Notes

# Determination of Antimony in Water by Electrothermal Atomic Absorption Spectrometry after Preconcentration on a Membrane Filter with a Finely Pulverized Anion-Exchange Resin

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It has become very important to determine heavy metals at low concentrations in environmental samples, especially antimony in natural water owing to its toxicity. There have been several reports on the determination of antimony by anodic stripping voltammetry[1], inductively coupled plasma atomic emission spectrometry[2,3], graphite-furnace atomic absorption spectrometry[4,5], and neutron activation analysis.[6,7] In these methods, hydride generation is mainly used for separation and pre-concentration. Other methods for the preconcentration of antimony are coprecipitation[7] and solvent extraction.[8]

In our previous studies, gallium(III) which formed a complex anion with 1,2-dihydroxybenzene-3,5-disul-fonic acid (Tiron) and was adsorbed on uniform anion-exchange beads, was determined by electrothermal atomic absorption spectrometry (ETAAS).[9] On the other hand, Ohzeki *et al.*[10] proposed a preconcentration technique based on the adsorption of trace amounts of copper as complexes with various chelating agents using finely pulverized anion- and cation-exchange resins of the macroreticular type. This preconcentra-tion technique was applied to the determination of gal-lium(III) with pyrocatechol sulfonphthalein (PV, Pyrocatechol Violet ) by ETAAS[11] and Fe(II) with 2-(5-nitroso-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropyl-amino)phenol (Nitroso-PAPS) by photoacoustic spec-trometry in mine-drainage and river-water samples.[12] Thus a sensitive method based on preconcentration on a membrane filter with a finely pulverized anion-exchange resin has been developed for the determina-tion of total antimony in river-water and snow-fall sam-ples by ETAAS. We found that antimony(III) and anti-mony(V) react with 5′,5″-dibromopyrogallolsulfon-phthalein (BPR, Bromopyrogallol Red) to form a water-soluble chelate anion, which is adsorbed on the resin at pH 2.0.

## Experimental

### Apparatus

The samples were analyzed on a Hitachi Model 180-80 polarized Zeeman-effect-type ETAAS equipped with a hollow-cathode lamp of antimony and a cup-type cuvette in a graphite furnace. Argon gas was used as a sheath gas. The instrumental operating conditions are summarized in Table 1. The pH of sample solutions was adjusted by a Horiba (Model M-13) pH meter. To collect finely pulverized anion-exchange resin with the antimony complex, a filter holder (Advantec Toyo KG-13) with membrane filter paper (Advantec Toyo, cellu-lose acetate type, 13 mm in diameter, pore size 0.8 μm) was used.

### Reagents

All of the reagents were of analytical grade, and dilu-tions were made with high-purity water (Millipore, Milli-QII). The antimony(III) and antimony(V) stan-dard solutions (1000 μg ml$^{-1}$) were prepared by dissolv-ing bis[(+)-tartrato]diantimonate(III) dipotassium trihy-drate (Wako) and potassium hexahydroxoantimonate (Wako) in water, respectively. The antimony(III) solu-tion was standardized based on oxidation–titration using a potassium bromate solution, and the antimony(V)

Table 1  Instrumental operating conditions

| Lamp current | 10.0 mA | | |
|---|---|---|---|
| Wavelength | 217.6 nm | | |
| Slit width | 0.4 nm | | |
| Furnace programmer settings | | | |
| | Drying | Ashing | Atomizing | Cleaning |
| Temp./°C | 110 | 860 | 2350 | 2800 |
| Time/s | 30 | 30 | 7 | 3 |
| Sheath gas/ml min$^{-1}$ | 150 | 150 | 0 | 150 |

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solution was standardized by comparing with the antimony(III) standard solution by atomic absorption spectrometry. A BPR solution (DOJINDO, $1.0\times10^{-3}$ M) was prepared by dissolving BPR in 30 v/v% ethanol. Both PV and Tiron solutions (DOJINDO) were used as a $1.0\times10^{-3}$ M aqueous solution.

A finely pulverized anion-exchange resin suspension (ARS) was prepared by following a method described in a previous paper.[11] As an anion-exchange resin, DIAION PA 316 (Mitsubishi Chemical Industry) was used and its ion-exchange capacity was 5.0 μequiv ml$^{-1}$.

*Procedure*

A 20 – 500 ml portion of a sample solution containing 0.02 – 0.20 μg of antimony was placed in a beaker; then, 1.0 ml of a $1.0\times10^{-3}$ M BPR solution, 2 ml of a buffer solution (pH 2.0) and 2 ml of a $1.0\times10^{-2}$ M EDTA solution were added successively. The pH of the solution was adjusted to 1.8 – 2.2 with 1 M hydrochloric acid. Then, 2.0 ml of ARS was added, and the mixture was stirred several times with a glass rod. The resin suspension was filtered under suction through a membrane filter and washed three times with 2 – 3 ml of a diluted buffer solution. A thin circular resin, which was retained on the membrane filter, was dried under silica gel in a desiccator for 15 min and fixed by sticking directly with a cellophaned tape (Nichiban) and divided into several 3 mm diameter disks by punching. Each disk was inserted into a cup-type cuvette for the determination of antimony by ETAAS. The absorbance was obtained as the mean of three measurements under the optimum conditions.

## Results and Discussion

*Effect of the pH and choice of chelating agents*

To find the optimum pH range for the adsorption of antimony complexes on the anion-exchange resin, the recoveries of antimony(III) and antimony(V) were examined. BPR, PV and Tiron were used as chelating agents. Figure 1 shows the relationship between the pH in the aqueous solution and the recovery of antimony. Antimony(III) was quantitatively adsorbed on the resin in the pH range 1.8 – 8.0, 2.0 – 6.0 and 6.0 – 8.0 with BPR, Tiron and PV, respectively. On the other hand, antimony(V) was completely adsorbed with BPR alone in the pH range 1.8 – 2.2. Therefore, it was found that the sum of antimony(III) and antimony(V) is determined with BPR at pH 2.0, and that the use of PV in the pH range 7.0 – 8.0 enables one to determine only antimony(III).

*Amounts of BPR solution and ARS*

The effects of the amounts of BPR solution and ARS on the absorbance for antimony were investigated. For 0.20 μg of antimony, the maximum and constant absorbance were obtained over the range 0.01 – 2.0 ml
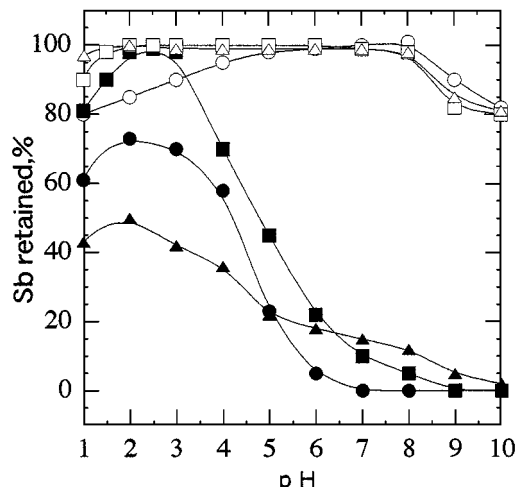


Fig. 1   Effect of the pH on the amount of antimony (0.20 μg) retained with 1.0 ml of $1.0\times10^{-3}$ M chelating agents (□ Sb(III)-BPR, ■ Sb(V)-BPR, ○ Sb(III)-PV, ● Sb(V)-PV, △ Sb(III)-Tiron, ▲ Sb(V)-Tiron) and 2.0 ml of 5.0 μequiv ml$^{-1}$ ARS in 20 ml of the sample volume.

of a $1.0\times10^{-3}$ M BPR solution for antimony(III) and 0.5 – 2.0 ml for antimony(V), respectively and 1.5 – 6.0 ml of 5.0 μequiv m$^{-1}$ ARS for both antimony(III) and antimony(V). Therefore, 1.0 ml of a $1.0\times10^{-3}$ M BPR solution and 2.0 ml of 5.0 μequiv ml$^{-1}$ ARS were used in subsequent studies.

*Calibration curve and detection limit*

A linear relationship through the point of origin between the absorbance and the concentration was obtained over the range 0.02 – 0.20 μg in 20 ml of antimony(III) or antimony(V) standard solution. The reproducibility of the proposed method for the absorbance obtained from five repeated determinations was 5.0% RSD for 0.1 μg of antimony(III) or antimony(V). The detection limit, defined as three-times the standard deviation of the reagent blank, was 4.9 ng of antimony(III) or antimony(V) in 500 ml (9.8 ng Sb l$^{-1}$) of water sample.

*Effect of the sample volume*

The enrichment of a 0.1 μg portion of antimony as the BPR complex from various sample volumes was examined following the above-described procedure. A constant absorbance for 0.1 μg of antimony was obtained at initial sample volumes of 20, 100, 200, 300, 400 and 500 ml. The reproducibilities for the signal intensity from five determinations were 7.0% RSD and 12.0% RSD in 200 ml and 500 ml, respectively.

*Effect of foreign ions*

The effects of commonly occurring foreign ions on the determination of 0.1 μg of antimony(III) or antimony(V) at pH 2.0 in 20 ml of sample solution were investigated. In this study, the tolerance limit was set as the amount which caused an error of ±5% in the

Table 2   Analysis of water samples

| Sample[a] | Sb/μg | | Recovery of Sb, % |
|---|---|---|---|
| | Added | Found | |
| River-water A | none | 0.069 | — |
| pH   4.7 | 0.020 | 0.085 | 96 |
| EC[b]   240 | 0.040 | 0.110 | 101 |
| | 0.060 | 0.126 | 98 |
| River-water B | none | 0.042 | — |
| pH   6.5 | 0.020 | 0.060 | 97 |
| EC   180 | 0.040 | 0.078 | 95 |
| | 0.060 | 0.115 | 96 |
| Snowfall A | none | 0.045 | — |
| pH   4.9 | 0.020 | 0.065 | 100 |
| EC   41 | 0.040 | 0.092 | 97 |
| | 0.060 | 0.119 | 95 |
| Snowfall B | none | 0.038 | — |
| pH   5.4 | 0.020 | 0.057 | 98 |
| EC   48 | 0.040 | 0.077 | 99 |
| | 0.060 | 0.093 | 95 |

The recoveries obtained are the average of three replicate determinations. a. Sample volume: river-water A, 50 ml; river-water B, 100 ml; snow-fall, 200 ml.
b. EC: electric conductivity ($\mu S\ cm^{-1}$).

recovery of antimony(III) or antimony(V). The concentrations of Na(I), K(I), Li(I), Ca(II), Mg(II), Sr(II), Ba(II), $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $F^-$, $Br^-$, $I^-$, $PO_4^{3-}$, $BO_3^{3-}$ and $CO_3^{2-}$ below 1000 μg, and those of Zn(II), Cd(II), Mn(II), Ni(II), Pd(II), Co(II), Sn(II), Pb(II), Nb(II), Al(III), Ga(III), In(III), Cr(III), As(III), As(V), Si(IV), Zr(IV), V(V) and Nb(V) below 100 μg did not interfere. The tolerable amounts of Fe(II), Fe(III), Ti(IV), Cr(VI), Mo(VI) and W(VI) were 5 μg, respectively. However, those of Fe(II), Fe(III), Ti(IV) and Cr(VI) were increased to 10 μg by adding 2 ml of $1.0 \times 10^{-2}$ M EDTA solution. These results suggest that the pro-

posed method should be suitable for the determination of antimony in river-water samples.

*Determination of the total antimony in water samples*

To evaluate the usefulness of the proposed method, it was applied to an analysis of the total antimony from river-water and snow-fall samples. The samples were filtered through a membrane filter as soon as possible after sampling, and acidified with hydrochloric acid to pH 2 for storage. The results are given as total antimony in Table 2.

The proposed method can be successfully applied to the determination of 0.1 μg l$^{-1}$ levels of antimony in river-water and snow-fall samples.

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