Trace and Ultratrace Analysis of Purified Water Samples and Hydrogen Peroxide Solutions for Phosphorus by Flow-Injection Method

Zenhai Li, Mitsuko Oshima, Akhmad Sabarudin, and Shoji Motomizu[†]

Department of Chemistry, Faculty of Science, Okayama University,
Tsushimanaka 3-1-1, Okayama 700–8530, Japan

A highly sensitive fluorescence-quenching method for the determination of phosphorus based on the formation of an ion associate between molybdophosphate and Rhodamine B (RB) was developed. A simple flow-injection system coupled with a fluorescence detector was used to measure the fluorescence intensity at 560 nm and 580 nm as an excitation and an emission wavelength, respectively. The calibration graph for phosphorus showed a good linearity in the range of $(0 – 1) \times 10^{-7}$ M (1 M = 1 mol L^{-1}), and a detection limit of 1×10^{-9} M ($S/N = 3$). The proposed method was successfully applied to the determination of ultratrace amounts of phosphorus in ultrapurified and purified water samples, and to the determination of trace amounts of phosphorus in commercially-available hydrogen peroxide solutions with satisfactory results.

Introduction

Nowadays, especially in semiconductor industries, large amounts of ultrapurified chemicals, such as water, hydrogen peroxide, acids, and bases, are required for manufacturing high-quality semiconductors in microelectronic industries.[1] The use of ultrapurified chemicals can help to fulfill two main objectives, namely the production of high-quality products and the minimization of rejects.[2] Consequently, there has been a growing demand for the sensitive and accurate determination of trace and ultratrace amounts of impurities, such as boron, phosphorus and silicon, in ultrapurified chemicals. In general, such nonmetallic elements/compounds are less sensitive to conventional atomic spectroscopic methods, such as AAS, ICP-AES and ICP-MS. For example, the limits of detection (LOD) of silicate and phosphate in ICP-MS, which is known to be one of the most sensitive instruments and is often used in semiconductor analysis, are about 1 ppb or larger. Therefore, its sensitivity is not sufficient for the determination of a sub-ppb or ppt level of such non-metallic substances.

The determination of trace and ultratrace amounts of phosphorus has become more and more important in such fields as semiconductor industry, ultrapurified chemicals (UPC) and ultrapurified water (UPW) manufactures *etc*.[3] The phosphomolybdenum blue method, either with or without solid-phase enrichment, has often been used for phosphorus and silicate determination,[4–8] though the procedures are sometimes troublesome and time-consuming, for improving the sensitivity they need filtration/collection procedures with membrane filters. Sensitive spectrophotometric and fluorometric methods based on ion-associate formation deserve much attention. Molybdophosphate forms ion-association complexes with bulky

cationic or basic dyes, which are the basis of sensitive detection methods for determining phosphorus spectrophotometrically. Malachite Green has found the widest application.[9–15] Motomizu *et al*.[16–18] have reported a highly sensitive spectrophotometric method for determining phosphorus at sub-ppb and ppt levels using relatively small volumes of the sample solutions, an organic solvent (methyl cellosolve: MC), and a tiny membrane filter for collecting the ion associate of molybdophosphate with Malachite Green. The absorbance of the collected ion associate dissolved in MC was measured by an off-line flow injection–spectrophotometric detection method, which is relatively simple and shows excellent sensitivity. However, the collection/concentration procedure with a tiny membrane filter and dissolution of the ion associate in MC is troublesome and time-consuming.

Highly sensitive fluorescence quenching methods for the determination of phosphate coupled with a flow-injection technique were also reported. These methods are based on the formation of an ion associate of molybdophosphate with Rhodamine 6G.[19,20] They are very sensitive with a detection limit of 0.1 ppb,[19] though the prepared reagent solution was not stable. Later, a method with Rhodamine B (RB) was developed to improve the stability of the reagent solution, and was applied to seawater analysis.[21]

In the present work, we reinvestigated the RB method proposed by Motomizu *et al*.[21] with respect to improving the sensitivity and reproducibility, and propose a versatile method coupled with a simple flow-injection system for the determination of ultratrace amounts of phosphorus in ultrapurified water based on the formation of an ion associate of molybdophosphate with Rhodamine B (RB). The proposed method was also applied to the analysis of commercially-available hydrogen peroxide solutions after dilution of the samples by at least 200 fold before injecting to the FIA system. The adopted wavelengths for the fluorescence measurement were 560 nm for excitation (λ_{ex}) and 580 nm for emission (λ_{em}). The proposed method resulted in a very low detection limit of 1×10^{-9} M.

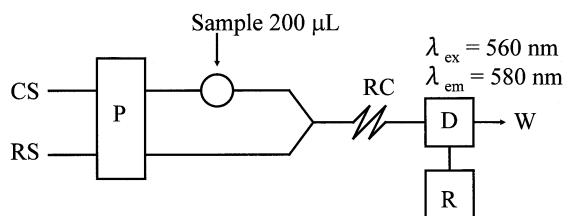[†] To whom correspondence should be addressed.
E-mail: motomizu@cc.okayama-u.ac.jp

Fig. 1 Flow system for phosphorus determination.   CS, ultrapurified water prepared by Elix 3/Milli Q Elements; RS, 1.0×10^{-2} M Mo + 0.8 M H_2SO_4 + 6.0×10^{-6} M RB + 0.05% PVA; P, double plunger micropump (flow rate 0.5 mL min^{-1}); RC, reaction coil (0.5 mm i.d. $\times$ 2.5 m PTFE tubing); R, recorder; D, fluorophotometric detector (λ_{ex}, 560 nm; λ_{em}, 580 nm).
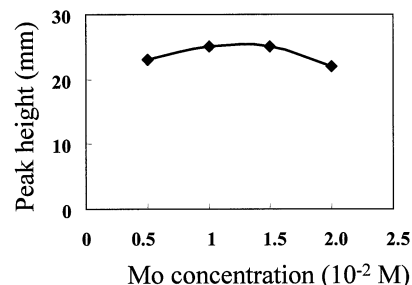

Fig. 2   Effect of the molybdate concentration on the determination of phosphorus.   Phosphorus concentration, 5×10^{-8} M; other conditions are the same as in Table 1, except for molybdate, which was varied in this study.

Experimental

Apparatus and reagents

The flow-injection manifold used in this work is shown in Fig. 1.   A carrier solution, ultrapurified water, was propelled with a PFA 300 (F·I·A Instruments, Tokyo), which consisted of two double-plunger pumps, a six-way injection valve with a loop (sample volume: 200 μl), and a reaction coil (RC: 0.5 mm i.d. $\times$ 2.5 m).   The flow rate of the pumping system was controlled using an electronic controller of the PFA 300 pump.   The carrier solution (CS) and the reagent solution (RS) were propelled at a flow rate of 0.5 mL min^{-1}.   A fluorophotometric detector (RF-10A$_{XL}$) equipped with a micro flow cell of 12 μL (Shimadzu, Kyoto), was installed after RC.   Flow signals were recorded with a Toa FBR-252 recorder.

In the FIA system proposed in this study, sample solutions were injected into the carrier stream of ultrapurified water and merged with the reagent stream to form an ion associate of molybdophosphate with Rhodamine B (RB) in RC.   Then, the fluorescence quenching of the ion associate formed was detected at λ_{ex} = 560 nm and λ_{em} = 580 nm.   This system is very simple and accompanied with an excellent performance.

All chemicals used were of analytical-reagent grade or the highest-quality commercially available grade.   Ultrapurified water obtained with ELIX 3/Milli Q element (Nihon Millipore, Tokyo) was used for preparing the reagent solution, as well as the sample solution, itself.   The samples, analytical reagent grade of hydrogen peroxide solutions, were purchased from Kanto Chemical Ltd. and Wako Pure Chemical Ltd., and the one of the electronic grade was purchased from Mitsubishi Chemical Ltd.

The reagent solution (RS) was prepared by dissolving molybdate salt (hexaammonium heptamolybdate tetrahydrate, Wako Pure Chemical), Rhodamine B, polyvinyl alcohol (PVA), and concentrated H_2SO_4 (Kanto Chemical) in ultrapurified water to give final concentrations of 1.0×10^{-2} M, 6×10^{-6} M, 0.05%, and 0.8 M, respectively.

A stock standard solution of phosphorus was prepared by dissolving potassium dihydrogenphosphate dried at 110°C in ultrapurified water to give a 2.0×10^{-2} M solution.   Working standard solutions for preparing a calibration graph were prepared by accurate dilution of the stock solution.

Sample preparations used for measuring phosphorus by FIA

Ultrapurified water samples were concentrated by evaporation before analysis.   Ultrapurified water samples, 100 mL, were transferred into clean PTFE beakers with a pipette, and kept on

a hot plate.   The samples were evaporated to about 10 ml.   The enrichment factor was calculated by using the weights of the residued samples measured after evaporation.   The concentrated samples were used for FIA measurements.

The enrichment procedure was unnecessary for hydrogen peroxide samples.   At least 200-fold dilution with ultrapurified water was required for the hydrogen peroxide samples before being injected to the FIA system.

Results and Discussion

Optimized conditions for the formation of ion association

The medium acidity was examined by using sulfuric acid, nitric acid, hydrochloric acid, and perchloric acid.   Sulfuric acid was selected because of the lower value of a reagent blank (background), higher sensitivity, and better linearity of a calibration graph.   The optimum concentration of sulfuric acid was found to be around 0.8 M.

The effect of the molybdate concentration on the reaction was examined by varying its concentrations from 5.0×10^{-3} to 2.0×10^{-2} M, the obtained results are shown in Fig. 2.   The peak heights increased with increasing the molybdate concentrations from 5.0×10^{-3} to 1.5×10^{-2} M.   At higher concentrations (> 1.5 $\times$ 10^{-2} M), the baseline became very noisy, the peak heights became shorter, and the linearity of the calibration graph became poor.   Such an inferior performance was caused by the formation of aggregates of ion associates formed between molybdate and RB, which adsorbed on the flow cell and the inner surface of the reaction coil.   In this work, 1.0×10^{-2} M of molybdate was selected as the optimum concentration.

The effect of the Rhodamine B (RB) concentration on the formation of the ion associate was investigated by varying its concentrations from 5×10^{-9} M to 3×10^{-5} M.   The results showed that an increase in the RB concentrations lead to an increase in the fluorescence quenching intensity, as shown in Fig. 3.   However, the baseline became increasingly noisy and the reproducibility of the peaks became unsatisfactory.   Therefore, 6×10^{-6} M of RB was adopted as a compromise.

The fluorophotometric and the spectrophotometric methods for the determination of phosphorus based on the formation of the ion associate between heteropolyacid anions and a cationic dye were very sensitive, compared with the molybdenum blue methods.   However, the ion associates tend to precipitate and adsorb on the reaction coil and the flow cell, which can lead to the baseline drift.   To prevent such adsorption, polyvinylalcohol (PVA: polymerization degree, 1750) was added to RS to stabilize the ion associate in the flow stream and to avoid

Table 1   Conditions adopted for the determination of phosphorus in ultrapurified water and hydrogen peroxide

Carrier solution (CS)	Water (ELIX 3/Miili Q Element)
Reagent solution (RS)	1.0×10^{-2} M Mo + 0.8 M H_2SO_4 + 6.0×10^{-6} M RB + 0.05% PVA
Flow rate of CS and RS	0.5 mL min^{-1}
Temperature of reaction coil	Room temperature
Sample volume	200 μL
Reaction coil (RC)	0.5 mm i.d. × 2.5 m PTFE tubing
Detection wavelength	λ_{ex}, 560 nm; λ_{em}, 580 nm

baseline drift. In the present work, 0.05% of PVA was chosen as the optimum concentration with respect to the lower baseline noise as well as higher sensitivity. When the concentration of PVA was higher than 0.05%, the solution became more viscous, the background became less stable and the linearity of the calibration graph became poorer.

Optimized conditions for the flow-injection system

The effect of the temperature in RC on the formation of the ion associate was examined by varying from 25°C to 100°C, where the peak heights were almost identical. This means that the formation of the molybdophosphoric acid and its ion associate with RB is very fast at room temperature, and seems to be essentially independent from the temperature. Therefore, room temperature (25°C) was selected for further experiments, which provided some benefit, such as excellent reproducibility of the peaks, low baseline noise, and no bubbles of air in the stream.

The effect of the length of the reaction coil (RC) on the peak height (negative peaks) was investigated by varying it from 1 m to 4 m; the obtained results are shown in Fig. 4. With increasing RC until 2.5 m, the peak height increased. Such increases were mainly due to an increase in the formation of molybdophosphate. By using a longer RC than 2.5 m, the peak height was decreased, which was due to dispersion of the sample zone. Thus, 2.5 m was chosen as the optimum length of the RC.

The optimum flow rate of the pump, which propels the reagent solution (RS) and the carrier (CS), was found to be 0.5 mL min^{-1}. Higher peak heights were obtained when a lower flow rate was used. This is because the formation of the ion associate proceeded more completely, and there was less dispersion of phosphorus. However, it took a very long time for the analysis. Therefore, 0.5 mL min^{-1} was adopted as a compromise of the analysis time and the sensitivity.

The experimental conditions optimized for the determination of phosphorus are summarized in Table 1.

Flow signals, calibration graph and detection limit

Flow signals of phosphorus for a calibration graph under the optimal conditions are shown in Fig. 5. The reaction of molybdophosphate with RB resulted in negative peaks, which were due to the fluorescence quenching of RB. The possible reaction mechanism is:

$$H_3PO_4 + \text{molybdate} \longrightarrow H_3PMo_{12}O_{40},$$

$$H_3PMo_{12}O_{40} + 3RB^+ \longrightarrow (RB^+)_3(PMo_{12}O_{40}^{3-}).$$

RB gave a strong fluorescence, while its ion associate resulted in weak fluorescence.[21]

The calibration graph showed good linearity from 0 to 1 ×

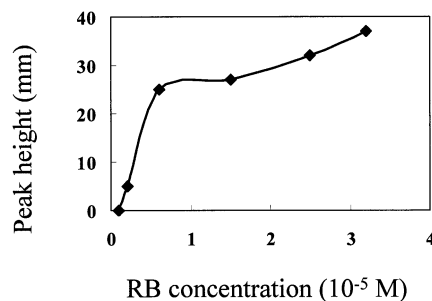Fig. 3   Effect of the Rhodamine B concentration on the determination of phosphorus. Phosphorus concentration, 5×10^{-8} M; other conditions are the same as in Table 1, except for Rhodamine B, which was varied in this study.
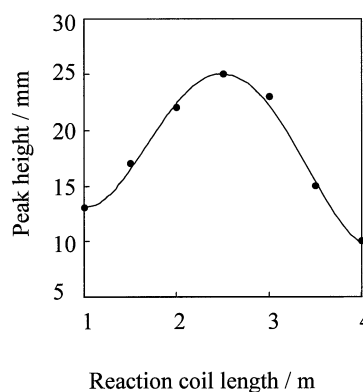
Fig. 4   Effect of the reaction coil length on the determination of phosphorus. Phosphorus concentration, 5×10^{-8} M; other conditions are the same as in Table 1.
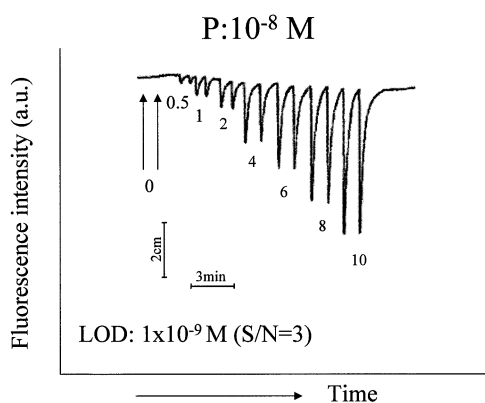
Fig. 5   Flow signals for the determination of phosphorus by the fluorescence quenching/FIA method. The experimental conditions were the same as in Table 1.

10^{-7} M of phosphorus.   The correlation coefficient of the calibration graph was 0.999, and the relative standard deviation of 10 measurements of 4×10^{-8} M phosphorus was 2.3%. The limit of detection (LOD) obtained with the peak height by three-times of the signal-to-noise ratio ($S/N = 3$) was 1×10^{-9} M, which corresponds to about 30 ppt of phosphorus; the LOD of the proposed method seems to be the most sensitive, compared to other FIA methods reported so far.

Table 2   Effect of silicate on the determination of phosphorus

Phosphorus/M	Silicate added/M	Peak height/mm
5×10^{-8}	0	14.5 ± 1.0
	5×10^{-8}	14.5 ± 1.0
	2×10^{-7}	14.5 ± 1.0
	3×10^{-7}	14.5 ± 1.0
	4×10^{-7}	14.6 ± 1.0
	5×10^{-7}	18.5 ± 1.0
	5×10^{-7}	23.0 ± 1.0
0	5×10^{-8}	0
	2×10^{-7}	0
	3×10^{-7}	0
	4×10^{-7}	0
	5×10^{-7}	5.0 ± 1.0
	5×10^{-6}	6.5 ± 1.0

Table 3   Effect of hydrogen peroxide on the determination of phosphorus

Sample	Peak height/mm
10^{-7} M P (phosphate)	25.2 ± 0.2
10^{-7} M P + 10^{-5} M H_2O_2	25.0 ± 0.4
10^{-7} M P + 10^{-4} M H_2O_2	24.5 ± 0.2
10^{-7} M P + 10^{-3} M H_2O_2	25.2 ± 0.2
10^{-7} M P + 10^{-2} M H_2O_2	55.5 ± 0.4
10^{-7} M P + 10^{-1} M H_2O_2	Double peak

Concentration of phosphorus in the 8.8 M H_2O_2 solution examined, 1.08×10^{-4} M. The experimental conditions were the same as in Table 1.

Interferences study

  Silicon as silicate can form molybdosilicate under similar conditions of the proposed method, and can form an ion associate with RB. The effect of silicate, as shown in Table 2, was examined by varying its concentrations from 0 to 5×10^{-6} M in the presence of 5×10^{-8} M of phosphorus. The results indicate that there is no interference from silicate up to 4×10^{-7} M. Similarly, when phosphorus was not added to the samples (the reagent blank), 4×10^{-7} M of silicate did not give any signals. As a result, the effect of silicate on the phosphorus determination could be neglected, because silicate in ultrapurified water samples is less than 10^{-8} M.[2] The concentrations of silicate in ultrapure, electronic, and analytical grade of concentrated hydrogen peroxide solutions are about 6.8×10^{-5} – 7.1×10^{-5} M. Therefore, for the determination of phosphorus in hydrogen peroxide, the samples should be diluted by at least 200 fold to avoid interference from silicate.

  The effect of the H_2O_2 concentration in sample solutions on the determination of phosphorus by the proposed FIA system is shown in Table 3. The results show that H_2O_2 up to 10^{-3} M did not interfere with the determination of phosphorus in the sample solution. However, when the concentration of H_2O_2 was more than 10^{-2} M, a positive error as well as a double peak of the flow signal occurred. The positive error was due to the decomposition of RB with H_2O_2. The concentrations of phosphorus in concentrated H_2O_2 (8.8 M) solutions examined in this work (Table 3) were about 1×10^{-4} M. Therefore, if concentrated H_2O_2 was diluted to 10^{-2} M, which was diluted by 880 fold, the concentration of phosphorus was about 1.2×10^{-7} M. This concentration could be easily determined by the proposed method without the any interference from silicate and H_2O_2. The double peak, which occurred at 10^{-1} M of H_2O_2, is

Table 4 Recovery test for phosphorus in the evaporation/enrichment step

Phosphorus added/ 10^{-9} M	Concentration factor	Phosphorus		Recovery, %
		Measured[a]/10^{-8}	Found[b]/10^{-9}	
0.00	9.48	1.08 ± 0.14	1.14	—
1.00	6.91	1.52 ± 0.05	2.20	106
2.00	6.98	2.22 ± 0.05	3.18	102
3.00	7.15	2.86 ± 0.06	4.00	95
4.00	9.48	5.07 ± 0.02	5.35	105

Sample: ultrapurified water prepared by Elix 3/ Milli Q Element. Samples, 100 mL, were evaporated to about 10 mL, whose weights were measured by a chemical balance. The density of the residual water was assumed to be 1.00 g mL^{-1}.
a. Results obtained by the proposed FIA method.
b. Phosphorus found: phosphorus measured divided by concentration factor.

attributed to silicate present in the sample. Silicate could interfere because its concentration in 10^{-1} M H_2O_2 was higher than the tolerable limit (> 4×10^{-7} M). A double peak could occur, because the formation of the ion associate of molybdosilicate-RB was slower than the formation of the ion associate of molybdophosphate-RB.

Determination of phosphorus in ultrapurified and purified water samples

  As mentioned in the sample-preparation section, ultrapurified and purified water samples were concentrated by about 10 fold before measurements. This procedure for ultrapurified water analysis was imperative for the present purpose because the concentration of phosphorus in the carrier stream (ultrapurified water prepared by ELIX 3/Milli Q Element) is identical to that in the ultrapurified water sample, and essentially no peak may occur when the sample, ultrapurified water, is injected in the carrier. The evaporation/concentration method was selected as an suitable enrichment method for phosphorus in ultrapurified water samples, because "a standard reference ultrapure water", which has a certified value for phosphorus, is not currently available. Furthermore, it is very difficult, or impossible, to obtain chemicals, reagents, and solvents that are completely free from phosphorus. Consequently, the enrichment method using some chemicals, reagent, and solvent can not be adopted. This is why a several-fold enrichment method for phosphorus determination in the ultrapurified water samples, which is also used as a carrier, without the addition of any reagents was adopted in this study, as well as in a previous analysis of ultrapurified water.[2,3,22,23]

  During the evaporation of samples, some elements in the samples may be lost because of vaporization of the elements to the air, such as Ti, Ge and Sb.[23,24] To make sure that phosphorus would not be lost during the evaporation/preconcentration step, the recovery test of phosphorus in the evaporation step was examined and the obtained results are given in Table 4. Phosphorus could be recovered in the range of 95% to 106%, which indicates that the contamination from the experimental circumstances or the vaporization of phosphate during the evaporation step was negligible. Also, a repeatability test for the evaporation/concentration procedure was investigated. The obtained results are given in Table 5. From Table 5, it can be concluded that the evaporation procedure was very reproducible, and in that procedure the contamination from the experimental circumstances was negligibly small compared

Table 5   Repeatability test of evaporation/concentration of ultrapurified water samples

Sample taken/mL	Residued sample/g	Concent-ration[a] factor	Phosphorus Measured/10^{-8}	Phosphorus Found/10^{-9}
A 100.00	10.54	9.49	1.08 ± 0.14	1.14
100.00	4.44	22.52	2.77 ± 0.08	1.23
100.00	6.38	15.67	1.88 ± 0.10	1.20
100.00	3.82	26.18	2.67 ± 0.06	1.02
100.00	4.87	20.53	2.77 ± 0.08	1.35
				1.19 (mean value)
B 100.00	7.43	13.46	3.00 ± 0.03	2.22
100.00	11.86	8.43	2.05 ± 0.07	2.43
100.00	11.78	8.49	1.70 ± 0.10	2.00
100.00	10.33	9.68	2.19 ± 0.08	2.26
100.00	8.47	11.81	3.15 ± 0.03	2.67
				2.32 (mean value)

a. The density of water was assumed to be 1.000 g mL^{-1}.

Table 6   Analytical results for the determination of phosphorus as phosphate in purified water samples

Sample[a]		Pretreatment[b]	Phosphorus found[c]/10^{-9} M
Deionized water	A	E/C	6.51 ± 0.06
	B	E/C	7.35 ± 0.04
	C	E/C	9.61 ± 0.07
	A	E/C	7.21 ± 0.08
	B	E/C	5.68 ± 0.04
	C	E/C	6.20 ± 0.08
Ultrapurified water	A	E/C	2.35 ± 0.06
	B	E/C	3.56 ± 0.07
	C	E/C	1.14 ± 0.10

a. Samples were sampled on different dates, and 100 mL of the samples were evaporated to about 10 mL, whose weights were measured by a chemical balance. The density of the residued water was assumed to be 1.000 g mL^{-1}.
b. E/C, evaporation/concentration procedure.
c. Results obtained by the proposed FIA method: mean values of 5-replicate measurements with standard deviations.

Table 7   Effect of the dilution of samples on the determination of phosphorus in H_2O_2 solutions

Dilution factor	Peak height/ mm	Phosphorus measured[a]/ 10^{-7} M	Phosphorus found[b]/ 10^{-4} M
100	Double peak		
200	28.8 ± 0.4	4.55 ± 0.07	0.91
400	17.2 ± 0.2	2.62 ± 0.03	1.05
600	13.2 ± 0.4	1.95 ± 0.07	1.17
800	10.1 ± 0.3	1.43 ± 0.05	1.14
1000	8.3 ± 0.3	1.13 ± 0.05	1.13

Sample, analytical grade of H_2O_2 solution.
a. Results obtained by the proposed FIA method.
b. Phosphorus found: (phosphorus measured) × (dilution factor).

Table 8   Recovery test of phosphorus in an H_2O_2 solutions

Phosphorus added[a]/ 10^{-7} M	Phosphorus/10^{-7} M Measured[b]	Found[c]	Recovery, %
0	3.33 ± 0.06	3.33	—
2	5.45 ± 0.05	3.45	104
4	7.28 ± 0.04	3.28	99
6	9.32 ± 0.03	3.32	100
8	11.25 ± 0.05	3.25	98
10	13.38 ± 0.06	3.38	102

Sample, analytical grade of H_2O_2 solution.
a. Samples were diluted by the factor of 250.
b. Results obtained by the proposed FIA method.
c. Phosphorus found: (phosphorus measured) – (phosphorus added).

with the amounts of phosphorus in the ultrapurified and purified water samples.

Table 6 shows the analytical results for the determination of phosphorus in purified water samples, such as deionized water and deionized/distilled water, as well as ultrapurified water. The phosphorus contents in all water samples examined were at 10^{-9} M levels. However, ultrapurified water contained lower phosphorus contents, compared with other purified water samples. The unavailability of a standard reference material for ultrapurified water, which has a certified phosphorus value, made it difficult to assess the accuracy of these results. However, compared with a reference,[3] where phosphorus in ultrapurified water was found to be about 2×10^{-9} M, the results obtained by the proposed method with fluorescence quenching/FIA method were comparable.

Determination of phosphorus in a hydrogen peroxide solution
In semiconductor industries, large amounts of hydrogen peroxide solutions have been used, and the impurities, especially such as phosphorus, silicon and boron, are the target elements to be analyzed quantitatively, rapidly and simply. For the determination of phosphorus by a conventional

molybdenum blue method, hydrogen peroxide in the sample must be decomposed prior to the measurement, because the oxidizing agent, H_2O_2, can seriously interfere with the coloration of the molybdenum blue.

Aoyagi *et al.* reported an off-line decomposition method for hydrogen peroxide using a heating system with a 20 m PTFE coil (i.d. 1 mm), including a 0.2 mm i.d. × 10 m platinum wire as a catalyst. The sample solutions, whose hydrogen peroxide was decomposed, were analyzed by FIA.[24,25] The decomposition method is time-consuming, and needs the extra system used for a higher temperature (100°C) and the Pt catalyst.

In the proposed FIA method, the reaction necessary for the fluorescence quenching will be less interfered from hydrogen peroxide, because it does not need a "reducing medium". Furthermore, highly diluted samples can be used for the determination of phosphorus in a H_2O_2 solution, because the detection sensitivity of the proposed method is sufficient for measuring phosphate in diluted solutions.

In the present method, hydrogen peroxide samples should be diluted before a measurement with the proposed FIA method. The effect of dilution of the samples for the determination of phosphorus in H_2O_2 solutions was examined; the results obtained are given in Table 7. The results indicate that 100-fold dilution of the samples resulted in double peaks, which were caused by the interference of silicate present in the sample, which was larger than the tolerable limit. Therefore, at least 200-fold dilution is recommended for the measurement of phosphorus in H_2O_2 samples. The recovery test for phosphorus was examined, and the results are given in Table 8. Phosphorus at concentrations of 10^{-7} M levels could be recovered almost

Table 9   Analytical results for the determination of phosphorus in H_2O_2 solutions

	Sample grade[a]	Found[b]/10^{-5} M
A	AR	6.20×0.22
B	AR	10.80×0.12
C	EL	7.93×0.20

a. AR, analytical reagent grade; EL, electronic grade.
b. Results obtained by the proposed FIA method.

completely.

Phosphorus existing as phosphate in a commercially available hydrogen peroxide solution (30%) was diluted by the factor of 200 before a measurement using the proposed FIA system. The obtained results are summarized in Table 9. Compared with the phosphorus contents in ultrapurified water to those in H_2O_2 solutions, it was found that the phosphorus content in H_2O_2 solutions were much higher than and about 10^5 times as much as the phosphorus contents in the ultrapurified and purified water. From these results, it can be predicted that the removal of phosphorus in hydrogen peroxide used for microelectronic industries will become an important topic of advanced research.

Conclusion

Ultratrace amounts of phosphorus in ultrapurified and purified water samples were successfully determined by using a fluorescence quenching FIA method coupled with the evaporation/enrichment method.   Ultrapurified and purified water samples were concentrated by bout 10 fold.   For the determination of phosphorus in H_2O_2 solutions, the samples were diluted by at least 200 fold before measurements. By using the proposed FIA system, trace amounts of phosphorus in hydrogen peroxide solution used in semiconductor industries can be carried out more easily and precisely.

Acknowledgements

References

1. Z. Li, M. Oshima, and S. Motomizu, *J. Flow Injection Anal.*, **2003**, *20*, 197.
2. A. Sabarudin, M. Oshima, N. Ishii, and S. Motomizu, *Talanta*, **2003**, *60*, 1277.
3. A. Sabarudin, M. Oshima, and S. Motomizu, *Anal. Chim. Acta*, **2003**, *481*, 311.
4. H. J. Heckemann, *Anal. Chim. Acta*, **2000**, *410*, 177.
5. C. X. Galhardo and J. C. Masini, *Anal. Chim. Acta*, **2000**, *417*, 191.
6. S. Taguchi, K. Goto, and H. Watanabe, *Talanta*, **1991**, *28*, 613.
7. S. Hoshi, S. Kanagami, M. Uto, and M. Matsubara, *Anal. Sci.*, **1992**, *8*, 103.
8. A. Yuchi, A. Ogiso, S. Muranaka, and T. Niwa, *Anal. Chim. Acta*, **2003**, *494*, 81.
9. K. Itaya and M. Ui, *Anal. Chim. Acta*, **1966**, *14*, 361.
10. S. Motomizu, T. Wakimoto, and K. Toei, *Analyst*, **1983**, *108*, 361.
11. C. Matsubara, Y. Yamamoto, and K. Takamura, *Analyst*, **1987**, *112*, 1257.
12. S. Motomizu, M. Oshima, and K. Araki, *Analyst*, **1990**, *115*, 1627.
13. A. Muñoz, F. M. Torres, J. M. Estela, and V. Cerda, *Anal. Chim. Acta*, **1997**, *350*, 21.
14. N. Goto, S. Motomizu, and M. Oshima, *Bunseki Kagaku*, **1993**, *42*, 151.
15. L. L. Kathryn and E. O. Carolyn, *Anal. Chim. Acta*, **2001**, *450*, 247.
16. J. P. Susanto, M. Oshima, and S. Motomizu, *Analyst*, **1995**, *120*, 187.
17. S. Motomizu, J. P. Susanto, M. Oshima, H. Mikasa, and H. Hori, *Anal. Sci.*, **1995**, *11*, 155.
18. J. P. Susanto, M. Oshima, and S. Motomizu, *Analyst*, **1995**, *120*, 2605.
19. S. Motomizu, H. Mikasa, M. Oshima, and K. Toei, *Bunseki Kagaku*, **1984**, *33*, 116.
20. T. Taniai, M. Sukegawa, A. Sakuragawa, and A. Uzawa, *Talanta*, **2003**, *61*, 905.
21. S. Motomizu, M. Oshima, and N. Katsumura, *Anal. Sci. Tech.*, **1995**, *8*, 843.
22. K. Takeda, S. Ikushima, J. Okuzaki, S. Watanabe, T. Fujimoto, and T. Nakahara, *Anal. Chim. Acta*, **2001**, *426*, 105.
23. K. Takeda, S. Watanabe, H. Naka, J. Okuzaki, and T. Fujimoto, *Anal. Chim. Acta*, **1998**, *377*, 47.
24. M. Aoyagi, Y. Yasumasa, and A. Nishida, *Anal. Sci.*, **1991**, *7*, 347.
25. M. Aoyagi, Y. Yasumasa, and A. Nishida, *Bunseki Kagaku*, **1990**, *39*, 131.