Preconcentration Method of Antimony Using Modified Thiol Cotton Fiber for Isotopic Analyses of Antimony in Natural Samples

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It is very important to investigate antimony geochemical behavior in order to identify its source, or reveal contamination processes, since antimony and its compounds are considered to be pollutants of high priority by the Environmental Protection Agency of the United States (USEPA). However, the concentration of antimony in most geological samples is very low, and its stable isotope mass difference is only 1.6%. An antimony preconcentration method for isotope analysis using modified Thiol Cotton Fiber has been developed. Using this new method, the recovery of antimony was $99.5 \pm 3.6\%$ ($n = 3$) and blank values were <0.1 ng. The standard error of the $\epsilon^{123}\text{Sb}$ isotope ratios in the proposed method is only 0.4‰, much smaller than those of the previous method. The proposed method is therefore effective in the preconcentration and separation of antimony for antimony isotope analysis.

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Introduction

Antimony is a naturally occurring element with more than 1.0×10^5 tons used annually in a variety of industrial applications, such as flame retardants, catalyst in plastics, pigment in paints, and additives in glassware, ceramics, ammunition, and battery.¹⁻³ Since antimony compounds were considered to be pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA), the concentration of antimony is regulated at less than $10 \mu\text{g L}^{-1}$ under the USEPA criteria.⁴ From a geochemical standpoint, typical concentrations of dissolved antimony in unpolluted water are less than $1 \mu\text{g L}^{-1}$.⁵ The average antimony concentrations in fresh water and seawater are 1.1 and $0.18 \mu\text{g L}^{-1}$, respectively.^{5,6} Due to its lower abundance and the relative insolubility of most of its compounds, environmental concern for antimony has sometimes been overlooked.⁷ Therefore, little information is available on its geochemical behavior or dynamics in the environment, which has been a scientific basis of recent studies on the environmental geochemistry of Sb.⁸⁻¹⁰ Accordingly, it is very important to investigate antimony geochemical behavior in order to identify its source and to reveal its contamination mechanisms. For this purpose, antimony isotope variations in natural systems can be useful geochemical tracers by considering the different antimony isotopes among deep-sea sediments, hydrothermal sulfides, environmental samples, seawater, basalt and silicate rocks.¹¹ Hence, it is possible that the antimony isotope can be used to identify the ultimate arsenic source in the hydrosphere. To apply such an isotopic method of source analysis of Sb, it is

very desirable to develop a preconcentration method for natural samples that contains trace amounts of antimony. Before any antimony stable isotope analysis, there are some problems that need to be overcome, as follows: (1) concentrations of Sb in most geological samples and seawater are low at less than 100 ng g^{-1} and 300 ng L^{-1} , respectively;¹¹ (2) considering their small mass difference of only 1.6% between two Sb stable isotopes (121 and 123), the preconcentration and separation of antimony from other elements are essential to determine precisely the isotope ratio using a multiple collector, ICP-MS (MC-ICP-MS); (3) in particular, the separation of antimony from tellurium is important, since Te has isobaric Te-123 on Sb-123, which cannot be separated using a mass spectrometer; (4) because antimony, especially the trivalent species, is very volatile,¹² antimony can be lost during evaporation in digestion and preconcentration processes; (5) high recovery is desirable to prevent isotopic fractionation through the preconcentration procedure.

Preconcentration and chemical separation methods for antimony commonly reported include chelating, coprecipitation and ion exchange.¹³⁻¹⁶ Thiol cotton fiber (TCF) is also used for the preconcentration and chemical separation of antimony.^{13,17} However, the results from the preconcentration and chemical separation for antimony using TCF varied among those studies. Therefore, we have developed an external correction method using tin isotopes.¹⁸ The measurement precision was 0.4‰, which is enough to distinguish antimony isotopes of sulfide ores, possible sources of antimony from usual terrestrial materials.¹¹ This method is effective in determining antimony isotope ratios in terms of a low standard deviation. Hence, the antimony and tin in samples should be separated completely. However, antimony separation from a combined antimony and tin solution has not been tested, and blank values have not been mentioned in the previous papers.^{11,13,17} Thus, the purpose of

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Fig. 1 Flow diagram of the proposed method for antimony preconcentration.

this study is to develop a preconcentration and separation method of antimony with high recovery for antimony isotope analyses using powdered Thiol Cotton Fiber (TCF).

Experimental

Reagents

A standard solution of 1000 mg L⁻¹ Sb(V) was prepared by adding an appropriate amount of K[Sb(OH)₆] (Wako Pure Chemical Industries, Ltd.) into 100 mL of ultrapure water (18.2 MΩ), and the solution was ultrasonicated for *ca.* 2 h in order to dissolve the standard reagent completely. A commercially available standard (Wako Pure Chemical Industries, Ltd.) was used for a Sn standard solution. A standard solution of 1000 mg L⁻¹ Te(VI) was prepared by adding an appropriate amount of Na₂H₄TeO₆ (Wako Pure Chemical Industries, Ltd.) into 100 mL of ultra pure water. Before use, the solutions were successively diluted in each experiment. All chemicals used in this study were ultrapure analytical reagents (Tama Chemicals Co., Ltd.) unless otherwise stated. A mixed reducing agent (10 w/v% potassium iodide and 10 w/v% ascorbic acid) for Sb(V) was prepared by dissolving an appropriate amount of >99.998% potassium iodide (Sigma-Aldrich Co.) and ascorbic acid (Kanto Chemicals Co., Inc.) into ultrapure water every time before use.

Preparation of TCF

Mercaptoacetic acid (100 mL) (Wako Pure Chemical Industries, Ltd.), 60 mL of acetic anhydride (Wako Pure Chemical Industries, Ltd.), 40 mL of acetic acid (36%) and 0.3 mL of sulfuric acid (18 mol L⁻¹) (Tama Chemicals Co., Ltd.) were mixed successively in a wide-mouth bottle, and the mixture was cooled to room temperature. Thereafter, 30 g of medical absorbent cotton (H153; PIP-FUJIMOTO Co., Ltd.) was thoroughly impregnated in the solution. After the top of the bottle was closed tightly, the bottle was kept at 40°C in an oven for 4 d. Thereafter, the TCF was washed fully with ultrapure water and then dried at 30°C.¹³ The TCF was stored at *ca.* 20°C in a sealed container protected from light. Before use, the TCF

Table 1 Chemical composition of reducer for antimony

Condition	HCl/ M	Ascorbic acid, w/v%	KI, w/v%	NH ₂ OH-HCl, w/v%	Rec., %
A	0.5	0.5	—	—	8.8
B	0.5	0.5	0.5	—	>95
C	0.5	0.5	—	0.5	13

was pulverized using a food processor with ceramic blades to minimize any variation of recovery during preconcentration using TCF. Thereafter, the TCF was rinsed by ultrapure water in a centrifugation tube and centrifuged (3000 rpm) several times for 5 min to remove suspended fractions.

Preconcentration and chemical separation procedure

The optimized procedure is shown in Fig. 1. After TCF (*ca.* 1.3 mL) was packed in a mini column (3.5 cm h, 7 mm i.d.; disposable 2 mL polystyrene columns, Thermo Fisher Scientific K.K.), the TCF was conditioned by introducing sequentially 25 mL of ultrapure water and 25 mL of 0.5 M HCl. Antimony in sample solutions adjusted to 0.5 M HCl was reduced to Sb(III) by adding a 10 w/v% KI-ascorbic acid mixed solution to make 0.5 w/v% of the final concentration for 3 h. Subsequently, the sample was passed through a column packed with TCF at *ca.* 100 mL h⁻¹. After the column was rinsed with 5 mL of 0.5 mol L⁻¹ HCl and 6 mL of 2.5 mol L⁻¹ HCl successively, the Sb fraction was collected by passing 5 mL of 6 mol L⁻¹ HCl through the column. The H₂O₂ (with final concentration of 3.5 w/v%) was added to an aliquot of the Sb fraction and evaporated to dryness at 95°C. The concentration of antimony was determined using an ICP-MS (7500; Agilent Technologies), and the Sb isotope was analyzed by a multicollector ICP-MS (Neptune; Thermo Fisher Scientific K.K.) coupled with an external correction method using Sn isotopes.¹⁸

Results and Discussion

Reducing conditions

Antimony(V) is the predominant species present in aerobic conditions while Sb(III) species increase to 93% only in the sample under the anoxic condition.⁵ Since TCF can retain Sb(III) selectively, but not so for Sb(V),^{13,17} reducing reagents for converting Sb(V) to Sb(III), such as (A) ascorbic acid solution, (B) KI-ascorbic acid mixed solution and (C) hydroxylamine hydrochloride-ascorbic acid mixed solution were tested. These reagents, adjusted to a 0.5 w/v% final concentration, were added to 100 mL of 0.45 µm filtered reservoir water (in Hiroshima University, Japan) samples (0.5 mol L⁻¹ HCl solution) spiked with 0.1 µg of Sb(V) and 0.1 µg of Sn(II). The recoveries of antimony were 8.8, 13 and >95% for the ascorbic acid solution, the hydroxylamine hydrochloride-ascorbic acid mixed solution and the KI-ascorbic acid mixed solution, respectively (Table 1). When only the KI-ascorbic acid mixed solution (0.5 w/v% final concentration) was used for antimony reduction, high recovery was achieved. However, KI reagent contains Sb and Sn as impurities. A blank test was conducted followed by this proposed method using a KI reagent produced by three companies in order to lower the blank from the reagents. The blank was lowest when using KI reagent (>99.998%) purchased from Sigma-Aldrich Co., which was subsequently used for following experiments.

The time required for reducing Sb was also investigated in the

Fig. 2 Change in the ratio of Sb(III) and (V) over time for reducing.

range of 0 to 4 h by KI and an ascorbic acid mixed solution (0.5 w/v% final concentration) as a reducing solution. The change of the Sb(III) and Sb(V) ratio over time was measured using LC-ICP-MS;¹⁹ 98% of Sb(V) was reduced in 3 h and the ratio was constant (Fig. 2). Thus, the time for the reduction was set to 3 h.

Separation conditions

The concentration of HCl for the separation of Sn from the Sb fraction was investigated in the range of 2.5 to 6 mol L⁻¹ HCl. Tin was eluted completely by a 2.5 mol L⁻¹ or more concentrated HCl solution. On the other hand, Sb did not elute by the HCl solution at a concentration less than 3 mol L⁻¹, and Sb was collected perfectly by introducing 6 mol L⁻¹ of HCl. Thus, Sb can be separated from Sn completely by introducing 2.5 mol L⁻¹ HCl.

The volume of the HCl solution introduced was also optimized to collect Sb. Antimony (0.1 µg) was introduced to a column packed with 1.3 mL of TCF, followed by the procedure shown in Fig. 1. When more than 4 mL of 6 mol L⁻¹ HCl was introduced into the column, Sb was collected completely (Fig. 2). The optimum volume of HCl solution was fixed at 5 mL to ensure complete recovery of Sb. On the other hand, the recovery of Sb upon introducing 10 µg of Sb sample loading was around 82%. Thus, 1.3 mL of TCF was used in the mini column, and the Sb retaining capacity of TCF was 6 µg mL⁻¹-TCF. Consequently, 5 mL of 0.5 mol L⁻¹ HCl and 6 mL of 2.5 mol L⁻¹ HCl were introduced successively to separate the reducing reagent and Sn before Sb collection; thereafter, the Sb fraction was collected by introducing 5 mL of 6 mol L⁻¹ HCl.

Tellurium contamination in the Sb fraction was investigated because tellurium has a 123 stable isotope, which is isobaric to ¹²³Sb. After about 0.1 µg of Te was loaded, the present method was performed as shown above. As a result, the concentration of Te in the Sb fraction was below the detection limit. Therefore, Te was also separated completely from Sb, and the effect of Te on Sb analysis was insignificant.

A blank test was also conducted following the same procedure. The blank value was less than 0.1 ng for Sb and less than 0.7 ng for Sn. These values are also negligible for the analysis of Sb in natural samples.

Evaporation conditions

After the elution of Sb using a 6 mol L⁻¹ HCl solution, the solution was converted into 2% HNO₃ prior to isotope analysis, since a HCl solution forms molecular ions of MCl (M: metal ion) in MC-ICP-MS analyses. Hence, the evaporation condition

Table 2 Recovery percentages of antimony under the various oxidizer condition

Condition	H ₂ O ₂ , %	HNO ₃ , %	HClO ₄ , %	Evaporation temp/°C	Recovery, %
A	3.5	—	—	95	97
B	17.5	—	—	95	99
C	3.5	6.8	—	95	89
D	3.5	—	23	120	50

Fig. 3 Recovery of antimony under various evaporation temperatures.

without Sb loss due to volatilization was validated. Antimony, especially the trivalent species, is very volatile,¹² and can be lost during digestion and evaporation processes. An oxidizer to prevent Sb from volatilization was tested using a 6 mol L⁻¹ HCl solution spiked with 0.1 µg of Sb, which was the same concentration of Sb in the Sb fraction after passing through TCF column. The oxidizer compositions tested in this study and antimony recovery are given in Table 2. The evaporation temperature under condition D was 120°C, since HClO₄ has a high boiling temperature of 203°C. The others were set at 95°C. When H₂O₂ was used as an oxidizer (= conditions A and B), a high recovery of Sb was achieved. HClO₄ was not suitable as an oxidizer in this case, because its boiling point was very high, thus causing the loss of Sb. The concentration of H₂O₂ was set at 3.5 w/v% as a final concentration because severe forming was observed at 17.5 w/v% and therefore, not prone to evaporation.

The absolute amount of Sb added into the column was tested within the range of 0.01 – 50 µg. Antimony was recovered well up to 15 µg, but its recovery decreased at more than 15 µg. Thus, the maximum amount of Sb under the evaporation process should be set at 15 µg. However, when the duration required for evaporation exceeded 6 h, its recovery decreased slightly. To prevent Sb loss, a large Teflon vessel should be used for the evaporation to have a larger contact area on the hot plate, by which we can shorten the duration required for evaporation.

The evaporation temperature was studied using a 6 mol L⁻¹ HCl solution spiked with 0.1 µg of Sb within the range of 60 – 120°C (Fig. 3). The recovery was optimum at 95°C, and decreased at lower or higher temperatures due to a longer evaporation time and volatilization during evaporation, respectively. Hence, the 95°C was selected for the evaporation process.

Table 3 Recovery of antimony

	Introduced/ μg	Detected/ μg	Recovery, %
RUN1	0.109	0.107	97.6
RUN2	0.110	0.107	97.1
RUN3	0.110	0.114	104.0
A.V.			99.5
SD			3.6
RSD, %			3.7

Fig. 4 ϵ values of Sb obtained using previous method and the proposed method developed in this study. Error bars are standard error.

Analytical performances

The recovery test was conducted with the results summarized in Table 3, showing that the recoveries of Sb from ultrapure water spiked with $0.1 \mu\text{g}$ Sb was more than 97%. The natural water samples collected from Ichinokawa river (Sb concentration, $113 \mu\text{g L}^{-1}$; loading, 3 mL), which is affected by significant antimony loads from the Ichinokawa abandoned mines, known to have one of the highest stibnite outputs in the world, located on Shikoku Island, southwestern Japan. Water samples from downstream of Kamo river (Sb concentration, $1.5 \mu\text{g L}^{-1}$; loading, 100 mL), which is also affected by antimony load from Ichinokawa river joining, were also tested. In both cases their recoveries were more than 95%. Antimony in water samples was collected effectively using the proposed method in the present study.

Antimony isotope analysis was conducted following previous reports,^{11,13,17} and the proposed method developed in this study (Fig. 4). The antimony isotope analysis was conducted at Kochi Institute for Core Sample Research using MC-ICP-MS (Thermo Finnigan Neptune). Since, the previous method cannot separate Sn from Sb completely, about 1–5 ng of Sn was contaminated in the Sb fraction. Therefore, an external correction method using Sn cannot be applied, and therefore the Bracketing method was performed instead of the external correction method in order to correct the mass distinction effect.²⁰ Consequently, the standard error of $\epsilon^{123}\text{Sb}$ isotope ratios show high values (1.7–2.7 ϵ). On the other hand, since the proposed method developed in this study can separate Sn from Sb completely, and the external correction method can be applied to Sb isotope analysis, the standard error of the $\epsilon^{123}\text{Sb}$ isotope ratios in the proposed method is only 0.4 ϵ , much smaller than those of the previous method. The proposed method is therefore effective in the preconcentration and separation of antimony for antimony

isotope analysis.

Conclusions

The proposed method is effective in the preconcentration and separation of antimony for isotope analysis in terms of its high recovery, and showing a small standard error coupled with the Sn external correction method.

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References

1. M. Filella and P. M. May, *Geochim. Cosmochim. Acta*, **2003**, 67, 4013.
2. K. A. Herbst, G. Rose, K. Hanusch, H. Schumann, and H. U. Wolf, "Antimony and Antimony Compounds", ed. K. Hunger, P. Mischke, and W. Rieper, **1985**, Wiley-VCH, Weinheim, 55.
3. X. Guo, Z. Wu, and M. He, *Water Res.*, **2009**, 43, 4327.
4. USEPA, "Antimony: an Environmental and Health Effects Assessment", **1984**, US Environmental Protection Agency, Office of Drinking Water, Washington, D.C.
5. M. Filella, N. Belzile, and Y. W. Chen, *Earth Sci. Rev.*, **2002**, 57, 125.
6. D. P. Kharkar, K. K. Turekian, and K. K. Bertine, *Geochim. Cosmochim. Acta*, **1968**, 32, 285.
7. M. Filella, N. Belzile, and Y. W. Chen, *Earth Sci. Rev.*, **2002**, 59, 265.
8. A. C. Scheinost, A. Rossberg, D. Vantelon, I. Xifra, R. Kretzschmar, A.-K. Leuz, H. Funke, and C. A. Johnson, *Geochim. Cosmochim. Acta*, **2006**, 70, 3299.
9. S. Mitsunobu, T. Harada, and Y. Takahashi, *Environ. Sci. Technol.*, **2006**, 40, 7270.
10. S. Mitsunobu, Y. Takahashi, and Y. Terada, *Environ. Sci. Technol.*, **2010**, 44, 1281.
11. O. Rouxel, J. Ludden, and Y. Fouquet, *Chem. Geol.*, **2003**, 200, 25.
12. J. Klein, S. Dorge, G. Trouvé, D. Venditti, and S. Durécu, *J. Hazard. Mater.*, **2009**, 166, 585.
13. M. Yu, G. Liu, and Q. Jin, *Talanta*, **1983**, 30, 265.
14. A. Erdem and A. E. Eroğlu, *Talanta*, **2005**, 68, 86.
15. Y. C. Sun and J. Y. Yang, *Anal. Chim. Acta*, **1999**, 395, 293.
16. K. W. W. Sims and E. S. Gladney, *Anal. Chim. Acta*, **1991**, 251, 297.
17. M. Yu, D. Sun, W. Tian, G. Wang, W. Shen, and N. Xu, *Anal. Chim. Acta*, **2002**, 456, 147.
18. M. Tanimizu, Y. Araki, S. Asaoka, and Y. Takahashi, *Geochem. J.*, in press.
19. S. Mitsunobu, T. Takahashi, and Y. Sakai, *Chemosphere*, **2008**, 70, 942.
20. A. Cocherie and M. Robert, *Chem. Geol.*, **2007**, 243, 90.