

Chemistry

Analytical Chemistry fields

Okayama University

Year 2003

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Novel Flow Injection-Fluorometric Method for the Determination of Trace Silicate and Its Application to Ultrapurified Water Analysis

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Abstract

A highly sensitive fluorescence quenching method for the determination of silicate based on the formation of an ion associate between molybdosilicate and Rhodamine B (RB) in nitric acid medium was developed. A flow injection system coupled with a fluorescence detector was used for the measurement of fluorescence intensity at 560 nm and 580 nm as excitation and emission wavelengths, respectively. The calibration graph for Si showed a linear range of 0.1 – 5 ng cm⁻³ with correlation coefficient of 0.9989, and the detection limit of 0.06 ng cm⁻³. The proposed method was successfully applied to the determination of silicate in ultrapurified water with satisfactory results.

Keyword : ultrapurified water, ion associate, molybdosilicate, Rhodamine B, flow injection, fluorescence quenching.

Introduction

The cleaning and etching processes in the manufacturing of high technology products such as semiconductors, data storage media, printed wiring board, etc consume significant amounts of ultrapurified water (UPW). The use of UPW helps to fulfill two main objectives, namely production of high quality products and minimization of rejects. Consequently, the need for more sensitive and accurate measurements of impurities in UPW has seen a rapid increase. Silicate is one of the most important substances for silicon surface reaction. The desired impurity level for Si in UPW used for high-tech products is currently less than 1 ng cm⁻³. Therefore, the analytical methods employed should accurately determine 0.1 ng cm⁻³ of Si.

The formation of an ion associate between molybdosilicate and cationic dyes has been successfully used to increase sensitivity for the determination of silicate. Motomizu *et al.* developed several spectrophotometric methods for highly sensitive determination of silicate based on the formation of an ion associate between molybdosilicate and Malachite Green (MG) by flotation-extraction method [1], flotation-dissolution and filtration-dissolution method [2], flotation-exchange-extraction method [3] and filtration-concentration

of the ion associate on a tiny membrane filter [4]. The filtration-concentration method with tiny membrane filter was also applied to the trace determination of phosphorus [5,6]. Takaku *et al.* [7] reported High Resolution ICP-MS (HR-ICP-MS) method for the determination of silicate in ultra-high-purity water. However, water samples had to be concentrated/evaporated to at least ten-fold to achieve satisfactory quantitative measurement, and the serious mass spectrometric (isobaric) interferences on all the Si isotopes were observed. Takeda *et al.* [8,9] also applied ICP-MS for the determination of ultra-trace elements in electronic-grade water, in which samples had to be concentrated by a non-boiling evaporation technique (500 cm³ to 5 cm³), and polyhydric alcohol (dulticol) was added to the samples to prevent vaporization loss of analytes such as Ti, Ge and Sb. Yoshimura and Hase [10] reported a flow analysis for the determination of silicate in highly purified water : the method was based on the adsorption of an ion associate on the Sephadex LH-20 gel. The method produced sensitive analytical results with the detection limit of 0.1-0.2 ng cm⁻³. However, the sample preparation was time consuming (1 day) and very complicated, including the addition of very high concentration of reagents (ammonia and sulfuric acid) before evaporation and suffering from an increase in

the reagent blank.

Chu and Balazs [11] developed three different analytical techniques, ICP-AES, ICP-MS and colorimetry with cold acid digestion, for the determination of silicate in high-purity water. With at least ten-fold concentration of the sample, the detection limits obtained for the ICP-AES and ICP-MS were 3 ng cm^{-3} and 1 ng cm^{-3} , respectively. Samples for colorimetry were concentrated to 20-fold and gave the detection limit of 0.25 ng cm^{-3} .

Motomizu *et al.* reported highly sensitive fluorophotometric methods for the determination of phosphate coupled with flow-injection technique. The method which was based on the formation of an ion associate of molybdophosphate with Rhodamine 6G gave the limit of detection (LOD) of about 0.1 ng cm^{-3} [12]. The method was improved by using Rhodamine B (RB) and applied successfully to the determination of phosphate in sea water [13].

In this paper, we propose a fluorescence quenching/flow-injection method for the determination of ultratrace amounts of silicate in ultrapurified water based on the formation of an ion associate of molybdosilicate with RB. The adopted wavelengths for the fluorescence measurement were 560 nm for excitation (λ_{ex}) and 580 nm for emission (λ_{em}), respectively. The detection limit was 0.06 ng cm^{-3} .

It is the first time for the determination of Si by fluorescence quenching/FIA with simple procedure, and to the best of our knowledge more sensitive than any other method already reported.

Experimental

Reagents. All chemicals used were of analytical-reagent grade or the highest-quality commercially available grade, and ultrapurified water treated with ELIX 3 / Milli Q element (Nihon Millipore, Tokyo) was used throughout. Hexaammonium heptamolybdate tetrahydrate (Wako Pure Chemical, Osaka) and ultrapure grade of nitric acid (Kanto Chemical, Tokyo) were used.

Standard silicate solution. A commercially available silicate standard solution for AAS (1000 mg dm^{-3} , Wako Pure Chemicals, Osaka) was used. The working solutions were prepared daily by accurate dilution with ultrapurified water.

Reagent solution 1 (RS1). The RS1 containing 0.01 mol dm^{-3} Mo, $0.025 \text{ mol dm}^{-3}$ HNO_3 , and 0.01% polyvinyl alcohol (PVA) was prepared as follows. Hexaammonium heptamolybdate tetrahydrate, $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}$ (1.77 g) was dissolved in about 500 cm^3 ultrapurified water, to which concentrated nitric

acid (1.9 cm^3) and PVA (100 cm^3 of 0.1% w/v) were added and made up to 1000 cm^3 by ultrapurified water. Before use, PVA solution was filtered through a cellulose membrane filter (pore size, $0.45 \mu\text{m}$; diameter, 25 cm).

Reagent solution 2 (RS2). The RS2 containing $6 \times 10^{-7} \text{ mol dm}^{-3}$ RB and $0.006 \text{ mol dm}^{-3}$ oxalic acid was prepared as follows. 10 cm^3 of RB solution ($0.0015\text{g C}_{28}\text{H}_{31}\text{O}_3\text{N}_2\text{Cl}/100\text{cm}^3$) and 100 cm^3 of oxalic acid solution ($0.7564\text{g (COOH)}_2 \cdot 2\text{H}_2\text{O}/100 \text{ cm}^3$) were transferred into 1000 cm^3 polypropylene calibrated flask and diluted to the mark with ultrapurified water. The solution was filtered through a cellulose membrane filter (pore size, 0.45 mm ; diameter, 25 cm) prior to use.

Apparatus. Figure 1 shows the flow injection manifold used in this study. The system was constructed by two double-plunger pumps PD-4000 (F.I.A. Instruments, Tokyo) and a fluorescence detector RF-10A XL equipped with a micro flow cell, $12 \mu\text{l}$ (Shimadzu, Kyoto). Flow lines were made of PTFE tubing (0.5 mm and 0.25 mm i.d.), and T-pieces made of PEEK were used as a mixing joint. The temperature controller, reactor 521, (F.I.A. Instruments, Tokyo) was used at RC1 (Fig.1). Flow signals were recorded with a Toa FBR-1 recorder.

Results and Discussion

Fundamental flow studies

Two- and three-channel systems were investigated. A two-channel system was examined by two different procedures. First, sample solutions were injected into carrier stream of ultrapurified water, which merged with a reagent solution containing molybdate, nitric acid, PVA, RB, and oxalic acid in reaction coil (0.5 mm i.d ; 8 m). Secondly, sample solutions were injected into a carrier stream containing an acidic molybdate solution. Then, the molybdosilicate formed reacted with the reagent solution containing RB, oxalic acid, and PVA to form the ion associate. In both procedures, the reaction coil was kept in a temperature controller and the ion associate was detected at $\lambda_{\text{ex}} = 560 \text{ nm}$ and $\lambda_{\text{em}} = 580 \text{ nm}$.

[The two-channel system generally showed poor sensitivity and reproducibility.](#)

For three-channel system examination as shown in Fig.1, sample solutions were injected into a carrier stream (CS) of ultrapurified water and merged with a RS1 stream to form molybdosilicate in RC1 (0.5 mm i.d ; 8 m). The RC1 was kept in the temperature controller at 100°C. Then, the molybdosilicate formed was merged with a RS2 stream to form the ion associate in RC2 (0.5 mm i.d. ; 2m). The fluorescence quenching was detected at $\lambda_{\text{ex}} = 560 \text{ nm}$ and $\lambda_{\text{em}} = 580 \text{ nm}$.

This system showed the best fluorescence signals, and was adopted for further experiments.

Experimental variables for the formation of ion association

Medium acidity was examined by using sulfuric acid and nitric acid. Nitric acid was selected because of a lower value of a reagent blank (background), a higher fluorescence signals and better linearity of a calibration graph.

The effect of nitric acid concentration was examined, and the results obtained are shown in Fig.2. The best linearity of the calibration graph and the largest difference in fluorescence intensity between the background and the samples, which corresponds to peak height of negative peaks, were achieved when $0.025 \text{ mol dm}^{-3}$ nitric acid was used. Therefore, $0.025 \text{ mol dm}^{-3}$ nitric acid was adopted. Higher concentration of nitric acid resulted in shorter peak heights because RB is converted into a protonated orange cation by an excess of nitric acid which resulting in decrease of fluorescence intensity. Decrease in fluorescence intensity at lower concentration of nitric acid was due to incomplete formation of molybdosilicate.

The effect of molybdate concentration was also examined by varying its concentrations from 0.006 to 0.02 mol dm^{-3} as shown in Fig.3. The fluorescence

intensity between the background and the linearity of calibration graph were improved with increasing molybdate concentrations from 0.006 to 0.01 mol dm⁻³. At higher concentration (> 0.01 mol dm⁻³), the baseline became very noisy, shorter peak heights, and the linearity of 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 inner surface of PTFE reaction coil. In this work, 0.01 mol dm⁻³ of molybdate was selected as an optimum concentration.

The fluorophotometric and spectrophotometric methods of silicate, as well as phosphate [12-14, 16-17,21] based on the formation of the ion associate between heteropolyacid anions and a cationic dye were very sensitive, however, the ion associates tend to precipitate and adsorb on the reaction coil and flow cell. To prevent these adsorptions, PVA was added to RS1 to stabilize the ion associate in the flow stream and to avoid the baseline drift. In this paper, 0.01% PVA was chosen as an optimum concentration with respect to the linearity of the calibration graph and low baseline noise. When the concentration of PVA was higher than 0.01%, the solution became more viscous resulting in reduced stability of background and poor linearity of the calibration graph.

The effect of RB concentration in RS2 was investigated by varying its concentration from 3×10^{-7} – 9×10^{-7} mol dm⁻³. The results showed that an increase in RB concentration, produced an increase in the fluorescence intensity as shown in Fig.4. However, the baseline became increasingly noisy and the reproducibility of the peaks became unsatisfactory. Therefore, 6×10^{-7} mol dm⁻³ RB was adopted as a compromise.

Molybdate can also react with phosphate under acidic condition. Interference from phosphate was eliminated by the addition of oxalic acid, which decompose any molybdophosphate. Oxalic acid can react with the excess of molybdate to form colorless molybdenum oxalate without affecting the molybdosilicate formation. 0.006 mol dm⁻³ of oxalic acid was found sufficient for the elimination of the effect of phosphate which is reported to be present at about 0.06-0.07 ppb as phosphorus in ultrapurified water [15].

Experimental variables for the flow injection system

The effect of temperature in RC1 on the formation of molybdosilicate was examined. Silicate present at sub-ppm levels did not form molybdosilicate at temperatures below 40°C. [As the temperature is raised above 40°C, There is a](#)

gradual increase in the amount of molybdosilicate which reach the required value at about 100°C [14,18]. The effect of temperature was examined from 40°C to 110°C and the results were displayed in Fig.5. The higher the temperature, the more extensive the formation of the molybdosilicate, and also the more accelerated the conversion rate of an unstable β -molybdosilicate to a stable α -molybdosilicate. In this work, the adopted temperature was 100°C, as a compromise for acceptable reproducibility of peaks and the baseline noise. The RC2 was kept at room temperature because the formation of the ion associate was much faster than that of molybdosilicate.

Effect of flow rate of the pump P1, which propelled the molybdate solution and the carrier, was investigated by varying the flow rate from 0.5 to 0.9 cm³ min⁻¹. Higher peak heights were obtained when lower flow rate was used. This is because the formation of molybdosilicate proceeded more completely and there was less dispersion of silicate. However, it took very long time for analysis. As a compromise of the analysis time and the sensitivity, 0.7 cm³ min⁻¹ was adopted. The flow rate of the pump P2, which delivered the RB solution, was also investigated by varying the flow rate from 0.4 to 1.0 cm³ min⁻¹. The peak height increased gradually from 0.4 to 0.7 cm³ min⁻¹, and the highest peak height was

achieved at the flow rate of 0.7 to 0.8 cm³ min⁻¹. In further experiments, 0.7 cm³ min⁻¹ was selected as an optimum flow rate for pump P2.

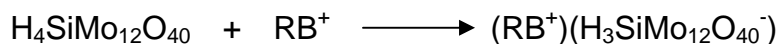
The effect of the sample volume was examined by varying the volume of sample loops from 100 to 500 mm³. The peak height increased as the injected volume increased from 100 to 400 mm³, and reached nearly constant height from 400 to 500 mm³. As the results, 400 mm³ was selected as an optimum sample volume.

The PTFE tubing (0.5 mm i.d ; 8 m) was sufficient for the completion of the molybdosilicate formation in RC1. The length of the RC2 was one fourth of the RC1 (0.5 mm i.d ; 2 m) because the ion associate formation is much faster than molybdosilicate formation.

The conditions optimized for the determination of silicate were summarized in Table 1.

Flow signals, calibration graph and detection limit

Figure 6 showed typical flow signals for silicate obtained by the proposed method. The reaction of molybdosilicate with RB resulted in negative peaks, which were due to the fluorescence quenching of RB. The possible reaction mechanism is :



The calibration graph showed a good linearity from 0.1 to 5 ng cm⁻³ of Si with equation, $Y = 10.378X + 2.523$, where Y is peak height (mm) and X is the concentration of silicate in ng cm⁻³. The correlation coefficient was 0.999 and the relative standard deviation of 6 measurements with 2 ng cm⁻³ silicate solution was 1.04 %. The sampling rate was 12 samples/h.

The detection limit attained by the proposed method was 0.06 ng cm⁻³, as determined by the equation : $\text{LOD} = 3.3(\sigma/S)$ where (σ) is the standard deviation of the response and (S) is the slope of the calibration graph. The standard deviation of the response can be determined based on the standard deviation of the blank or the standard deviation of Y intercept of the regression line. This calculation method can reduce the bias which sometimes occurs when the detection limit is determined by using signal-to-noise ratios (S/N).

Interference from arsenate and phosphate

In the most cases, the amounts of interfering ions present in ultrapurified water are very small and can be assumed as tolerable/negligible. For example, the concentration of some anions e.g. Cl^- , NO_2^- , Br^- , NO_3^- and SO_4^{2-} in

ultrapurified waters appear in the range of 0-9 pg cm^{-3} . The range of concentrations of some metals, such as Li, Na, Mg, Al Cr, Mn, Fe, Co, Ni, Cu, and Pb is 0.034-0.94 pg cm^{-3} , while K, Ca and Zn are present in the range 4.4-6.8 pg cm^{-3} [19, 20]. From these data, it can be expected that there is no interference from coexisting ions in ultrapurified water.

Phosphate and arsenate can form molybdophosphate and molybdoarsenate under similar conditions of this method, and can form an ion associate with RB.

Effect of arsenate on the determination of silicate was examined by varying its concentrations from 0 to 2 ng cm^{-3} . The result showed no interference from arsenate (the concentration of arsenate in ultrapurified water is lower than 0.01 ng cm^{-3}).

Effect of phosphate was similarly examined by varying its concentrations as phosphorus from 0 to 1 ng cm^{-3} where the sample contained 1 ng cm^{-3} of Si. The results indicated that there was no interference from phosphate. When Si was not added to the samples (the reagent blank), 0.3 ng cm^{-3} of phosphorus did not give any error. As a result, the effect of phosphate on silicate determination can be neglected because phosphorus in ultrapurified water was present in the concentration range of 0.06-0.07 ng cm^{-3} .

Sample enrichment method

All ultrapurified water samples were concentrated by evaporation before analysis. This procedure was imperative for the present purpose because concentration of silicate in the carrier stream (ultrapurified water prepared by ELIX 3 / Milli Q Element) was nearly the same (identical) as that in the ultrapurified water samples. Besides being used as carrier stream, the ultrapurified water prepared by ELIX 3 / Milli Q element, was also used as a sample solution as well as in the preparation of chemical reagents. The evaporation/concentration method was selected as an enrichment method for silicate in ultrapurified water samples, because “a standard reference ultrapurified water”, which has a certified value for silicate, is not currently available. Furthermore, it is very difficult or impossible to obtain chemicals, reagents, and solvents which are completely free from silicate. Consequently, an enrichment method which uses some chemicals, reagent and solvents can not be adopted. This is why a several-fold enrichment method for silicate in ultrapurified water samples without the addition of any reagents was adopted in this study, and probably in all previous analysis of ultrapurified water [7-11].

Ultrapurified water samples were transferred into clean PTFE beakers and

kept in a small evaporation chamber on a hot plate. During the evaporation, nitrogen gas was delivered into the chamber. The evaporation chamber used in this work was an almost closed system, which had only 2 small holes for the flow of N₂ in and out. By using this system, the contamination from the atmosphere was avoided. All procedures were carried out in a class 100 clean room. Only two-fold concentration was sufficient for the proposed method, which resulting in excellent sensitivity (LOD : 0.06 ng cm⁻³ of Si).

To evaluate the original concentration of silicate in ultrapurified water samples, we define concentration factor (F) as follows ;

$$F = x_0/x \quad (1),$$

where x_0 is an initial mass of the sample and x is a final mass of the sample after evaporation. The relationship between the original concentration (C_0) and the observed concentration after the evaporation (C), which can be calculated by using calibration graph, is represented in the following equation ;

$$C + a = fC_0 \quad (2),$$

where a is the concentration of silicate in the carrier stream (background). In which a sample is the same as the water in a carrier stream, equation 2 can be modified to ;

$$a = C_o = C/(f-1) \quad (3)$$

In this work, equation 3 was applied to evaluate the silicate concentration in ultrapurified water prepared by ELIX 3 / Milli Q Element.

Determination of silicate in ultrapurified water

The proposed method was applied to the determination of silicate in ultrapurified waters prepared by ELIX 3/Milli Q Element, Milli Q-Labo, and YAMATO Millipore WQ 500. The results obtained were shown in Table 2. All the ultrapurified waters were sampled in our laboratory on July 17th, 2002. The samples were treated as described in a sample enrichment method before injection into the carrier stream. [On the basis of the reproducibility test by using the same sample, the proposed method can be declared to be highly reliable and accompanied by good precision.](#) Unavailability of the standard reference material for ultrapurified water which has certified silicate value makes it difficult to assess the accuracy of this method. [However, by comparing the various analytical methods for the determination of silicate in ultrapurified water as shown in Table 3, it can be concluded that the proposed method exhibits better accuracy and higher sensitivity than any other method previously reported.](#)

Acknowledgement

The present work was partially supported by Grant-in-Aid for Scientific Research (B) No. 13440220 from Japan Society for the Promotion of Science (JSPS), Japan, and by the Venture Business Laboratory of Okayama University.

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Figure captions

Fig.1 Flow injection manifold for silicate determination

CS : ultrapurified water (ELIX 3/Milli Q Element) ;

RS1 : 0.01 mol dm^{-3} Mo, $0.025 \text{ mol dm}^{-3}$ HNO₃, and 0.01% PVA ;

RS2 : $6 \times 10^{-7} \text{ mol dm}^{-3}$ RB and $0.006 \text{ mol dm}^{-3}$ Oxalic acid ;

P1, P2 : double plunger pump , $0.7 \text{ cm}^3 \text{ min}^{-1}$;

RC1 : 0.50 mm i.d., 8m ; RC2 : 0.5 mm i.d., 2m ;

BPC : 0.25 mm i.d , 0.3m ; CC : 0.5 mm i.d, 1m ;

D : fluorescence detector (λ_{ex} 560 nm , λ_{em} 580 nm) ; R : recorder.

W : waste

Fig.2 Effect of nitric acid concentration on the linearity of calibration graphs

Mo : 0.01 mol dm^{-3} , PVA : 0.01% , RB : $6 \times 10^{-7} \text{ mol dm}^{-3}$, oxalic acid : $0.006 \text{ mol dm}^{-3}$, P1 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, P2 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, T : 100°C , sample volume : 300 mm^3 . (1) $0.025 \text{ mol dm}^{-3}$ HNO₃ , (2) $0.050 \text{ mol dm}^{-3}$ HNO₃ , (3) 0.10 mol dm^{-3} HNO₃. The linear correlation coefficients of (1), (2), (3) are 0.999 , 0.998 , 0.996 , respectively.

Fig.3 Effect of molybdate concentration on the linearity of calibration graphs

HNO₃ : $0.025 \text{ mol dm}^{-3}$, PVA : 0.01% , RB : $6 \times 10^{-7} \text{ mol dm}^{-3}$, oxalic acid : $0.006 \text{ mol dm}^{-3}$, P1 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, P2 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, T : 100°C , sample volume : 300 mm^3 . (1) $0.006 \text{ mol dm}^{-3}$ Mo , (2) $0.010 \text{ mol dm}^{-3}$ Mo , (3) 0.02 mol dm^{-3} Mo. The linear correlation coefficients of (1), (2), (3) are 0.998 , 0.999 , 0.992 , respectively.

Fig.4 Effect of Rhodamine B (RB) concentration on the linearity of calibration graphs

HNO_3 : $0.025 \text{ mol dm}^{-3}$, Mo : 0.01 mol dm^{-3} , PVA : 0.01% , oxalic acid : $0.006 \text{ mol dm}^{-3}$, P1 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, P2 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, T : 100°C , sample volume : 300 mm^3 . (1) $3 \times 10^{-7} \text{ mol dm}^{-3}$ RB , (2) $6 \times 10^{-7} \text{ mol dm}^{-3}$ RB , (3) $9 \times 10^{-7} \text{ mol dm}^{-3}$ RB. The linear correlation coefficients of (1), (2), (3) are 0.997 , 0.999 , 0.990 , respectively.

Fig.5 Effect of temperature on the linearity of calibration graphs.

HNO_3 : 0.05 mol dm^{-3} , Mo : 0.01 mol dm^{-3} , PVA : 0.005% , RB : $6 \times 10^{-7} \text{ mol dm}^{-3}$, oxalic acid : $0.006 \text{ mol dm}^{-3}$, P1 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, P2 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, sample volume : 300 mm^3 . (1) 40°C , (2) 60°C , (3) 90°C , (4) 100°C , (5) 110°C . The linear correlation coefficients of (1), (2), (3), (4), (5) are 0.991, 0.993 , 0.995 , 0.997, 0.996, respectively.

Fig. 6 Flow signals for the determination of silicate by fluorescence quenching-FIA .

HNO_3 : $0.025 \text{ mol dm}^{-3}$, Mo : 0.01 mol dm^{-3} , PVA : 0.01% , RB : $6 \times 10^{-7} \text{ mol dm}^{-3}$, oxalic acid : $0.006 \text{ mol dm}^{-3}$, P1 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, P2 : $0.7 \text{ cm}^3 \text{ min}^{-1}$, sample volume : 300 mm^3 , carrier : ultrapurified water prepared by ELIX 3 / Milli Q Element.

Figure and table

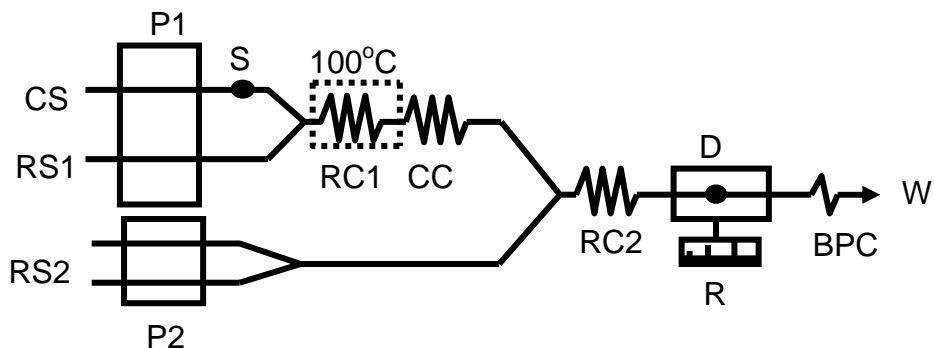


Fig.1 Flow injection manifold for the determination of silicate

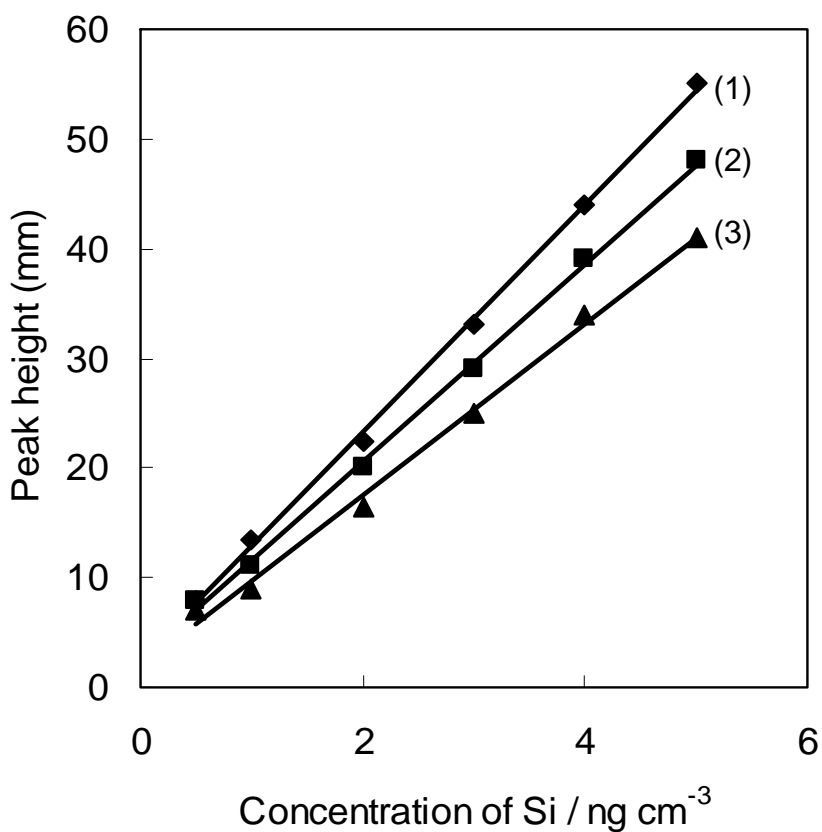


Fig.2 Effect of nitric acid concentration on the linearity of calibration graphs

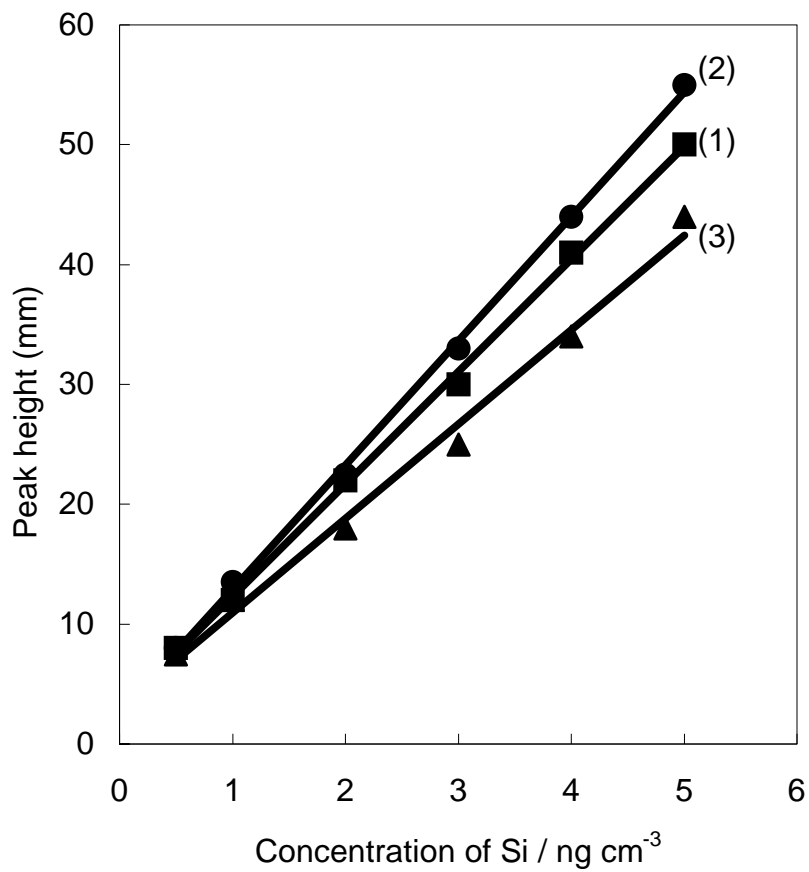


Fig.3 Effect of molybdate concentration on the linearity of calibration graphs

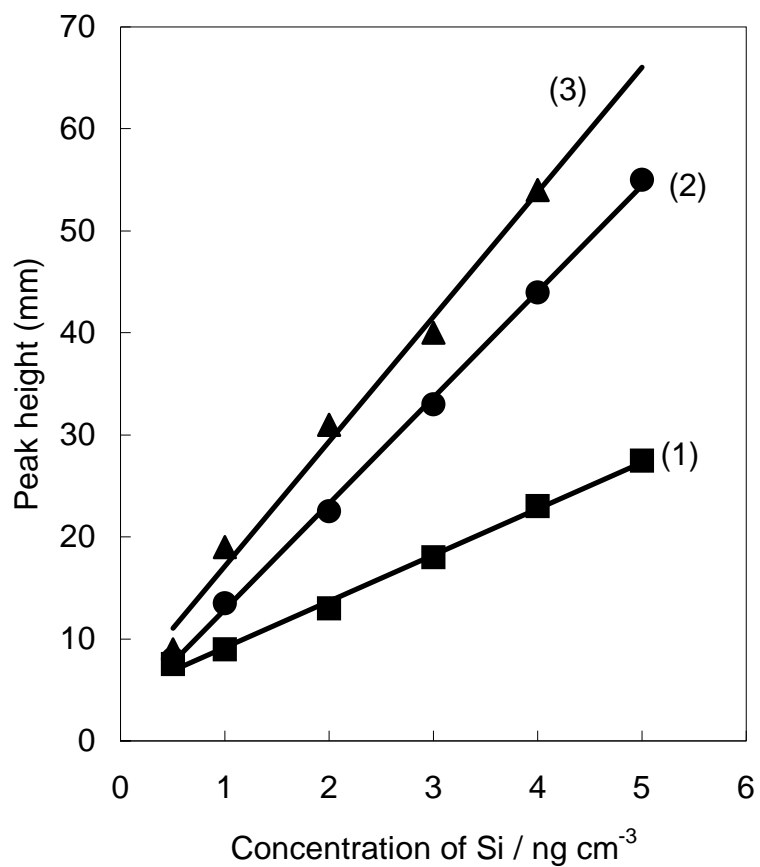


Fig.4 Effect of Rhodamine B concentration on the linearity of calibration graphs

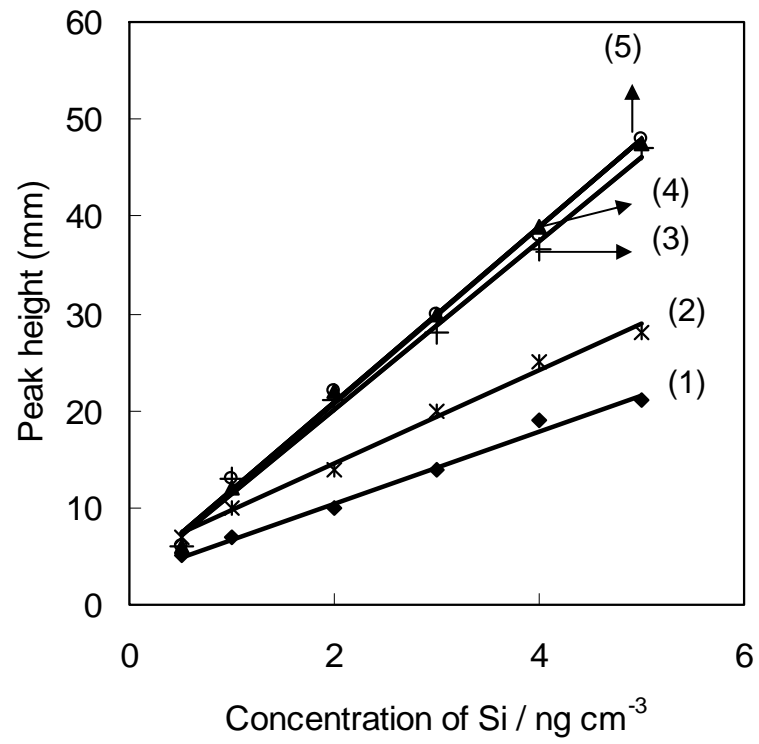


Fig.5 Effect of temperature on the linearity of calibration graphs

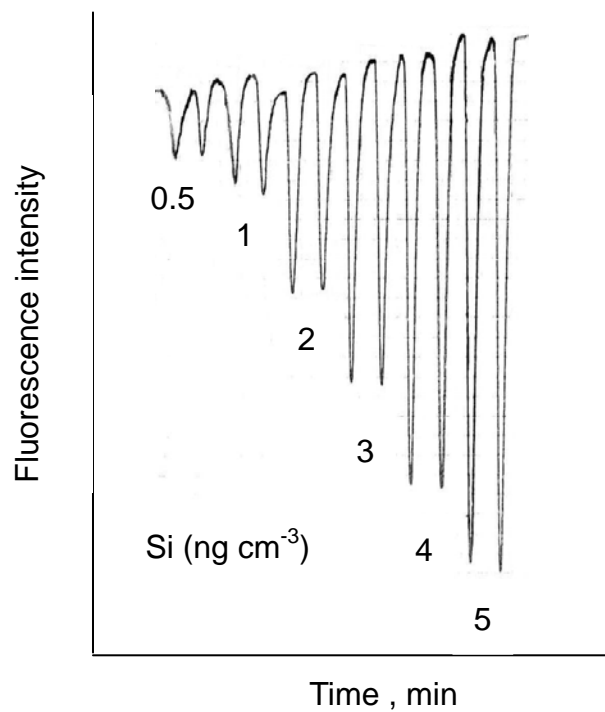


Fig. 6 Flow signals for the determination of silicate by fluorescence quenching-FIA

Table 1 Conditions adopted for the determination of silicate in ultrapurified water

Carrier solution	Water (ELIX 3 / Milli Q Element)
Reagent solution 1 (RS1)	0.01 mol dm ⁻³ Mo + 0.025 mol dm ⁻³ HNO ₃ + 0.01% PVA
Reagent solution 2 (RS2)	6 x 10 ⁻⁷ mol dm ⁻³ RB + 0.006 mol dm ⁻³ oxalic acid
Flow rate of pump1 (P1)	0.7 cm ³ min ⁻¹
Flow rate of pump 2 (P2)	0.7 cm ³ min ⁻¹
Temperature of reaction coil 1 (RC1)	100°C
Sample volume	400 mm ³
Reaction coil 1 (RC1)	0.5 mm i.d. x 8 m PTFE tubing
Reaction coil 2 (RC2)	0.5 mm i.d. x 2 m PTFE tubing
Cooling coil (CC)	0.5 mm i.d. x 1 m PTFE tubing
Back pressure coil (BPC)	0.25 mm i.d. x 0.3 m PTFE tubing
Wavelength	λ_{ex} : 560 nm ; λ_{em} : 580 nm

Table 2 Analytical results for the determination of silicate in ultrapurified water

Sample	Replication	Concentration factor	Si found / ng cm^{-3}	Mean value / ng cm^{-3}
Ultrapurified water 1 ^{*a}	1	2.2655	0.41	0.41 \pm 0.02
	2	2.2333	0.39	
	3	5.4620	0.43	
Ultrapurified water 2 ^{*b}	1	2.3682	0.87	0.94 \pm 0.05
	2	2.3300	0.97	
	3	5.1025	0.98	
Ultrapurified water 3 ^{*c}	1	2.5442	0.42	0.44 \pm 0.02
	2	2.2890	0.46	
	3	5.2892	0.45	

*a : Prepared by ELIX 3 / Milli Q Element

*b : Prepared by Milli Q labo

*c : Prepared by YAMATO Millipore WQ 500

These ultrapurified waters were sampled at Laboratory of Analytical Chemistry, Okayama University on July 17th, 2002.

Table 3 Comparison of the various analytical methods for the determination of silicate in ultrapurified water.

Method	Sample pretreatment ^{*a}	Minimum concentration factor	Detection limit / ng cm^{-3}	Range of Si concentration found ^{*b} / ng cm^{-3}	Reference
ICP-AES	C/E	10	3	0.2-0.9	11
ICP-MS	C/E	10	1	0.2-0.9	11
Colorimetry	C/E	20	0.25	0.2-0.9	11
HR-ICP-MS	C/E	10	-	0.5-1.0	7
Gel-phase absorptiometry	C/E	>10	0.1-0.2	0.3-0.9	10
Flow injection-fluorophotometry	C/E	2	0.06	0.4-0.9	This work

*a: C/E : concentration/evaporation

*b: The range of Si concentration in various ultrapurified water samples.