Voltammetric Determination of Antimony in Natural Waters

D. RÚRIKOVÁ and M. POČUCHOVÁ

Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, SK-842 15 Bratislava

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A procedure for determining Sb(III) and total dissolved Sb in natural waters using differential pulse voltammetry (DPV) in enriched solution with hanging mercury drop electrode in the presence of catechol is described. The DPV involves three steps: electrochemical reduction to elemental antimony at −1.0 V, reoxidation to Sb(III), and accumulation in the form of catechol complex after fast potential change to −0.1 V and cathodic scan from −0.1 V to −1.0 V The Sb(III) may be determined with a detection limit 0.1 μg dm^{-3} and a linear response in the range 0.5 to 8 μg dm^{-3} for a 480 s deposition. This voltammetric technique responds to Sb(III) only. Therefore Sb(V) must be converted to Sb(III) with chemical reduction prior to its determination. The precision and accuracy of the pretreatment procedure and DPV technique were evaluated by analyzing synthetic water spiked with known amounts of Sb(III) and Sb(V). The relative standard deviations ranged from 1.3 to 9.8 % and the recoveries were > 90 % for both Sb species in most cases. Finally, the developed method was successfully applied to the analysis of Sb in natural waters.

The concentration of total antimony in most natural waters varies in the range 0.01 to 5 μg dm^{-3} The predominant antimony species found in natural water are: inorganic Sb(III) and Sb(V). The ratio Sb(III)/Sb(V) in most natural waters was reported to be of the order 10^{-2} The contents of organic methylantimony compounds are on very low concentration levels (< 13 ng dm^{-3}) [1].

The low content of Sb in waters demands a high sensitivity of the analytical method used for its determination. Among instrumental analytical methods which can be applied for the determination of traces of Sb, electroanalytical technique such as stripping voltammetry is important. This method besides allowing the determination of the element at μg dm^{-3} levels is also suitable for speciation studies. Speciation of the oxidation states of Sb in environmental samples is important as each state may exhibit significant differences in toxicity.

Anodic stripping voltammetry (ASV) is the most often used electroanalytical method for the determination of traces of Sb in waters. The antimony was accumulated on hanging mercury drop electrode (HMDE) [2—4], mercury-coated graphite electrode [5, 6], and gold film electrode [7]. Antimony can also be determined by cathodic stripping voltammetry (CSV) after adsorptive collection in the form of complexes with the aromatic *o*-dihydroxy groups (*e.g.* catechol [8], gallic acid [9]) on HMDE or in the form of sparingly soluble ionic associates formed with triphenylmethane dyes [10] and rhodamine B [11] on the surface of a graphite electrode.

In the present work we used complexes with catechol for a voltammetric determination of dissolved Sb in natural waters. A voltammetric behaviour of Sb depended on the oxidation state of the element. Therefore a procedure was developed for selective determination of different inorganic forms of this element at nanogram level.

EXPERIMENTAL

Hydrochloric (Lachema) and sulfuric (Merck) acids of highest purity were used. Catechol (Lachema) was purified by recrystallization. All other chemicals used were of anal. grade from Lachema and were not further purified. Water was deionized with mixed ion exchangers and then distilled.

The standard stock solution of Sb(III) was prepared by dissolving Sb_2O_3 in concentrated hydrochloric acid and diluting to give a 2 × 10^{-3} mol dm^{-3} Sb(III) solution in 2 M-HCl. A stock solution of Sb(V) (1 × 10^{-4} mol dm^{-3}) was prepared by oxidation of Sb(III) stock solution by addition of bromine solution and by suitable dilution. Working standard solutions of lower concentrations 2 × 10^{-6} to 8 × 10^{-6} mol dm^{-3} Sb(III) or Sb(V) were prepared by dilution of the stock solutions. A stock solution of 0.1 mol dm^{-3} catechol in deaerated distilled water was prepared daily. A stock pH buffer solution was prepared from 1 M-CH_3COOH by pH adjustment to 6.0 with 1 M-NaOH. Synthetic water spiked with known amount of Sb was used as model sample. Its composition was: 0.294 g dm^{-3} $CaCl_2$ $2H_2O$, 0.216 g dm^{-3} NaCl, 0.086 g dm^{-3} $MgSO_4$ $7H_2O$, 9.5 mg dm^{-3} KCl, 7.3 mg dm^{-3} $(NH_4)_2HPO_4$ [12].

The polarographic Analyzer PA 4 with X—Y recorder 4103 and Static Mercury Drop Electrode SMDE 1 (Laboratorní přístroje, Prague) were used for voltammetric measurements. The electrochemical cell was equipped with Ag/AgCl reference electrode (saturated KCl), the platinum auxiliary electrode, and the working electrode which was used in the HMDE mode. Voltammetric measurements were made either by fast scan differential pulse voltammetry (FSDPV) in enriched solution or FSDPCSV under the following conditions: drop size 160 ms (2.3 mg), deposition time 120 to 480 s, pulse amplitude −50 mV, scan rate 50 mV s^{-1}, sensitivity 2 to 10 nA cm^{-1}, time constant of memory 10 ms, deposition potential −1.0 V and −0.2 V for FSDPV and FSDPCSV, respectively, reoxidation potential −0.1 V, and reoxidation time 20 s for FSDPV

Voltammetric Determination of Sb

The water sample (1—10 cm^3) was pipetted into the polarographic cell and diluted to 10 cm^3, 50 mm^3 of 0.1 mol dm^{-3} EDTA was added and pH was adjusted to 6 by addition of 200 mm^3 of acetate buffer. After deaeration of the sample by nitrogen purified with an acidic vanadium(II) solution 200 mm^3 of the catechol stock solution was pipetted to measured solution. The Sb(III) peak was recorded at the conditions mentioned above by fast scan differential pulse record of reduction of adsorbed Sb—catechol complex. The Sb(III) peak in these conditions was located at −0.58 V. For determination of Sb(III) the method of standard additions was used. It was realized by three additions (20 to 50 mm^3) of 2×10^{-6} to 8×10^{-6} mol dm^{-3} Sb(III) standard solutions. The height of the Sb(III) peak was used for its quantification. The Sb content was found by treatment of concentration dependence by linear regression as intercept on the concentration axis.

For the determination of Sb(III) water samples without pretreatment were used. The content of total antimony was estimated after a preconcentration and a reduction of Sb(V) to Sb(III). After dilution pH of pretreated sample was adjusted to *ca.* 6 by addition of NH_3 solution. The synthetic water spiked with standard solutions of Sb(III) and Sb(V) and natural waters were analyzed.

Reduction with $NH_2NH_2 \cdot H_2SO_4$

The standard 7.6×10^{-6} mol dm^{-3} Sb(V) solution (0.3 to 0.9 cm^3) was mixed with H_2SO_4 solution in 25 cm^3 flask so that final concentration of H_2SO_4 in this solution was 0.5 to 2 mol dm^{-3} After adding of NH_2NH_2 H_2SO_4 (10 to 40 mg cm^{-3}) the mixture was maintained in water bath at 70—80 °C for 10 to 30 min.

Reduction with Na_2SO_3 in Acidic Medium

In preliminary tests of the reduction process, portions (0.3 to 0.9 cm^3) of standard 7.6×10^{-6} mol dm^{-3} Sb(V) solution were introduced into 10 cm^3 flasks. To each flask 5 cm^3 of 1.0 to 1.4 mol dm^{-3} HCl (0.4 to 1 mol dm^{-3} H_2SO_4) and 0.1 g of Na_2SO_3 were added. The mixture was maintained in water bath at 70—80 °C for 20 to 40 min. The excess of sulfur dioxide was removed by nitrogen bubbling (10 min). Then the mixture was cooled to room temperature and diluted to 10 cm^3 For one determination 0.5 to 1 cm^3 of this solution was pipetted.

Reduction with Ascorbic Acid

The standard 3.8×10^{-6} mol dm^{-3} Sb(V) solution (0.02 to 0.6 cm^3) or 2 to 3 cm^3 of treated water sample (filtration, preconcentration by evaporation) was mixed with HCl solution in 25 cm^3 flask so that final concentration of HCl in this solution was 1 mol dm^{-3} After adding of ascorbic acid (2 to 6 mg cm^{-3}) the flask was placed in a boiling water bath for 5 to 20 min. Then the solution was cooled to room temperature, diluted to the volume of 10 cm^3 and pipetted into the polarographic cell for the voltammetric measurement.

To prevent possible adsorption of Sb vessels were washed out with solution of $CaCl_2$ and $MgCl_2$ (w = 0.001) prior to pretreatment procedure. The preconcentration by evaporation was carried out at 70 to 80 °C and continued until the volume was reduced to one tenth or twentieth.

RESULTS AND DISCUSSION

In ASV the peaks Bi(III) and Cu(II) are situated very close to the peak of antimony. It can cause very serious interferences (especially Cu(II)) because the concentration of Sb is very low in natural waters. The difficulties connected with ASV of trace amounts of Sb led to an examination of the possibilities of adsorptive stripping voltammetry (AdSV). Among the ligands forming stable complexes with Sb one of the most promising is catechol. Sb—catechol complexes were studied by DC-polarography and cyclic voltammetry and used for determination of total Sb in sea waters in paper [8].

The optimum experimental conditions (catechol concentration, pH, deposition potential, scan rate, *etc.*) for the determination of Sb at trace levels by AdSV were studied first, and then the effects of some possible interfering elements were examined. The adsorption of catechol complexes of antimony onto the HMDE is controlled by catechol concentration and pH. The peak height increased with catechol concentration up to the Sb/catechol mole ratio 1:8000. Optimum pH values for the formation of Sb(III)—catechol

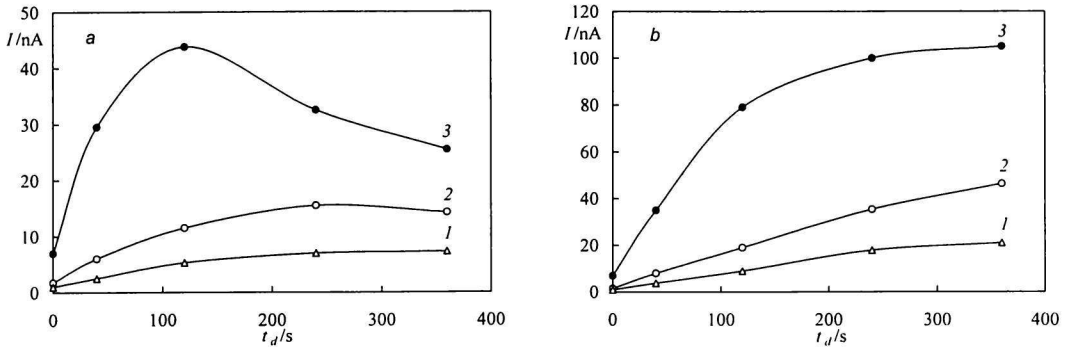

Fig. 1. Effect of the increase of the deposition time on the peak height obtained using FSDPCSV (*a*) and FSDPV (*b*) in enriched solution for Sb(III) concentration: *1.* 2.4 μg dm^{-3}, *2.* 6.1 μg dm^{-3}, *3.* 24.4 μg dm^{-3}

complexes were found to be in the range 5 to 6.5. The decrease of Sb(III) signal at lower and higher pH values is caused by competitive equilibrium with H^+ and OH^- ions, respectively. The slope of the linear E_p *vs.* pH plot between pH 3.7 and 7.1 was found to be 60.2 mV/pH and it confirms participation of protons at the reduction of the accumulated Sb(III)—catechol complexes.

AdSV of Sb(III) can be realized by two techniques: CSV and DPV in enriched solution. In conjunction with chemical parameters, instrumental parameters such as deposition potential, reoxidation potential, duration of the deposition time, and scan rate were also studied. The influence of these parameters on the voltammograms was investigated systematically in order to optimize experimental conditions for determination of Sb(III) by CSV and DPV in enriched solution.

The catechol complex formed is adsorbed on the surface of the HMDE and further reduced during the cathodic polarization. The accumulation of this complex on the electrode surface in the potential range 0 to −0.4 V using CSV showed maximum efficiency at the potential −0.2 V and this deposition potential was considered optimum.

Influence of various deposition and reoxidation potentials on the determination of Sb(III) was investigated in order to determine optimum parameters for DPV in enriched solution. In the first experiment was optimized the deposition potential which was varied in the range −0.6 to −1.3 V whereas each scan was initiated at −0.1 V The most favourable deposition potential for determination of Sb(III) was found to be in the range −0.9 to −1.1 V where the least change in the peak height was observed. In the second experiment the reoxidation potential was varied whereas the deposition potential was kept constant at −1.0 V. The measurements showed that a reoxidation potential of −0.1 V gave the largest peak height.

On the basis of these results, for the determination of Sb(III) by FSDPV in enriched solution the following conditions were applied. The Sb(III) had been previously deposited at the deposition potential of −1.0 V on the HMDE for 120 to 480 s by reduction to Sb(0). Then this amalgamated Sb was during 20 s reoxidized to Sb(III), complexed by catechol and subsequently adsorbed when the potential was set to −0.1 V immediately prior to the cathodic scan. The Sb was stripped by reduction at the potential of −0.58 V

Plots of Sb(III) signals *vs.* deposition time for concentrations 2.4 μg dm^{-3}, 6.1 μg dm^{-3}, and 24.4 μg dm^{-3} were measured using both techniques and are shown in Fig. 1. When short deposition times were applied (up to 120 s or 240 s at $\leq$ 6 μg dm^{-3}) the peak current depended linearly on deposition time. A nonlinear increase of I_p values at longer deposition times is common to all techniques measuring trace element concentrations using adsorptive collection, and is caused by saturation of the surface of the HMDE. The increasing sensitivity for Sb as a function of the deposition time is obviously beneficial for the determination of low antimony concentrations. In Fig. 2 are shown voltammetric peaks of both techniques for vari-

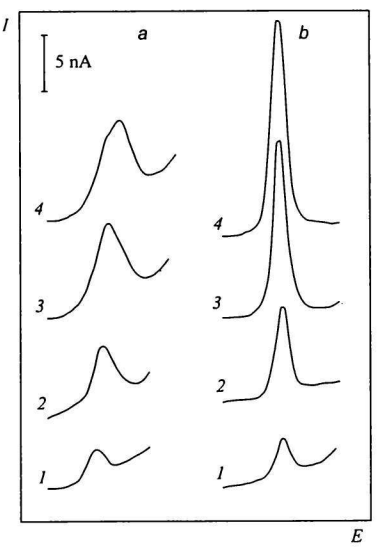

Fig. 2. Voltammograms for 2.4 μg dm^{-3} Sb(III) recorded by FSDPCSV (*a*) and FSDPV (*b*) in enriched solution at various deposition times: *1.* 40 s, *2.* 120 s, *3.* 240 s, *4.* 360 s.

ous deposition times. From the voltammograms it can be concluded that DPV in enriched solution should be preferred when trace amounts of antimony (below 2 μg dm^{-3}) have to be determined. It was therefore applied in all further measurements.

The peak currents and peak potentials were found to depend on the scan rate. The peak height increased four times when the scan rate was increased from 10 to 100 mV s^{-1} The peak potential gradually shifted to more negative values when the polarization rate was increased from 10 to 200 mV s^{-1}, the peak potential being -0.54 V at 10 mV s^{-1}, -0.64 V at 200 mV s^{-1} The polarization rate of 50 mV s^{-1} is most suitable because it enables sufficient sensitivity and Sb(III) peaks are not distorted.

The observed peak current at the scan rate 50 mV s^{-1} increased linearly with amplitude over the range of 12.5 to 50 mV At higher amplitude a departure from linearity occurs. The use of an amplitude of 50 mV enabled sufficient sensitivity and is recommended for the Sb determination.

Under conditions mentioned above linearity of the dependence of the peak height on Sb(III) concentration was tested by standard additions of Sb(III) to synthetic water in the concentration range from 0.4 to 100 μg dm^{-3} The results showed that the current peak increased linearly with the concentration up to 60 μg dm^{-3} at the deposition time of 120 s. Similar test carried out at longer deposition time of 480 s showed that the response was linear up to 8 μg dm^{-3} At enhanced Sb(III) concentration the response became nonlinear as a result of saturation of the electrode surface with adsorbed complex. The linear portion of these plots is characterized with a sensitivity 0.43 nA dm^3 μg^{-1} and 4.2 nA dm^3 μg^{-1} (correlation coefficients 0.9998 and 0.9989), respectively. The detection limits are 0.5 μg dm^{-3} and 0.1 μg dm^{-3} Sb for 120 s and 480 s deposition, respectively.

For the application of the analytical method to natural waters it is necessary to consider the effects of any inorganic or organic interferents that may be found in the sample. Other trace metals can interfere if their catechol complexes adsorb on the HMDE and occupy the available surface area of the drop (*e.g.* Fe(II), Fe(III)) or if these metals (*e.g.* Pb(II), Cd(II)) accumulate at the potential of -1.0 V and produce a reduction peak near that of antimony. The effect of heavy metals on the determination of Sb(III) was studied by applying the method to standard Sb sample containing various amounts of Cd(II), Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Fe(II), and Fe(III). No peaks were obtained with nickel, cobalt, and copper. The potentially serious interference was found from Pb(II) and especially Cd(II) as its peak is situated very close to that of antimony. All metal ions caused depression of the Sb(III) peaks. The influence of inorganic matrix can be suppressed by addition of EDTA as a masking agent to the solution. In our experiments the concentration of about 5×10^{-4} mol dm^{-3} EDTA was used.

Among the organic interferents, humic acids are the most important, especially because of their capacity to give nonelectroactive complexes with several metal ions and a competition between adsorption of organic matter and Sb—catechol complex at the electrode surface. The results of our measurements showed that the Sb(III) signal was practically unaffected by the presence of humic acid up to the concentration of 3 mg dm^{-3} The content of Sb(III) determined in synthetic water sample in the presence of humic acid (3 mg dm^{-3}) agreed well with the actual content if the measurement was realized immediately after preparation. The low recovery of only 50 % of the actual value was obtained after standing overnight. Therefore, these organics should be destroyed by ultraviolet irradiation or heating with mineral acids prior to voltammetric determination of Sb(III).

The precision and the accuracy of this method for Sb(III) determination in water were evaluated by analysis of spiked synthetic water and the results are shown in Table 1. From the results presented it can be concluded that trace amounts of Sb(III) $\geq$ 0.4 μg dm^{-3} can be determined by this method directly.

Table 1. Determination of Sb(III) in Synthetic Water Samples

c(Sb, given)/(μg dm^{-3})		c(Sb(III), found)/(μg dm^{-3})	$s_{\bar{x}}$/%	Recovery/%	Number of measurements
Sb(III)	Sb(V)				
13.9	13.9	12.7 ± 1.0	3.3	91.4	6
9.2		8.2 ± 0.6	3.0	89.2	7
8.3	27.8	8.9 ± 0.6	2.6	107.2	8
5.5		5.8 ± 0.8	4.6	105.4	4
5.5	13.9	5.3 ± 0.4	2.7	95.6	9
5.5	20.8	5.4 ± 0.2	1.3	96.4	6
2.8		2.9 ± 0.2	2.1	104.3	6
1.4	5.6	1.3 ± 0.1	3.4	96.4	10
0.46		0.39 ± 0.04	5.4	84.8	12
0.46	0.46	0.44 ± 0.03	2.4	95.7	6

Since contents of Sb(III) in natural waters are generally extremely low, its determination is not possible in these samples without pretreatment by a suitable preconcentration procedure.

In contradiction with the literature [8] under conditions mentioned above only Sb(III) is the electroactive form of Sb for DPV based on adsorption of the antimony—catechol complex on the HMDE. In our experiments no signal of Sb(V) was found and the oxidation states of Sb in original sample can be distinguished. This was confirmed both by addition of Sb(V) to Sb(III) standard solution which did not increase the peak of Sb(III) and by analysis of synthetic waters spiked with known amounts of Sb(III) and Sb(V) because certified reference materials for Sb(III) and/or Sb(V) were not available. The experimental values agree well with the actual content of Sb(III) (Table 1) and show that this method can be used for differentiating Sb(III) and Sb(V) species.

In order to determine the concentration of total dissolved Sb in a water sample, Sb(V) species must be converted to Sb(III) with chemical reduction prior to the determination. It was therefore necessary to establish the best conditions for transforming Sb(V) to Sb(III). Of the many reduction procedures available for Sb(V), those based on the use of NH_2NH_2 H_2SO_4, SO_2 generated from Na_2SO_3 in acidic medium, and ascorbic acid were chosen. The possibility and reliability of these reduction procedures were tested. The results of reduction with $NH_2NH_2 \cdot H_2SO_4$ under various conditions were unsatisfactory. The Sb(V) gave generally low erratic values.

Sulfur dioxide is an effective reducing agent which is frequently used for reduction pretreatment. The advantage of this reagent is that its excess can be easily removed by passing nitrogen. In our experiments the reduction was realized with Na_2SO_3 in HCl (H_2SO_4) solution. The optimum conditions were chosen on the basis of the study of the Sb(V)—Sb(III) reduction process with SO_2 under various conditions. The effect of different parameters as amount of Na_2SO_3, concentration of mineral acids, reaction time, temperature was investigated with standard samples containing varying amounts of Sb(V) (278 to 780 ng). The results of these experiments indicated that the highest recovery was obtained in 0.05 M-H_2SO_4 (0.1 M-HCl) medium at temperature 70 °C and reaction time 30 min. The elevated temperature speeds up the reduction of Sb(V) and simultaneously the removing of SO_2 from solution by the stream of nitrogen. The determination itself has to be preceded by absolute removing of SO_2 because of its serious interference in voltammetric analysis.

However, some difficulties were encountered in obtaining quantitative reduction under these conditions. Measurements showed recoveries of 40 to 96 %. This led to a systematic study of the conditions. Similar low recoveries were obtained when the experiments were repeated with the addition of KI which was recommended as a powerful catalyst for the reduction reaction by *Lanza* [13]. Reductions with different Sb(V) standards gave recoveries which were dependent on the initial amounts of Sb(V). It was found that Sb(V) standards gave quantitative recoveries when the amount of Sb(V) was above 800 ng. This suggested that probably some Sb remains fixed on the walls of the glass vessel used for this step. The effect of the adsorption was confirmed by comparing the results of numerous experiments made with or without rinsing of vessels with the solution of $CaCl_2$ and $MgCl_2$ (w = 0.001) prior to the reduction process. This precaution produced significant improvements in recovery. Therefore before use each vessel was conditioned by soaking with this solution for several hours. The losses of Sb by adsorption were higher in hydrochloric acid medium.

Ascorbic acid is an effective reducing agent for complete reduction of Sb(V). The reduction of Sb(V) to Sb(III) in acidic solution is fast, only several minutes (5 min) are necessary to complete the reduction at 100 °C [3]. If the reaction is carried out at lower temperature than that of boiling water, the reduction is incomplete even with an excess of reducing agent. The efficiency of the reduction process appeared to decrease at higher pH. *Piccardi* and *Udisti* [3] recommended for reduction of Sb(V) with ascorbic acid the medium of 1 M-HCl. In our experiments the reduction process was reexamined in 1 M-HCl solutions at 100 °C. The effect of the quantity of ascorbic acid and the reaction time on the reduction of Sb(V) (278 ng) is shown in Fig. 3. From the results it follows that the reduction of Sb(V) is finished during 10 to 15 min (53 to 66 % of the original Sb(V) was converted to Sb(III) after 5 min) and concentration 2 mg cm^{-3} of ascorbic acid is sufficient. The lower results at the heating time above 15 min can be due to reoxidation of Sb(III). To ensure an adequate supply of reductant for quantitative production of Sb(III) and to allow for potential competitive reaction with oxidants other than Sb(V), 3 mg cm^{-3} of ascorbic acid was applied. The results of Sb(V) standard samples of various concentration

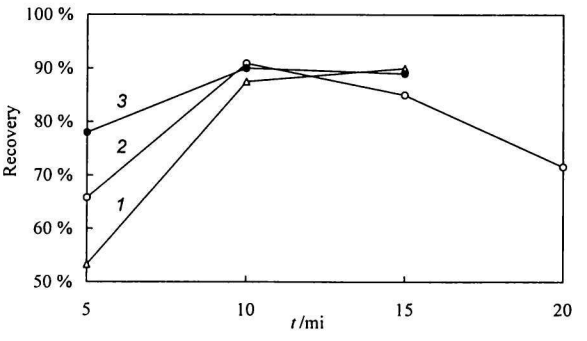

Fig. 3. Influence of reaction conditions on the reduction of Sb(V) with ascorbic acid. Concentrations of ascorbic acid: *1.* 2 mg cm^{-3}, *2.* 4 mg cm^{-3}, *3.* 6 mg cm^{-3}

Table 2. Determination of Sb(V) in Standard Samples after Reduction with Ascorbic Acid

m(Sb(V), given)/ng	m(Sb(V), found)/ng	$s_{\bar{x}}$/%	Recovery/%	Number of measurements
556.3	542.6 ± 24.2	1.3	97.5	6
278.2	253.0 ± 9.2	1.5	90.9	7
139.1	117.6 ± 9.0	3.4	84.5	10
92.7	78.1 ± 14.2	5.7	84.3	6
9.3	8.6 ± 3.5	10.8	80.0	3

Table 3. Determination of Sb(V) in Synthetic Water Samples

c(Sb(V), given)/(μg dm^{-3})	c(Sb(V), found)/(μg dm^{-3})	$s_{\bar{x}}$/%	Recovery/%	Number of measurements
14.8	13.9 ± 0.7	2.2	93.9	8
5.6	5.6 ± 0.6	4.3	100.0	6
4.6	4.5 ± 0.3	3.6	97.8	8
2.3	2.2 ± 0.1	2.3	95.6	10
1.4	1.1 ± 0.2	9.8	78.6	8

Table 4. Determination of Total Sb in Various Water Samples

Sample	c(Sb)/(μg dm^{-3})	$s_{\bar{x}}$/%
Tap water 1	0.4 ± 0.05	15.2
Tap water 2	0.3 ± 0.10	15.1
Tap water 3	0.1 ± 0.02	6.6
Surface water 1	0.4 ± 0.10	9.8
Surface water 2	0.2 ± 0.06	10.3
Surface water 3	0.9 ± 0.16	4.6

summarized in Table 2 confirm that the proposed procedure allows quantification of Sb(V) at the low levels (> 9 ng). The successful recoveries of Sb(V) were obtained and the relative standard deviations were between 1.5 and 0.8 % ($s_{\bar{x}}$ calculated for $\alpha = 0.05$). The lower recoveries ($\approx$ 80 %) at very low concentration can reasonably be ascribed to the adsorption of Sb on the walls of the glass vessels.

Of the reduction procedures tested that based on the use of ascorbic acid seemed to be the most suitable and was applied in all further work for the reduction. To establish the suitability of the procedure for determination of Sb in environmental water samples, the recovery of Sb(V) from synthetic water spiked with various amounts of Sb(V) was investigated. The blank-corrected results are given in Table 3. If concentration of Sb(V) was very low, the pretreatment included also the preconcentration step by evaporation. From our experiments with synthetic waters spiked with known amounts of Sb(V) satisfactory recoveries (> 90 %) were obtained in most cases as shown in Table 3. These results demonstrate the utility of the method for determination of Sb at nanogram level in waters.

The proposed procedure for Sb determination has been applied to analysis of tap and surface waters. The measurement applied directly to the water sample yields the concentration of Sb(III). The corresponding determination after reduction of the sample represents the sum of the concentrations of Sb(III) and Sb(V). The total antimony concentrations found in natural water were below 0.5 μg dm^{-3} This means that the analyte has to be preconcentrated prior to its determination. Of several preconcentration procedures the decrease of sample volume by evaporation was used in the work. The results of determination of Sb in various types of natural waters using the proposed procedures are presented in Table 4. From the presented data it follows that the precision of determination at this low concentration level is good. The relative standard deviations of total Sb obtained from three to six determinations of each sample are in the range 4.6 to 15.2 %. An initial study of each of the samples showed that Sb(III) concentrations were below the detection limit in analyzed water samples.

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