Visual Colorimetry for Trace Antimony(V) by Ion-Pair Solid-Phase Extraction with Bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) on a PTFE Type Membrane Filter

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A new visual colorimetry for trace antimony(V) based on ion-pair solid-phase extraction to a PTFE-type membrane filter with bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) ion ($[\text{Co}(\text{5-Cl-PADAP})_2]^+$) has been developed. Experiments showed that hexachloroantimonate(V) ion (SbCl_6^-) was adsorbed with $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ to the front surface of the PTFE filter. The adsorption of antimony(V) ion was promoted by the addition of lithium chloride as a source of chloride ion. The excess reagent of $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ was eluted by rinsing with a 10 wt% methanol aqueous solution. In this case, the slow rate of the hydrolysis reaction of SbCl_6^- and the difference of the hydrophobicity of the ion pairs were important for adsorption and separation with a PTFE-type membrane filter. The antimony(V) concentration was determined through a visual comparison with a standard series. The visual detection limit was 0.10 μg . The calibration curve assessed with the reflection spectrometric responses at 580 nm was linear in the concentration range of 0.10 – 1.2 μg ($r = 0.996$). The proposed method has been applied to the determination of sub-microgram levels of antimony(V) ion in water samples.

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Introduction

The development of simple analytical methods with high sensitivity and selectivity is an urgent necessity in various analytical fields. Especially, the daily monitoring of antimony in natural water, drinking water, and wastewater is needed because of concern over its toxicity.¹⁻³ The WHO guideline value of the antimony concentration for drinking-water quality is 0.02 mg l^{-1} . Antimony has been specified as a precautionary monitoring target in Japan. Antimony determination techniques, including anodic stripping voltammetry,^{4,5} inductively coupled plasma atomic emission spectrometry,⁶ atomic absorption spectrometry,^{5,7} neutron activation analysis,⁸ and flow-injection analysis,⁹ have been developed. Our previous studies have demonstrated the determination of trace antimony by electrothermal atomic absorption spectrometry after preconcentration on a membrane filter.^{10,11} However, a determination method that is simple, relatively inexpensive, utilizes little or no electrical energy, and applicable to field work is still lacking. Although solvent-extraction spectrometry has also been long used,¹²⁻¹⁵ these methods are unsuitable for processing many samples in short time.

This study is intended to develop a non-instrumental analytical method for the detection of trace antimony with high sensitivity and selectivity. Over the past decades, great effort has been expended towards the development of solid-phase

extraction systems using membrane filters, which are very useful media for the preconcentrations of various analytical tools.^{10,11,16-26} Visual methods based on comparing the coloration on a membrane filter were also developed for the determination of trace phosphate ion,^{27,28} human serum albumin,^{29,30} urinary protein,³¹ or formaldehyde.³² Herein, we describe a new solid-phase visual colorimetry of trace antimony(V) based on ion-pair solid-phase extraction to a PTFE-type membrane filter with bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) ion ($[\text{Co}(\text{5-Cl-PADAP})_2]^+$). The cobalt(III) complex, $[\text{Co}(\text{5-Cl-PADAP})_2]^+$, which is stable even in 3 mol dm^{-3} of hydrochloric acid and is too inert to be replaced by other metal ions or ligands, has been used as a counter ion in the extraction and spectrometric determination of anions.³³⁻³⁵ Furthermore, the extraction behavior of ion pairs with $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ to membrane filters was studied in detail by Taguchi *et al.*³⁶ It is well-known that hexachloroantimonate(V) ion (SbCl_6^-), which is formed in a hydrochloric acid medium, can be extracted to various organic solvents with cationic dyes.¹²⁻¹⁵ In the flow-injection analysis reported by Watanabe *et al.*,⁹ SbCl_6^- was adsorbed on a PTFE tube inner surface as an ion pair with $[\text{Co}(\text{5-Cl-PADAP})_2]^+$, and the excess reagent of $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ was removed by rinsing with a methanol-aqueous solution. In the current study, we found that SbCl_6^- was extracted to a PTFE membrane filter with $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ when lithium chloride was used as a source of chloride ion. Furthermore, the ion pair was retained and separated perfectly from excess reagent of $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ by rinsing with a 10 wt% methanol aqueous solution. Antimony(V) was determined visually by comparing the color intensity. The visual detection limit was 0.10 μg . The proposed

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method was applied to water samples.

Experimental

Materials

A standard solution of antimony(V) ion ($0.001 \text{ mol dm}^{-3}$) was prepared by dissolving potassium hexahydroxoantimonate(V) (Merck KGaA, Darmstadt, Germany) in deionized water. Bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]-cobalt(III) chloride (Dojindo Laboratories, Kumamoto, Japan) was dissolved in water to prepare a $1 \times 10^{-4} \text{ mol dm}^{-3}$ solution. All other reagents used were of analytical grade. Membrane filters (25 mm diameter) made of PTFE (pore size $0.50 \mu\text{m}$), cellulose acetate (pore size $0.45 \mu\text{m}$), and mixed cellulose ester (pore size $0.45 \mu\text{m}$) were purchased from Advantec Toyo Kaisha Ltd. (Tokyo, Japan).

Apparatus

Reflection spectrometric measurements were made using a tristimulus colorimeter (Model NF-777; Nippon Denshoku Industries Co. Ltd., Tokyo, Japan), which was calibrated using a white standard reference plate. Solution absorbance measurements were made using a spectrophotometer (U-3000; Hitachi Ltd., Tokyo, Japan). A graphite furnace atomic absorption spectrometer was used (Z-5010; Hitachi Ltd., Japan). A filter holder (230 mm² effective filtration area, KG-25; Advantec Toyo Kaisha Ltd.) was used under suction with an aspirator. A PTFE-type membrane filter, which was set on the glass filter holder, was conditioned prior to the filtration procedure by rinsing with 1 mL of ethanol twice and 10 mL of 1 mol dm^{-3} hydrochloric acid solution.

Typical procedure

To a 10-mL aliquot of a sample solution containing 0–1.2 μg of antimony(V), 6.0 g of lithium chloride and 5 mL of 36 wt% hydrochloric acid were added and let stand for 2 min. After dilution with 50 mL of water, 0.25 mL of $1 \times 10^{-4} \text{ M}$ $[\text{Co}(5\text{-Cl-PADAP})_2]^+$ solution was added. The mixture was filtered under suction (0.03 MPa) through a PTFE-type membrane filter, which was conditioned as described in the apparatus section. After rinsing twice with 5 mL of a 10 wt% methanol aqueous solution, the filter paper, on which blue circular flecks were retained, was dried at room temperature for 10 min. The antimony concentration was determined through a visual comparison with a standard series of 0, 0.10, 0.20, 0.30, 0.60, and 1.2 μg . Reflection spectrometry was also used at 580 nm to estimate the color intensity. The colored filters could be kept in the dark for at least 7 days without any change.

Results and Discussion

Adsorption behavior of antimony(V) ion on membrane filters

Ion pairs with a blue cobalt complex, $[\text{Co}(5\text{-Cl-PADAP})_2]^+$, were completely adsorbed when the solution, prepared as described above, was filtered through a PTFE-type membrane filter. The filter paper color after rinsing twice with 5 mL of 10 wt% methanol aqueous solution was dependent on the antimony(V) content. The adsorption of antimony(V) ion was promoted by the addition of lithium chloride as a source of chloride ion. In a separate experiment without lithium chloride, more than 10 mol dm^{-3} of hydrochloric acid had to be present in the initial sample solution to achieve filter coloration. In Neumann's report,³⁷ SbCl_6^- was the predominant species in 12

Fig. 1 Effects of the added amount of lithium chloride on the color intensity. ○, 0.60 μg of antimony(V); □, reagent blank; △, the difference in the reflection spectrometric response between 0.60 μg of antimony(V) and reagent blank. The added amount of hydrochloric acid was 5 mL. The standing time after the addition of hydrochloric acid was 2 min. The membrane filters were rinsed twice with 5 mL of 10 wt% methanol aqueous solution.

mol dm^{-3} hydrochloric acid solution with an absorption band at around 272 nm. The rate of hydrolysis of SbCl_6^- was known to be slow.³⁸ Neumann and Ramette studied the rate of hydrolysis in detail, and reported it to be about 1% per minute in 6 mol dm^{-3} hydrochloric acid at room temperature.³⁹ Furthermore, the rate constant for hydrolysis became smaller by reducing the hydrochloric acid concentration. In a separate experiment, the absorption band, as reported by Neumann, appeared in the aqueous solution, which was prepared by adding 6.0 g of lithium chloride and 5 mL of 36 wt% hydrochloric acid solution to a 10-mL aliquot of the sample solution containing 0.12 or 1.2 mg of antimony(V). The decreased absorbance value was within 4% after dilution with 50 mL of water within 10 min, and the spectrum shape changed only slightly. Consequently, the hydrolysis of SbCl_6^- was not a serious hindrance to the proposed method because the analytical procedure was completed rapidly: within several minutes after dilution with water.

Hexachloroantimonate(V) ion (SbCl_6^-) was adsorbed with $[\text{Co}(5\text{-Cl-PADAP})_2]^+$ to the front surface of the PTFE filter. The back of the filter was not colored. In contrast, the colored filtrate was observed at the filtration with membrane filters made of cellulose acetate, or mixed cellulose ester, because a part of the cobalt complex was passed through the filters; the backs were also colored. Antimony(V) ion in a hydrochloric acid medium is well known to be extracted using various organic solvents with cationic dyes.^{12–15} In this study, we also examined ion-pair solid-phase extraction to membrane filters with cationic dyes, such as methylene blue, rhodamine B, brilliant green, and malachite green. However, the effective adsorption to membrane filters made of cellulose acetate and mixed cellulose ester was not achieved under 1–3 mol dm^{-3} of hydrochloric acid condition. Filters made of cellulose acetate or mixed cellulose ester were remarkably damaged with greater than 4 mol dm^{-3} of hydrochloric acid. Although the cationic dyes were adsorbed to the PTFE membrane filters, the effective signal for the antimony(V) concentration was not obtained by rinsing with a methanol aqueous solution. Consequently, the cationic cobalt complex, $[\text{Co}(5\text{-Cl-PADAP})_2]^+$, and PTFE-type membrane filter were the best combination among counter cations and filters used in this study for the ion-pair solid-phase extraction of antimony(V) ion.

Fig. 2 Effects of the added amount of 36 wt% hydrochloric acid on the color intensity. The antimony(V) content was 0.60 μg . The added amount of lithium chloride was 6.0 g. The standing time after addition of hydrochloric acid was 2 min. The membrane filters were rinsed twice with 5 mL of 10 wt% methanol aqueous solution.

Fig. 3 Effects of the standing time after the addition of 36 wt% hydrochloric acid on the color intensity. The antimony(V) content was 0.60 μg . The added amounts of lithium chloride and hydrochloric acid were 6.0 g and 5 mL, respectively. The membrane filters were rinsed twice with 5 mL of 10 wt% methanol aqueous solution.

Optimum conditions for antimony(V) detection

The effect of the amount of lithium chloride is shown in Fig. 1. The reflection spectrometric response for 0.60 μg of antimony(V) increased as the added amount of lithium chloride increased. On the other hand, the blank signal rose slightly with lithium chloride addition of 7.0 g or more. For that reason, 6.0 g of lithium chloride was added to the sample solution. The effects of the amount of 36 wt% of hydrochloric acid solution are shown in Fig. 2. The highest and almost constant signal was obtained in reflection spectrometric measurements when more than 4 mL was added. For this study, 5 mL of a 36 wt% hydrochloric acid solution was used. Figure 3 shows the effects of the standing time after the addition of a hydrochloric acid solution on the reflection spectrometric response. The maximum and constant response was obtained after 2 min. It was necessary to control the hydrochloric acid concentration with water before adding the cobalt complex solution, because $[\text{Co}(\text{5-Cl-PADAP})_2]^+$ was unstable at greater than 3 mol dm^{-3} of hydrochloric acid solution. The reflection spectrometric response was also remarkably reduced when the cobalt complex solution was added at a concentration of hydrochloric acid greater than 3 mol dm^{-3} . For this study, the mixture had been diluted with 30–50 mL of water before adding the cobalt complex solution. In solid-phase extraction with a membrane filter, the contact time between the sample solution and the extraction medium is much shorter than that of solvent extraction or flow-injection analysis equipped with PTFE tube concentration.⁹ As described above, in order to obtain a filter coloration that was dependent on the antimony(V) content, SbCl_6^- in the mixture should be made predominant among the antimony(V) species, because of the slow rate of formation of SbCl_6^- (see Fig. 3). Therefore, the concentration of chloride ion in the mixture before dilution had to be made more than 10 mol dm^{-3} , and lithium chloride, which has a high solubility in water, is a suitable material as a source of chloride ion in the proposed method. The effects of the methanol concentration in the rinsing solution are shown in Fig. 4. The difference in the reflection spectrometric response between 0.60 μg of antimony(V) and the reagent blank by rinsing twice with a 5-mL methanol aqueous solution in the concentration range of 0–20 wt% was remarkable. These ion pairs were eluted completely with methanol. This result agrees with the phenomena in the rinsing or washing step in flow-injection analysis equipped with PTFE tube concentration.⁹ As shown in

Fig. 4 Effects of the methanol concentration in the rinsing solution on the color intensity. ○, 0.60 μg of antimony(V); □, reagent blank; Δ, the difference in the reflection spectrometric response between 0.60 μg of antimony(V) and reagent blank. The added amounts of lithium chloride and hydrochloric acid were 6.0 g and 5 mL, respectively. The standing time after the addition of hydrochloric acid was 2 min.

Fig. 4, the blank signal was gradually reduced in the concentration range up to 10 wt%. The lowest and constant blank signal was obtained when more than 10 wt% methanol aqueous solution was used; then, the filter was not colored on externals. For that reason, a 10 wt% methanol aqueous solution was used in subsequent experiments. Taguchi *et al.* suggested that a steric cation, $[\text{Co}(\text{5-Cl-PADAP})_2]^+$, interacted with PTFE through hydrophobic forces.³⁶ The large size of ions is an important factor for the ion association and hydrophobicity of ion pairs.^{40,41} In the proposed method, the separation of the ion pair ($\text{SbCl}_6^- \cdot [\text{Co}(\text{5-Cl-PADAP})_2]^+$) from excess reagent, which was formed of ion pairs with other inorganic anions, aside from SbCl_6^- , was probably based on the difference of hydrophobicity among these ion pairs.

Calibration curve and detection limits

The color transitions of the membrane filters with relation to the antimony(V) concentration are shown in Fig. 5. The visual detection limit was 0.10 μg , defined as the minimum concentration that was visually distinguishable against the reagent blank. The color intensity was decreased rapidly at less than 0.10 μg . The calibration curve assessed with the reflection

Fig. 5 Color transition of the membrane filters with relation to the antimony(V) content. The added amounts of lithium chloride and hydrochloric acid were 6.0 g and 5 mL, respectively. The standing time after the addition of hydrochloric acid was 2 min. The membrane filters were rinsed twice with 5 mL of a 10 wt% methanol aqueous solution.

Table 1 Effect of foreign ions

Substance	Added as	Molar ratio	Sb(V) found ^a / µg	Recovery, %
Sodium	NaCl	1000	0.32	106
Potassium	KCl	1000	0.31	103
Magnesium	MgCl ₂	1000	0.29	96
Calcium	CaCl ₂	1000	0.33	110
Copper	CuCl ₂	100	0.24	80
		50	0.29	97
Aluminum	AlCl ₃	1000	0.33	110
Manganese	MnCl ₂	1000	0.30	99
Cobalt	CoCl ₂	1000	0.31	103
Iron	FeCl ₃	100	0.21	69
		50	0.29	98
		1000 ^b	0.27	90
Zinc	ZnCl ₂	1000	0.31	103
Lead	PbCl ₂	1000	0.30	100
Chromium	CrCl ₃	1000	0.29	97
Tin	SnCl ₂	100	0.32	106
Bismuth	Bi ₂ O ₃	100	0.30	99
Arsenate	As ₂ O ₃	100	0.33	110
Ammonium	NH ₄ Cl	1000	0.33	110
Sulfate	K ₂ SO ₄	1000	0.31	102
Nitrate	KNO ₃	1000	0.31	105
Thiocyanate	KSCN	1000	0.32	106
Perchlorate	NaClO ₄	50	0.32	108
Sodium		50	0.37	123
dodecylsulfate		0.1	0.28	94
Sodium		100	0.39	130
octylsulfate		50	0.32	106

a. Sb(V) taken: 0.30 µg. Reflection spectrometric measurement.

b. The dilution water in the typical procedure was 30 mL.

spectrometric responses at 580 nm was linear in the concentration range of 0.10 – 1.2 µg ($r = 0.996$). The RSD for reflection absorbance at 0.60 µg was 8.3% ($n = 8$).

Interference

The effect of commonly occurring foreign ions on the determination of 0.30 µg of antimony(V) in 10 mL of the sample solution was assessed. The results are summarized in Table 1. In this study, the tolerance limit was set as the amount that caused an error of $\pm 10\%$ in the recovery of antimony(V). The concentrations of sodium(I), potassium(I), magnesium(II), calcium(II), aluminum(III), manganese(II), cobalt(II), zinc(II), lead(II), chromium(III), ammonium ion, sulfate ion, and nitrate ion below a 1000:1 molar ratio, and those of tin(II), bismuth(III), and arsenate(III) below a 100:1 molar ratio did not

Table 2 Analytical results of water samples

Sample	Sb(V) concentration/ $\mu\text{g l}^{-1}$				Recovery, ^d %
	Added	Found			
		Visual method ^{a,b}	Reflection spectrometry ^a	GF- AAS	
River	0	0	< 10 ^c	< 4 ^c	—
water 1	30	30	28 $\pm$ 1 ^d	—	93
	60	60	57 $\pm$ 2 ^d	—	95
River	0	0	< 10 ^c	< 4 ^c	—
water 2	30	30	32 $\pm$ 1 ^d	—	107
	60	60	56 $\pm$ 1 ^d	—	93
Tap water	0	0	< 10 ^c	< 4 ^c	—
	30	30	31 $\pm$ 5 ^d	—	103
	60	60	60 $\pm$ 1 ^d	—	100

a. The dilution water in the typical procedure was 30 mL.

b. The visual detection limit is 10 µg L⁻¹.

c. The detection limits of each method.

d. Average value of three replicate analyses.

interfere. Although a large amount of iron(III) will cause a negative error, this interference can be eliminated by reducing the dilution water in the typical procedure to 30 mL. The proposed method is highly selective for antimony(V); however, water samples contaminated with significant amounts of ionic surfactants could cause problems.

Application

The analysis of antimony(V) in tap water and river water was undertaken to evaluate the practical usefulness of the proposed method. The river-water samples taken from a mountain area were used because a large amount of anionic surfactants interfered with the determination of antimony, as shown in Table 1. In this study, the visual determination and reflection spectrometry were performed after the addition of known amounts of antimony(V) ion. The results are summarized in Table 2. The recovery of antimony(V) gave sufficient results.

Conclusions

In conclusion, a sensitive and selective method for the visual detection of trace antimony(V) ion was demonstrated. The reasons for the capability of adsorption and separation on the membrane filter include (i) the slow rate of the hydrolysis reaction of SbCl₆⁻, and (ii) the difference in the hydrophobicity of the ion pairs. This proposed method using neither expensive instrumentations nor organic solvents harmful to the human body is suitable for processing many samples, and will provide valuable information related to the behavior of antimony in environmental science.

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References

1. H. A. Schröder, M. Mitchener, and A. P. Nason, *J. Nutr.*, **1970**, *100*, 59.
2. R. Poon, I. Chu, P. Lecavalier, V. E. Valli, W. Foster, S. Gupta, and B. Thomas, *Food Chem. Toxicol.*, **1998**, *36*, 21.
3. B. S. Lynch, C. C. Capen, E. R. Nestmann, G. Veenstra, and J. A. Deyo, *Regul. Toxicol. Pharm.*, **1999**, *30*, 9.
4. G. Gillain, G. Duyckaerts, and A. Disteche, *Anal. Chim. Acta*, **1979**, *106*, 23.
5. S. Costantini, R. Giordano, M. Rizzica, and F. Benedetti, *Analyst*, **1985**, *110*, 1355.
6. D. D. Nygaard and J. H. Lowry, *Anal. Chem.*, **1982**, *54*, 803.
7. M. O. Andreae, J.-F. Asmodé, P. Foster, and L. Van't dack, *Anal. Chem.*, **1981**, *53*, 1766.
8. W. M. Mok and C. M. Wai, *Anal. Chem.*, **1987**, *59*, 233.
9. K. Watanabe, T. Osawa, and M. Itagaki, *Tetsu to Hagane*, **2003**, *89*, 920.
10. J. Shida and S. Umeki, *Anal. Sci.*, **1999**, *15*, 1033.
11. J. Shida and S. Umeki, *Bunseki Kagaku*, **2001**, *50*, 143.
12. W. G. Fredrick, *Ind. Eng. Chem. Anal. Ed.*, **1941**, *13*, 922.
13. R. E. Van Aman, F. D. Hollibaugh, and J. H. Kanzelmeyer, *Anal. Chem.*, **1959**, *31*, 1783.
14. E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., **1959**, Interscience Publishers, Inc., New York, 254.
15. R. W. Burke and O. Menis, *Anal. Chem.*, **1966**, *38*, 1719.
16. K. Hiiro, T. Tanaka, A. Kawahara, M. Adachi, and K. Fukushi, *Bunseki Kagaku*, **1982**, *31*, E401.
17. K. Ohzeki, Y. Sato, Y. Kawamura, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 2618.
18. S. Taguchi, E. Ito-oka, and K. Goto, *Bunseki Kagaku*, **1984**, *33*, 453.
19. S. Taguchi, E. Ito-oka, K. Masuyama, I. Kasahara, and K. Goto, *Talanta*, **1985**, *32*, 391.
20. J. Shida, H. Satake, N. Ono, and T. Fujikura, *Talanta*, **1990**, *37*, 633.
21. J. Shida and S. Matsuzaki, *Anal. Sci.*, **1997**, *13*, 41.
22. J. Shida and I. Masuda, *Anal. Sci.*, **1998**, *14*, 333.
23. M. Endo, F. Yokota, and H. Mizuguchi, *Bunseki*, **2002**, *9*.
24. K. Goto and S. Taguchi, *Anal. Sci.*, **1993**, *9*, 1.
25. S. Taguchi, I. Kasahara, and N. Hata, *Bunseki Kagaku*, **1995**, *44*, 505.
26. S. Taguchi, H.-F. Sun, N. Hata, and I. Kasahara, *Bunseki Kagaku*, **2000**, *49*, 941.
27. J. Shida and H. Takahashi, *Anal. Sci.*, **1991**, *7*(Supplement), 675.
28. J. Shida, H. Takahashi, and Y. Sakamoto, *Talanta*, **1994**, *41*, 143.
29. K. Yoshimoto, E. Kaneko, and T. Yotsuyanagi, *Chem. Lett.*, **2000**, *6*.
30. K. Yoshimoto, E. Kaneko, and T. Yotsuyanagi, *Bunseki Kagaku*, **2000**, *49*, 363.
31. M. Hashimoto, N. Teshima, T. Sakai, and S. Kato, *Bunseki Kagaku*, **2005**, *54*, 783.
32. S. Taguchi, E. Seki, K. Murai, N. Hata, and H. Kuramitz, *Bunseki Kagaku*, **2006**, *55*, 525.
33. S. Taguchi and K. Goto, *Talanta*, **1980**, *27*, 289.
34. S. Taguchi, I. Kasahara, Y. Fukushima, and K. Goto, *Talanta*, **1981**, *28*, 616.
35. S. Taguchi, I. Kasahara, and K. Goto, *Bunseki Kagaku*, **1981**, *30*, 513.
36. S. Taguchi, K. Takayoshi, Y. Yotsu, and I. Kasahara, *Analyst*, **1996**, *121*, 1621.
37. H. M. Neumann, *J. Am. Chem. Soc.*, **1954**, *76*, 2611.
38. R. F. Weiland and H. Schmid, *Z. Anorg. Chem.*, **1905**, *44*, 37.
39. H. M. Neumann and R. W. Ramette, *J. Am. Chem. Soc.*, **1956**, *78*, 1848.
40. S. Motomizu, *Bunseki Kagaku*, **1989**, *38*, 147.
41. S. Motomizu, *Bunseki Kagaku*, **1999**, *48*, 151.