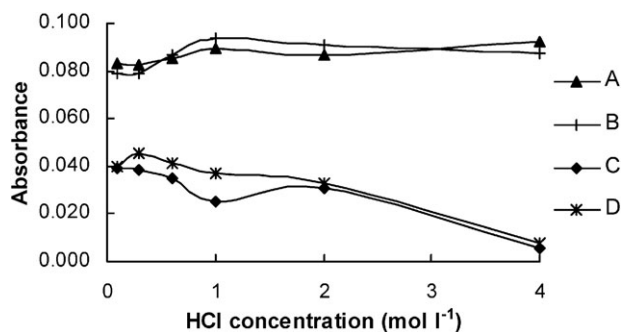


Fig. 2 Effect of HCl concentration in presence or absence of L-cysteine on the signal peak height (absorbance) of $10 \mu\text{g l}^{-1}$ Sb(III), 50 mm \times 3.3 mm column. (A) Multiple injections with L-cysteine, (B) single injection with L-cysteine, (C) multiple injections without L-cysteine, (D) single injection without L-cysteine.

observed. The second peak was attributed to the remobilization of antimony from the previous sample, which had been deposited on the hot side arm close to the entrance to the atomizer tube by reaction with the hydrogen liberated from the decomposition of excess borohydride. This phenomenon has been observed by other researchers.²⁴⁻²⁶ An argon flow rate of 540 ml min^{-1} was chosen as optimal.

The effect of acid concentration, in the presence or absence of L-cysteine, on the signal of antimony is shown by traces A, B, C and D in Fig. 2. It can be seen that for the samples without L-cysteine, the signal decreased as the acid concentration increased to 4 mol l^{-1} . In contrast, in the presence of L-cysteine, the antimony signal was not affected by the concentration of the acid. In the presence of 4 mol l^{-1} HCl, the signal for $10 \mu\text{g l}^{-1}$ antimony remained constant while the L-cysteine concentration was varied between 1 and 10% (m/v) and thus concentrations of L-cysteine as low as 1% prevented the signal suppression due to the high acid concentration. Similar results for thiourea were observed. The effect of sample ionic strength is shown in Fig. 3. A decrease of the signal was observed when the sample ionic strength was increased from 1 to 4 by adding chloride salts to samples containing $20 \mu\text{g l}^{-1}$ Sb(III) in 0.61 mol l^{-1} HCl. As the effect of

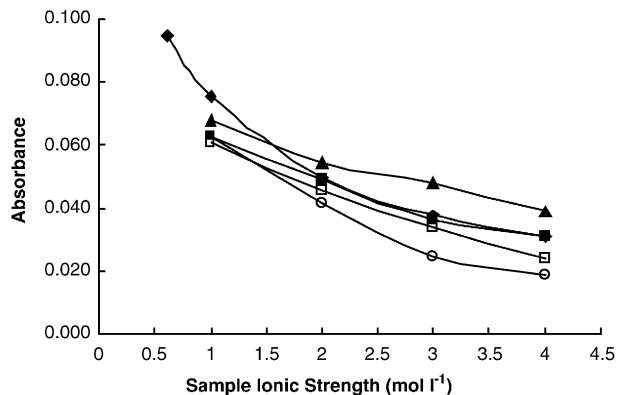


Fig. 3 Effect of sample ionic strength on the signal (peak height absorbance) for $20 \mu\text{g l}^{-1}$ Sb(III) in 0.61 mol l^{-1} HCl and chloride salts: (◆) HCl, (■) NaCl, (▲) KCl, (□) CaCl₂, (○) MnCl₂, 150 mm \times 3.3 mm column.

acid is very similar to the effects of the various salts, it is proposed that with immobilized borohydride the generation of stibine is not so much affected by the hydrogen ion concentration as by the sample ionic strength.

Analytical performance

The equations (unweighted linear least squares fit) of the calibrations were $y = 0.0099x + 0.0006$ (L-cysteine) and $y = 0.0089x + 0.0033$ (thiourea), where y is the peak height absorbance and x is the concentration in $\mu\text{g l}^{-1}$. The peak height LOD (3 σ) were 0.55 and 0.54 ($300 \mu\text{l}$) for solutions containing 4 mol l^{-1} HCl and 10% (m/v) L-cysteine, and 4 mol l^{-1} HCl and 10% (m/v) thiourea, respectively. The precision, expressed as %RSD ($n = 5$) was 5.9, 4.9, 3.8, 2.6 and 1 for 5.0, 10.0, 20.0, 40.0 and $60.0 \mu\text{g l}^{-1}$ in 4 mol l^{-1} HCl and 10% (m/v) L-cysteine and 8.1, 5.0, 1.5, 1.2 and 1.4 for 5.0, 10.0, 20.0, 40.0 and $60.0 \mu\text{g l}^{-1}$ in 4 mol l^{-1} HCl and 10% (m/v) thiourea. Peak height LOD of 1.3, 1.1, 0.95, 0.71, 0.55 and $0.37 \mu\text{g l}^{-1}$ were obtained for 56, 100, 200, 256, 300 and $500 \mu\text{L}$ sample volumes, respectively. The plot of these data resembles a straight line rather than the complete half of a rectangular hyperbola that is typical for the flow injection detection limit relationship.²⁸ Under the conditions given in Table 1, the throughput was 60 h^{-1} .

Interferences and masking agents

No interference, up to 100 mg l^{-1} , was seen for Zn(II), Fe(II), Mn(II), Cd(II), Pb(II) in 0.61 mol l^{-1} acid. Nickel(II), at concentrations greater than 50 mg l^{-1} , produced an enhancement. Selenium(IV) affected the antimony signal only when added at concentrations higher than 5 mg l^{-1} . Cobalt(II) affected the antimony signal when added at concentrations as low as 5 mg l^{-1} when replicate measurements were made without reloading the column. On the other hand, Co(II) did not interfere, even at a concentration of 100 mg l^{-1} , when borohydride was loaded onto the column after each injection. The effect of As(III) concentration on the determination of Sb(III) was studied for solutions containing up to $50 \mu\text{g l}^{-1}$ Sb(III) and 20 mg l^{-1} As(III). There was no effect for solutions containing up to $10 \mu\text{g l}^{-1}$ of antimony and 20 mg l^{-1} of arsenic. The antimony signal decreased for solutions containing between 20 and $50 \mu\text{g l}^{-1}$ antimony and between 2 and 20 mg l^{-1} arsenic. Of all the interfering elements studied, Cu(II) was the worst, causing at least 50% depression of the signal when added at concentrations between 50 and 100 mg l^{-1} . Concentrations of copper between 10 and 50 mg l^{-1} caused changes in the color of the resin: a yellow or black color was formed when the copper concentration was higher than 10 or 50 mg l^{-1} , respectively. These colors were probably due to the formation of elemental copper or copper complexes, which attached to the resin.^{18,29,30} These deposits were difficult to wash away and affected subsequent measurements. Therefore, new resin was packed inside the column after injecting samples containing high concentrations of copper. Several possible masking agents were evaluated, including 8-hydroxyquinoline, potassium iodide, thiourea and L-cysteine. 8-Hydroxyquinoline and potassium iodide were not effective. Preliminary studies with L-cysteine and thiourea showed that both compounds

Table 2 Determination of antimony in natural waters

Sample	Antimony added/ $\mu\text{g l}^{-1}$	Antimony found ^a / $\mu\text{g l}^{-1}$		Recovery ^a (%)	
		L-Cysteine	Thiourea	L-Cysteine	Thiourea
Well-water (Pelham, MA)	0	<0.55	<0.55	—	—
	3.0	3.1 \pm 0.4	3.0 \pm 0.2	102 \pm 12	99 \pm 8
	5.0	5.1 \pm 0.5	5.1 \pm 0.4	102 \pm 9	102 \pm 8
Sea-water (Chesapeake Bay, MD)	0	<0.55	<0.55	—	—
	3.0	3.4 \pm 0.2	3.1 \pm 0.2	114 \pm 7	104 \pm 6
	5.0	5.5 \pm 0.4	5.2 \pm 0.2	110 \pm 8	104 \pm 5

^a Values are mean ($n = 3$) \pm one standard deviation.

enhanced the signal, reduced the interferences from copper, and eliminated signal suppression at high ionic strength.

The simultaneous signal enhancement and reduction of interferences by L-cysteine has been observed previously for the determination of antimony by HG-AES²⁷ and by AAS.³¹ The effect is attributed to the formation of an intermediate compound between L-cysteine with borohydride, which has a greater hydride-forming efficiency than borohydride itself.³² However, there have been no previous reports of this effect for thiourea, though a number of researchers have masked interferences from other matrix components with this reagent in the determination of antimony by HG.^{33–36} The possible benefits of these two reagents for the elimination of ionic strength effects has not been reported. We also found that L-cysteine or thiourea removed the interferences from Se(IV), Co(II) and Cu(II), and allowed at least three replicate measurements without reloading the column. No interferences were observed at the optimum conditions for samples containing 10 $\mu\text{g l}^{-1}$ of antimony and up to 100 mg l^{-1} of the interfering element. On the contrary, the signal was enhanced for samples containing 10 $\mu\text{g l}^{-1}$ antimony and up to 100 mg l^{-1} As(III) or Ni(II). When L-cysteine was present, one more replicate measurement could be made before reloading the column than when thiourea was present.

Determination of antimony in natural waters

The results of the application of the proposed method to the determination of antimony in sea- and well-water are given in Table 2. The recoveries are calculated on the assumption that the original concentration is 0.0 $\mu\text{g l}^{-1}$, which of course may not be the case, as it is only possible to report that the concentrations of antimony in sea- and well-water were below the LOD of 0.55 $\mu\text{g l}^{-1}$. The recoveries of spikes at 3 and 5 $\mu\text{g l}^{-1}$ indicated that no significant interferences from the water matrices were encountered, apart from the result for sea-water spiked at 3.0 $\mu\text{g l}^{-1}$ with L-cysteine as making agent. Typical concentrations of dissolved antimony in unpolluted waters are less than 1 $\mu\text{g l}^{-1}$.¹ For sea-water, the concentration is around 0.2 $\mu\text{g l}^{-1}$; the prevalent forms are mainly inorganic Sb(III) and Sb(V), as methylated antimony compounds represent less than 10% of total antimony in the open ocean.³⁷ We are currently working on combining solid-phase extraction preconcentration with HG from the borohydride-form anion exchanger. If the measurement technique were AFS or ICP-MS, then the LOD would be considerably decreased.

Conclusions

As has been shown for the determination of lead and cadmium, the consumption of reagents is considerably decreased for generation from a borohydride-form anion exchanger compared with the consumption for homogeneous reaction procedures. In the particular case of antimony, we have shown that further economy is possible, as up to 6 injections (0.61 mol l^{-1} acid) may be made before the column needs to be reloaded with borohydride. The extent of interferences is decreased compared with those encountered in HG by homogeneous solution reaction, and the LOD are comparable to those of other HG quartz-tube atomizer AAS procedures. However, the LOD is still not low enough to determine Sb at naturally occurring concentrations in water samples, and thus preconcentration is needed if quantification is to be by AAS.

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