

Trace Analysis of Hydrogen Peroxide Solution for Boron Determination by Flow-Injection Technique after the Catalytic Decomposition of Hydrogen Peroxide

Zhenhai Li, Mitsuko Oshima and Shoji Motomizu

Department of Chemistry, Faculty of Science, Okayama University, Tsushimanaka, Okayama 700-8530 Japan

Abstract

Trace amounts of boron in commercially-available highly-pure hydrogen peroxide solutions were determined by a fluorometric flow-injection analytical method (FIA) with chromotropic acid as a complexing agent. In the proposed FIA, large amounts of hydrogen peroxide (H_2O_2) could interfere with the determination of trace amounts of boron, and therefore H_2O_2 in the sample solutions (about 8.8 M) were decomposed by catalytic methods with metal oxides and platinum metal, prior to the measurement of boron existing as boric acid / borate by the proposed FIA. In a batch-wise decomposition method, H_2O_2 in a commercially available electronic- and an analytical reagent-grade hydrogen peroxide solution was effectively decomposed by adding the powder of silver oxide, whereas in a continuous decomposition method with a catalyst, H_2O_2 was effectively decomposed by flowing the sample solutions in a platinum tube (0.5 mm i.d. x 100 cm) at 95 °C. Boron existing as boric acid / borate in the H_2O_2 solutions, where H_2O_2 was decomposed almost completely, was determined by the proposed FIA. The boron contents in the H_2O_2 solutions examined were around 10^{-8} M.

Keywords: boron determination, hydrogen peroxide solution, catalytic decomposition of hydrogen peroxide, silver oxide, platinum tubing, batch-wise method, continuous decomposition, fluorometric flow injection analysis, chromotropic acid.

1. Introduction

Recently, large amounts of ultrapurified chemicals, such as hydrogen peroxide solution, acids and bases, and water are required for manufacturing high-quality semiconductors in semiconductor-relating industries. In such fields, highly-purified chemicals are necessary and their contaminants / impurities must be regulated below some regulated values of each contaminant. Therefore, the demands for sensitive and accurate determination methods for trace (ppb levels: 1 ppb = 1 ng ml⁻¹) and ultratrace (ppt levels: 1 ppt = 1 pg ml⁻¹) amounts of the contaminants / impurities in ultrapurified chemicals are now growing rapidly. In these days, ultratrace analyses have been carried out by an inductively coupled plasma-mass spectrometric method (ICP-MS), which is said to be the most sensitive detection method of all instruments being now available: the limits of detection for common metal ions are usually around several ppt or sometimes sub-ppt levels by direct

ICP-MS measurement. However, the sensitivity for nonmetallic substances, such as boron, phosphorus and silicon, is not enough for the determination of sub-ppb and ppt-levels of such substances by ICP-MS. Furthermore, ICP-MS has several disadvantages: it is a big-scale and difficult-to-move, very expensive, highly costly apparatus, and samples are easy to be contaminated by an experimental circumstances.

The determination of trace and ultratrace amounts of boron has become more and more important in such fields as semiconductors, metallurgical products, advanced material substances, and industrial and purified water supplier industries. Boron as boric acid / borate in aqueous solutions reacts with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid: CA) to form a complex anion [1-3]; the complex anion formed is very stable in aqueous solutions, as well as in an organic solution. However, the absorption spectrum of boron complex with CA is very similar

to that of CA itself; therefore, for the absorptiometric detection of boron, the boron complex and the excess of the reagent must be separated prior to the measurement of absorbances. For the separation of the boron complex from the excess reagents, the complex can be extracted into an organic solvent as an ion associate with a quaternary ammonium ion[3]. Also, the separation can be achieved by high performance liquid chromatographic methods[4-6]. For the absorptiometric detection of boron, other reagents, such as azomethine H[7,8] and H-resorcinol[9], have been used; the former is less stable in aqueous solutions, and the latter is rather time-consuming for the complexation reaction with boric acid in aqueous solutions. H-resorcinol was successfully used for the highly sensitive determination of boron by the spectrophotometric ion-exchange chromatography: the LOD of boron was 20 ppt [10]. Later, a sensitive method for boron was developed by on-line complexation / anion exchange chromatography with H-resorcinol [11].

Chromotropic acid shows a very interesting spectroscopic phenomenon: it shows strong fluorescence near 350 nm [12-14], and can react rapidly with boric acid in aqueous solutions.

Motomizu et al. first developed FIA coupled with a fluorometric detection: the LOD was about 0.2 ppb of boron. Later, Motomizu et al. developed more sensitive method for boron determination by re-examining the experimental conditions of the fluorometric FIA method with respect of sensitivity improvement: the LOD was 50 ppt (5×10^{-9} M) of boron [15]. The method is probably the most sensitive one of all the methods now available for the direct determination of boron existing as boric acid in aqueous solutions by a rapid and simple procedure without any concentration techniques and with an excellent advantages in terms of the versatility, an easy-to-assemble system, and a cost-performance and less expensive instrumentation.

Hydrogen peroxide can interfere with the determination of boron, because of its oxidizing ability. Therefore, prior to the measurement by the fluorometric FIA, H_2O_2 must be decomposed. In the previous paper, silver oxide was used for the decomposition of H_2O_2 [16]. Aoyagi et al. reported the H_2O_2 decomposition system, which consisted of PTFE tube (1.0 mm i.d. x 10 m) containing platinum wire (0.3 mm o.d. x 10 m) heated at 100 °C [17,18]. By using this decomposition system, they could decompose H_2O_2 in hydrogen peroxide solutions (30%), and determined trace amounts of phosphate. In this work, the decomposition methods

for H_2O_2 in samples were examined to develop a convenient decomposition procedure used for the determination of trace and ultratrace amounts of boron. By using catalysts, a simple and a rapid procedure for the decomposition were developed. By coupling the newly developed decomposition procedures with the fluorometric FIA with CA, trace and ultratrace amounts of boron in hydrogen peroxide solutions were determined successfully.

2. Experimental

2.1 Apparatus and reagents

The flow diagram for the fluorometric FIA system used in this work is shown in Fig. 1.

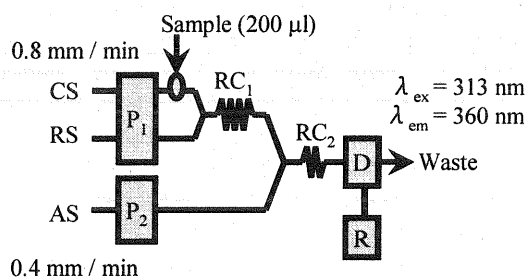


Fig.1 Flow system for boron determination

RS : reagent solution, 2.0×10^{-4} M chromotropic acid + 0.01 M EDTA + 0.1 M acetate buffer (pH 6.0);
 CS : carrier solution, ultrapure water;
 AS : ammonia (0.1 M); RC₁ : reaction coil (2 m);
 RC₂ : reaction coil (1 m); P₁ : pump (0.8 ml min^{-1});
 P₂ : pump (0.4 ml min^{-1}); D : detector; R : recorder.

A carrier, a reagent solution and an alkaline solution were propelled with a PFA 300 (F.I.A. Instruments, Tokyo), which consisted of two double-plunger pumps, a six-way sample injection valve with a loop (sample volume: 200 µl), and a reaction coils (RC₁: 0.5 mm i.d. x 2 m; RC₂: 0.5 mm i.d. x 1 m). The flow rates of the pumping systems were controlled by a controller of the main pumping system. The carrier (CS), the reagent solution (RS) and the alkaline solution were propelled at the flow rate of 0.4 ml min^{-1} . After the reaction coil (RC₂), a fluorometric detector (JASCO FP-920, Tokyo) equipped with a flow cell (8 µl) was installed: the excitation and emission wavelength were 313 nm and 360 nm, respectively. Flow signals were recorded with a strip chart recorder (TOA FBR-252, Tokyo).

For the continuous decomposition of hydrogen peroxide, a flow system shown in Fig. 2 was used. A platinum tube (0.5 mm i.d. x 1 m) and a PTFE cooling coil (0.5 mm i.d. x 2 m) were installed in the flow line. Samples (commercially available

hydrogen peroxide solutions, 30%) were propelled with a double-plunger micro pump (Sanuki Kogyo DM2M-1024, Tokyo) at a total flow rate of 0.4 ml min⁻¹. During the flow in the Pt tube, which was heated with an aluminum heating block at 95 °C, H₂O₂ in the sample solutions was decomposed almost completely.

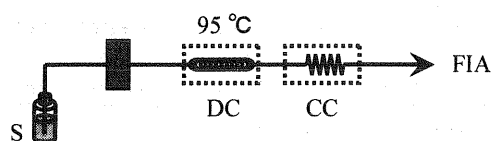


Fig.2 Flow diagram of the continuous decomposition system of hydrogen peroxide with platinum tube

S : sample (H₂O₂); P : pump (0.4 ml min⁻¹); DC : decomposition coil (Pt, ϕ 0.5 mm, 1 m); CC : cooling coil (2 m)

The reagent solution (RS) was prepared by dissolving chromotropic acid (Dojindo Laboratories, Kumamoto), EDTA (disodium salt, Dojindo Lab.) and acetate buffer (pH 6.0) in ultrapure water to give the concentrations of 2.0×10^{-4} M, 0.01 M and 0.1 M, respectively. The diluted ammonia solution (0.1 M) was used as the alkaline solution.

The stock solution of the standard boron was prepared by dissolving the boric acid dried in an air bath at 110 °C for 1 h in water to give 10^{-3} M. Working solutions for preparing a calibration graph were prepared by the accurate dilution of the stock solution.

Metal oxides (Ag₂O, MnO₂ and MoO₃), metal salts (Zn(CH₃COO)₂ and Co(CH₃COO)₂) and metals (Fe, Cu and Pt) were investigated as a catalyst for decomposing H₂O₂ in samples. Platinum tubes (0.5 mm i.d. and 1.0 mm i.d.) and platinum wire (0.3 mm o.d.) were also investigated as a catalyst for decomposing H₂O₂.

The reagents used in this work were of an analytical reagent grade. Through the experiments, water used was the one purified with a system of an Elix 10 / Milli Q Element (Millipore Japan, Tokyo).

2.2 Procedure for the determination of boric acid in sample solutions

Boric acid in the sample solutions, in which almost all of H₂O₂ was decomposed by a batchwise method or a continuous flow method, was determined by injecting the sample solutions using the injection valve in Fig. 1 and calculating the concentrations of boric acid from the calibration graph. The calibration graph was prepared by injecting the standard working solutions of boric acid at concentrations of 10^{-8} M level.

2.3 Procedure for the decomposition of hydrogen peroxide by the batchwise method and the continuous flow method

The hydrogen peroxide in the sample solutions was decomposed by adding small amounts of metal oxides, metal salts and metals to hydrogen peroxide solutions. After standing for several minutes, the sample solutions were analyzed by the proposed FIA system in Fig. 1.

In the continuous flow method, the sample solutions were flowed into the platinum tube heated at 95 °C in Fig. 2, where H₂O₂ in the sample solutions were decomposed during flowing through the heated platinum tube within 40 s. The sample solutions thus treated were analyzed as in the batchwise method.

3. Results and Discussion

3.1 Decomposition of H₂O₂ by the batchwise and the continuous flow methods

Table 1 shows the effect of H₂O₂ concentration in sample solutions on the determination of boron by the proposed FIA system in Fig.1. From the results shown in Table 1, less than 10^{-4} M of H₂O₂ does not interfere with the determination of boron in the sample solutions, whereas more than 10^{-3} M of H₂O₂ interfere with the determination of boron, and can give negative errors because of the oxidative decomposition of CA with H₂O₂ remaining in the sample. As a result, the amounts of H₂O₂ remaining in the sample solutions after the decomposition must be lowered below 10^{-4} M.

Table 1 Effect of hydrogen peroxide on the determination of boron as boric acid

Sample	Peak height / mm
10^{-7} M B (borate)	18.2 ± 0.2
10^{-7} M B + 10^{-6} M H ₂ O ₂	18.0 ± 0.2
10^{-7} M B + 10^{-5} M H ₂ O ₂	18.5 ± 0.2
10^{-7} M B + 10^{-4} M H ₂ O ₂	18.2 ± 0.2
10^{-7} M B + 10^{-3} M H ₂ O ₂	15.5 ± 0.4
10^{-7} M B + 10^{-2} M H ₂ O ₂	2.0 ± 0.4
10^{-7} M B + 10^{-1} M H ₂ O ₂	-12.2 ± 0.2

*Concentration of boron in 8.8 M H₂O₂ solution examined : 4.0×10^{-8} M, which can be neglected compared with the amounts of boron (1.0×10^{-7} M).

Several kinds of metals, their oxides and salts were examined as a catalyst for decomposing H₂O₂: 0.01g of the catalysts was added to 10.0 g of the hydrogen peroxide solution (30%), and after standing them for 30 min, the solutions were analyzed by using the proposed FIA system in Fig.1.

The results obtained are shown in Table 2. It was found that Ag_2O was useful for decomposing H_2O_2 , and boron could be determined by using the sample solutions treated with it, whereas boron could not form the complex with CA after treating with metals, such as Cu and Pt and MoO_3 . From such results, Ag_2O can decompose H_2O_2 , and the residual H_2O_2 does not interfere with the determination of boron. In case of metals, large amounts of H_2O_2 will remain in the sample solutions after treating with these metals, and oxidize CA, which results in the difficulty of the formation of the boron complex with CA. Double peaks appeared in case of the solutions treated with MnO_2 , Fe, $\text{Co}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{CH}_3\text{COO})_2$, which means that most parts of H_2O_2 were decomposed, metal complexes of CA formed and showed fluorescence.

Table 2 Effect of metals, metal salts and metal oxides on the decomposition of hydrogen peroxide

Catalyst ^{*1}	Peak height (mm) ^{*2}
Ag_2O (powder)	55
MnO_2 (powder)	60 (high blank)
$\text{Co}(\text{CH}_3\text{COO})_2$ (crystal)	45 (high blank)
$\text{Zn}(\text{CH}_3\text{COO})_2$ (crystal)	40 (double peaks)
Fe (powder)	10 (double peaks)
Cu (powder)	0
Pt (plate)	0
MoO_3 (crystal)	- (minus peak)

Sample: H_2O_2 solution (30%: 8.8 M)

*1 To 10.0 g of hydrogen peroxide solution(30%), 0.01g of catalysts was added. After 30min, the solutions were analysed by the FIA system in Fig. 1.
*2 Obtained by using the FIA system in Fig.1.

In Table 3, the effect of catalysts on the decomposition of H_2O_2 in a hydrogen peroxide solution was summarized; the residual concentrations of H_2O_2 in the sample were determined by the method recently reported [19]. Manganese dioxide can decompose most of H_2O_2 in the hydrogen peroxide solution, and the residual amounts (3.0×10^{-6} M) are less than 10^{-4} M, which seems not to interfere with the determination of boron. However, as can be seen in Table 2, MnO_2 itself shows a high blank value, while silver oxide does not show any blank value and double peaks. As a result, Ag_2O is the best catalyst for decomposing H_2O_2 in the determination of boron in hydrogen peroxide solutions.

Table 3 Effect of catalysts on the decomposition of hydrogen peroxide

Catalysts	Temp. (°C)	Decomposition time / min	Residual conc. of H_2O_2 (M)	Method ^{*4}
Platinum - wire ^{*1} (ϕ 0.3 mm, 1 m)	100	2.0	2.7	C.F
PTFE tube (ϕ 0.5 mm, 4 m)	100	2.0	8.1	C.F
Platinum tube (ϕ 0.5 mm, 1 m)	100	1.2	1.1×10^{-7}	C.F
Ag_2O ^{*2}	RT ^{*3}	10.0	2.7×10^{-6}	B
MnO_2 ^{*2}	RT	30.0	3.0×10^{-6}	B
$\text{Co}(\text{CH}_3\text{COO})_2$ ^{*2}	RT	60.0	6.2×10^{-5}	B

Sample: H_2O_2 solution (30%)

*1 Platinum-wire is inserted into PTFE tube(ϕ 1.0 mm).

*2 Catalysts : 2×10^{-3} g ml⁻¹ H_2O_2 (30%) solution.

*3 Room temperature.

*4 Decomposition method: C.F.: continuous flow method; B: batchwise method.

Figure 3 shows the effect of amounts of Ag_2O on the decomposition of H_2O_2 in the hydrogen peroxide solution (30%). The amounts of H_2O_2 remaining in the solution after treating with more than 0.001 g of Ag_2O per 1 ml of H_2O_2 solution (30%) does not interfere with the determination of boron. Figure 4 shows the effect of the standing time on the decomposition of H_2O_2 : 5 min is enough for the decomposition of H_2O_2 . In the further experiments, 10-min standing time was adopted for safety.

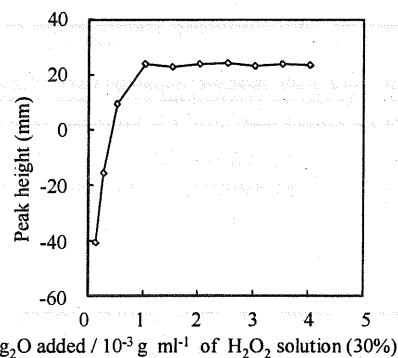


Fig.3 Effect of silver oxide on the decomposition of hydrogen peroxide in boron determination

The effect of heating time on the recovery of boron in sample solutions was examined; the results are shown in Table 4. The results show that the boron content obtained by the procedure of 10-min standing time is almost identical with those obtained by heating on the hot plate and concentrating it to about 2-3 fold. Such results indicate that 10-min standing time is enough for the determination of boron in the hydrogen peroxide solutions.

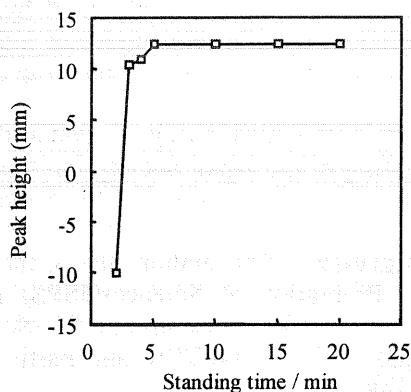


Fig.4 Effect of time on the decomposition of H_2O_2 in hydrogenperoxide solution

Ag_2O added : 2×10^{-3} g per 1 ml of H_2O_2 solution (30%)

Table 4 Effect of heating time on enrichment of boron in hydrogen peroxide

Sample	Enrichment ratio	Boron / 10^{-8} M	
		Measured*3	found
A*1	1.00	4.3 ± 0.2	4.3
B*2	2.20	9.3 ± 0.5	4.2
C*2	2.25	9.9 ± 0.3	4.4
D*2	3.12	13.9 ± 0.4	4.5
E*2	3.44	14.8 ± 0.3	4.3

Sample: 30% hydrogen peroxide solution.

Vessel for the decomposition of hydrogen peroxide : PTFE beaker.

*1 To 10.0 g of a hydrogen peroxide solution, 0.01g of Ag_2O was added and the solutions was stood for 10min at room temperature.

*2 To 10.0 g of the hydrogen peroxide solution, 0.01g of Ag_2O was added, heated on a hot plate and concentrate the solutions.

*3 Results obtained by the proposed FIA method.

Table 5 Recovery test for boron by the batchwise decomposition procedure with Ag_2O

Boron added*	Boron / 10^{-8} M		Recovery (%)
	measured	recovered	
10^{-8} M			
0.00	2.12 ± 0.23	2.12	
2.00	4.19 ± 0.16	2.19	103.3
4.00	6.06 ± 0.16	2.06	97.2
6.00	8.21 ± 0.16	2.21	104.2
8.00	10.16 ± 0.08	2.16	101.9
10.00	12.11 ± 0.08	2.11	99.5

* Adequate amounts of boron as boric acid were added to 5ml of the hydrogen peroxide solution in 10ml volumetric flasks. The solutions in the volumetric flasks were diluted two - fold with ultrapure water, and then the diluted hydrogen peroxide solutions were decomposed with 0.01 g Ag_2O .

By using Ag_2O as a catalyst in the batchwise decomposition method, the recovery test for boron was examined; the results obtained are shown in Table 5. From the results obtained, boron at concentrations of 10^{-8} M levels could be recovered successfully.

In the continuous flow decomposition methods, the platinum tube system is very effective for decomposing H_2O_2 , compared with the platinum wire system and the PTFE tube system, and also with the batchwise method with Ag_2O , as can be seen from Table 3.

Figure 5 shows the effect of the temperature of the platinum tube in the aluminum block on the decomposition of H_2O_2 by using the system in Fig.2. As can be expected, the decomposition ratio of H_2O_2 increased with increasing the temperature of the Pt tube, and the Pt tube with 0.5 mm i.d. was more effective for the decomposition than the Pt tube with 1.0 mm i.d.

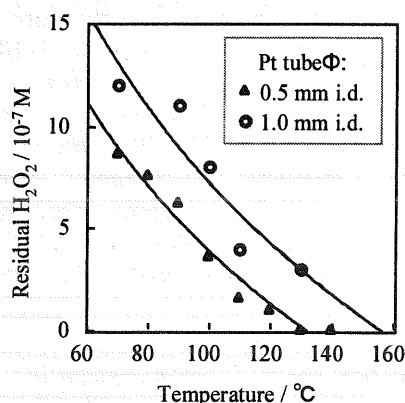


Fig.5 Effect of temperature on the decomposition of H_2O_2 in hydrogen peroxide solution

Sample: 30% H_2O_2 solution; decomposition time : 0.5 min.

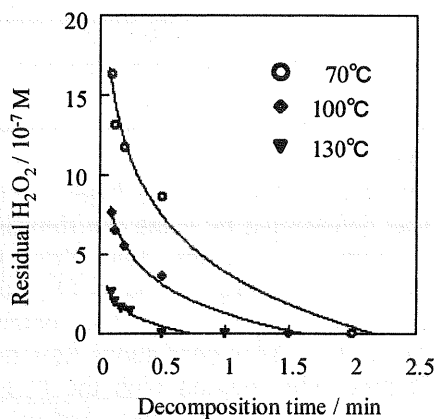


Fig.6 Effect of decomposition time

* Pt tube: 0.5 mm i.d. x 1 m

For the boron determination using the proposed FIA method, 70 °C is enough for lowering the amounts of H₂O₂ in the sample solutions below 10⁻⁴ M: for safety, 95 °C was adopted. Figure 6 shows the effect of time on the decomposition of H₂O₂ using the decomposition system (Fig.2); the results were obtained by varying the flow rate of samples in the system (Fig.2). For the boron determination, several seconds of the time flowing in the Pt tube is enough, which means that higher flow rate, for example, 2 ml min⁻¹, can be used.

3.2 Application to real samples

Boron contents existing as boric acid / borate in commercially available hydrogen peroxide solutions (30 %) were obtained by using the sample solutions treated with the Pt tube decomposition system shown in Fig.2 and the proposed FIA system. The results obtained are summarized in Table 6. In such hydrogen peroxide solutions, boron at concentrations of 10⁻⁸ M level or sub-ppb level is present as boric acid / borate. The ultrapure water used in this work contained boron at 3-10 ppt. Compared with such boron content values, boron contents in the hydrogen peroxide solutions are much higher and about 100-fold. Probably, in commercially available hydrogen peroxide solutions, some stabilizing substances are added to protect H₂O₂ from the auto-decomposition; such stabilizers contaminate the hydrogen peroxide solutions.

Table 6 Analytical results of boron contents in commercially available hydrogen peroxide solutions

Sample grade ^{*1}	Found / 10 ⁻⁸ M
A AR	7.5 ± 0.1
B AR	4.3 ± 0.1
C EL	5.6 ± 0.1

*1 AR : analytical reagent grade ; EL : electronic grade

4. Conclusion

Trace amounts of boron in hydrogen peroxide solutions was determined by using the fluorometric FIA system with chromotropic acid. Prior to the measurement of boron, large amounts of hydrogen peroxide were decomposed by the batch-wise method with Ag₂O and the continuous flow method with the Pt tube. The method with the Pt tube is very convenient and useful for trace and ultratrace analysis because of less contamination from other chemicals. By using the proposed decomposition

methods, trace and ultratrace analyses of hydrogen peroxide solutions used in semiconductor industries will be carried out more easily and more rapidly.

Some parts of this work was presented at the 52nd Annual Meeting of the Japan Society for Analytical Chemistry on September 23-25, 2003 in Sendai.

Acknowledgement The authors thank the Japan Society for Promotion of Sciences(JSPS) for the support of this work: Grant-in-Aid for Scientific Research (B)(2) (No.13440220), and partly (C)(2) (No.15550138).

- [1] K.Andress, W.Toph, *Anorg.Allg.Chem.*, **254**, 52 (1947).
- [2] D.F.Kummel, M.G.Mellon, *Anal.Chem.*, **29**, 378 (1957).
- [3] T.Korenaga, S.Motomizu, K.Toei, *Analyst*, **103**, 745 (1978).
- [4] S.Motomizu, I.Sawatani, M.Oshima, K.Toei, *Anal.Chem.*, **55**, 1629 (1983).
- [5] Z.Jun, M.Oshima, S.Motomizu, *Analyst*, **113**, 1631 (1988).
- [6] Z.Jun, M.Oshima, S.Motomizu, *Bunseki Kagaku*, **37**, T228 (1988).
- [7] R.A.Edwards, *Analyst*, **105**, 139(1980).
- [8] F.J.Krug, J.Mortatti, L.C.R.Pessenda, E.A.G.Zagatto, F.Bergamin Filho, *Anal.Chim.Acta*, **125**, 29 (1981).
- [9] K.Toei, S.Motomizu, M.Oshima, M.Onoda, *Bunseki Kagaku*, **35**, 3448 (1986).
- [10] S.Motomizu, M.Oshima, Z.Jun, *Analyst*, **115**, 389 (1990).
- [11] J. Zou, S.Motomizu, M.Oshima, H.Fukutomi, *Anal. Sci.*, **8**, 719 (1992).
- [12] J.Lapid, S.Farhi, Y.Koresh, *Anal.Lett.*, **9**, 355 (1976).
- [13] S.Motomizu, M.Oshima and K.Toei, *Bunseki Kagaku*, **32**, 458 (1983).
- [14] M.Oshima, S.Motomizu, Z.Jun, *Anal.Sci.*, **6**, 627(1990).
- [15] S.Motomizu, M.Oshima, Z.Jun, *Anal.Chim.Acta*, **251**, 269 (1991).
- [16] J.Li, P.K.Dasgupta, G.Li, S.Motomizu, *Anal.Chem.*, **75**, 6753 (2003).
- [17] M.Aoyagi, Y.Yasumasa, A.Nishida, *Anal.Sci.*, **7**, 347 (1991).
- [18] M.Aoyagi, Y.Yasumasa, A.Nishida, *Bunseki Kagaku*, **39**, 131 (199).
- [19] Z.Li, M.Oshima, S.Motomizu, Abstracts of the 64th Symposium on Analytical Chemistry, p.97 (2003).

(Received: October 30, 2003)

(Accepted: November 10, 2003)