Slope comparison method (SCM) for the determination of trace amounts of silicate in ultrapurified water

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SLOPE COMPARISON METHOD (SCM) FOR THE DETERMINATION OF TRACE AMOUNTS OF SILICATE IN ULTRAPURIFIED WATER

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ABSTRACT

A sensitive analytical method for the determination of trace amounts of silicate in ultrapurified water was developed. The method is based on the formation of an ion associate of molybdosilicate with Malachite Green (MG) and the collection of the ion associate on a tiny membrane filter (diameter : 5 mm, and effective filtering diameter : 1 mm). The ion associate formed on the membrane filter is dissolved together with the membrane filter in 1 ml of methyl cellosolve (MC) and the absorbance of MC solution is measured at 627 nm by a flow injection-spectrophotometric detection technique. In this method, silicate in the original sample (ultrapurified water) is concentrated as the ion associate into a small volume of MC to get high sensitivity. As sample concentration takes place, the small amounts of silicate contained in the reagents used also become concentrated as the ion associate into MC. The original sample volumes are varied and evaporated to an identical volume. Therefore, the reagent added is fixed to the same volume. The absorbance increase linearly with increase in the original sample volume will be due only to silicate in the original samples (ultrapurified water). The resulting slopes obtained by varying the sample volumes are compared with the slope of the calibration graph, and thus named the slope comparison method (SCM). The SCM facilitates a more sensitive and accurate evaluation of silicate concentration in the samples than either common calibration method (CCM) or standard addition method (SAM) because it compensates for the influence of trace amounts of silicate contained in chemicals, reagent solution and solvent used. The calibration graph was constructed from 0 to 0.25 ng ml^{-1} of Si and the detection limit was 10 pg ml^{-1} (ppt) when 30 ml of samples was used. The standard deviation and relative standard deviation from six measurements of the reagent blanks were 0.0012 and 3.5%, respectively.

Keyword: Slope comparison method, ultrapurified water, ion associate, molybdosilicate, malachite green, membrane filter.

Introduction

In various advanced fields, such as material science, environmental science and bioscience, the improvement of sensitivity, precision and accuracy in chemical analysis methods is one of the most important areas in their advancements. The use of ultrapurified water is of crucial importance for cleaning and etching semiconductors in microelectronic industries [1]. The world market for ultrapurified water (UPW) is estimated at around US$ 2.3 billion per year [2] and is expected to grow to US$ 2.6 billion by 2006 [3]. In the semiconductor industry, a large bulk of UPW is required in the manufacture of high-quality semiconductors [4], thereby creating a growing demand for sensitive and accurate determination of trace and ultratrace amounts of impurities, such as boron, phosphate and silicate [5-7]. The desired impurity level for Si in semiconductor grade UPW is less than 1 ng ml^{-1} and expected to be further lowered in the near future. Therefore, a highly sensitive analytical method for controlling Si levels in ultrapure water, with the capability of determining 0.1 ng ml^{-1} Si is required [8].

Chu and Balazs [9] developed and evaluated three different analytical methods for the determination of silicate in UPW. These methods were based on ICP-AES, ICP-MS, and spectrophotometry coupled with cold acid digestion. The detection limits obtained for the ICP-AES and ICP-MS were 3 ng ml^{-1}and 1 ng ml^{-1}, respectively, after ten-fold enrichments of the sample by evaporation. Samples for spectrophotometry were concentrated at least 20-fold by evaporation before analysis; the detection limit of the spectrophotometric method was found to be 0.25 ng ml^{-1}. The flow analysis for the determination of silicate in highly purified water by gel-phase spectrophotometry has also been reported [10]; the method was based on the adsorption of the ion associate of molybdosilicate with Malachite Green (MG) on the Sephadex LH-20 gel. A sensitive analytical result for Si was obtained with detection limit of 0.1 ng l^{-1}. Ion exclution chromatography with conductivity detection [11] for the determination of silicate was also reported. Alhough the detection limit was about 36 ng ml^{-1}, it is not sufficiently sensitive to be applied for UPW analysis because silicate in an eluent was retained and eluted, and sometime big system peaks and silicate peak appeared at the same retention time.

The formation of an ion associate between molybdosilicate and cationic dyes has been successfully used to increase detection sensitivity for the determination of silicate [12-16]. Motomizu *et.al*. [17-18] have reported a highly sensitive spectrophotometric method for the determination of silicate as well as phosphate at sub-ppb and ppt levels using relatively small volumes of sample solutions, an organic solvent (methyl cellosolve : MC) for dissolution of the ion associates, and a tiny membrane filter for collecting the ion associate of molybdosilicate with Malachite Green. The absorbance was measured by a flow injection-spectrophotometric detection method, which is relatively simple and shows excellent sensitivity and LOD. However, trace- and ultra-trace amounts of silicate in ultrapurified waters cannot be determined because “ the standard certified ultrapurified water “, “the silicate-free water “ or “the purified water containing negligibly small amount of silicate compared with the samples” are not currently available.

In this paper, a highly sensitive method for the determination of ultratrace amounts of silicate in ultrapurified water is proposed. It involves improving the previous method [17-18] and coupling the improved method with an evaporation of ultrapurified water under flowing clean air and/or nitrogen gas. Since the calibration strategy undertaken affects the precision and accuracy of analytical results, we applied the slope comparison method (SCM) [19] to silicate determination in the present study; the method was originally developed to determine trace emounts of phosphate in ultrapurified water and has enable evaluation of silicate concentration in ultrapurified water with higher sensitivity and accuracy than the conventional common calibration method (CCM) and standard addition method (SAM). In the SCM, the influence of trace amount of silicate arising from chemicals, reagent solutions and the solvent added to samples can be fully compensated.

Experimental

Reagents

Ultrapurified water was prepared by an ELIX 3 / Milli Q Element System (Nihon Millipore, Tokyo), and was used as a sample solution, and reagent solution preparations. Ammonium heptamolybdate tetrahydrate purchased from Wako Pure Chemicals (Osaka) was used to prapare a 0.52 mol l^{-1} of molybdate solution. A stock solution of Si (1000 mol l^{-1}) was a commercially available standard for AAS (Wako Pure Chemicals, Osaka), and working solutions were prepared by accurate dilution of the stock solution with the ultrapurified water. A concentrated sulfuric acid was purchased from Kanto Chemical Co. Ltd (Tokyo) for preparation of a 1.7 mol l^{-1} sulfuric acid solution. Malachite Green oxalate (Tokyo Kasei Kogyo, Tokyo) was used to prepare a 3.4×10^{-4} mol l^{-1} Malachite Green solution in a 6.1 mol l^{-1} sulfuric acid. After standing this solution for 12 h, it was filtered through a cellulose nitrate membrane filter (pore size 0.45 μm ; diameter 25 mm) under suction to remove trace amounts of silicate, which may be present as a contaminant in the chemicals used.

Apparatus

The filtration-preconcentration apparatus used in the present work is assembled with a plastic syringe, a three-way valve, a filtering housing, an upper and lower filtering supporter as shown in Fig. 1. All parts of the filtering apparatus were made of plastics. The present apparatus was different from that used in the previous work [15] by some modifications: the effective filtering diameter was reduced from 2 mm to 1 mm. Furthermore, a lower filtering supporter was changed from a simple pinhole type to a pinhole with several radial grooves, which accelerated the flowing of filtrate and resulted in better filtration efficiency. The filtration was carried out by suction with an aspirator. A membrane filter with a diameter of 5 mm and an effective filtering diameter of 1 mm, prepared by punching a commercially available cellulose nitrate membrane (45 mm diameter; Advantec Toyo, Tokyo) with a steel punch (5 mm diameter), was placed on the filtration apparatus. The diameter of membrane filter was much smaller than those used in common filtration methods, resulting in more effective enrichment and a lower reagent blank.

A simple flow injection system used in this work was the same as that used in the previous work [15]. A double-plunger micropump (DMX-2000, Sanuki Kogyo) was used for propelling a carrier of MC at a flow rate of 0.5 ml min^{-1}. A six-way valve (SVM-6M2, Sanuki Kogyo) connected with PTFE tubing (0.5 mm i.d.) was used for injecting samples of 200 μl. The absorbances at 627 nm were measured with a Soma Kogaku S-3250 spectrophotometer equipped with an 8-μl flow cell (optical path length, 10 mm) and recorded with a Ross Model 201/B-1278 recorder (Topac, Massachusetts, USA)

PTFE beakers (100 ml) were used as evaporating vessels for ultrapurified water samples.

Sample Preparation

Aliquots, 15-60 ml of ultrapurified water samples, were transferred into the

PTFE beakers, placed in an evaporation chamber (Sanai Kagaku, Nagoya). Then the samples were evaporated to 5 ml or to near dryness. While the evaporation was taking place, nitrogen gas or clean air was continuously delivered into the chamber. The evaporation chamber used in this work was almost a closed system, with only 2 small holes for flowing air and/or nitrogen in and out as shown in our previous work [19]. By using this system, the contamination from the experimental atmosphere can be avoided almost completely. After the evaporation, the samples were quantitatively transferred to the filtration apparatus. The PTFE beakers used were washed with 5 ml of 0.003 mol l^{-1} H_2SO_4 and transferred into the filtration apparatus. Finally, the solutions were diluted to 10 ml, prior to treatment by the procedure described in the next section. Polymethyl pentene (PMP) beakers were also tested as evaporating vessesl. However, the beakers were found to adsorb some silicate in water samples and were not used any further for the present purpose.

Experimental Procedure

Water samples,15-30 ml, containing 0-0.25 ng ml^{-1} Si were transferred into the filtration apparatus. A 0.25 ml of 1.7 mol l^{-1} H_2SO_4 and 0.52 mol l^{-1} Mo solution per 15 ml of the sample volume were then added to each sample. The mixed solutions were allowed to stand for 25 min to allow a complete formation of the molybdosilicate, after which, 1 ml of 3.4×10^{-4} mol l^{-1} MG solution per 15 ml of the water samples was added to the each solution. The solutions were thereafter allowed to stand for 30 min to allow a complete formation of the ion associate, and then filtered through the membrane filter under suction. The ion associates collected on the membrane together with the membrane filter itself were dissolved in 1 ml of methyl cellosolve (MC). The filtrates obtained from the first filtration were re-filtered in the manner previously explained and the ion associates were dissolved in the MC. Then, the absorbance of the MC solutions was measured at 627 nm by flow injection technique. Re-filtering procedure for the filtrate was aimed at ascertaining a cause of the absorbance as well as amount of the reagent blank. In this method, the cause of reagent blank is the ion associate formed between MG with sulfate and isopolymolybdate as well as silicate present in the reagent solution and the solvent used.

Result and Discussion

Contamination of water, reagents and vessel with silicate

Although the highest-quality chemicals currently available were used in the present study, it was very difficult or practically impossible to obtain the reagent blank completely free from the silicate contamination, which may have originated from the reagents used, as well as the solvent (ultrapurified water) and vessels. All chemicals and reagents were dissolved in the ultrapurified water prepared by ELIX 3/Milli Q Element System, which was also used as a sample solution. The contamination of PTFE beakers with silicate, which were used as a vessel for evaporating samples, was controlled to negligible levels by soaking the beakers in 1 mol l^{-1} nitric acid for 24 h, and washing them with the ultrapurified water. In order to reduce a contamination of the reagents and the solvent with silicate, the Malachite Green solution in sulfuric acid was prepared and treated as described in the reagent section. In this case, the mixed reagent solution was filtered with cellulose nitrate membrane after standing for 12 h; the filtrate was used for further experiments. By this scheme of treatments, the absorbance of the reagent blank could be minimized to about 0.034 A.U. The reagent blank values may be attributed to the ion associate of such anions as isopolymolybdate and sulfate, as well as molybdosilicate with Malachite Green. In addition to the complexity of the reagent blank, the reason why a conventional calibration graph method and a standard addition method can not be applied to the direct determination of silicate in ultrapurified water samples, is that the certified standard silicate solution for ultrapurified waters or the silicate-free water is not currently available anywhere in the world.

Due to the fore mentioned reasons, a procedure for enriching silicate in water samples without the addition of any chemicals is imperative. For such reasons, it is necessary to concentrate the ultrapurified water samples by factor of at least two folds. By coupling the “classical concentration method by evaporation without any chemicals under the conditions of non-contamination”, a slope comparison method (SCM) was developed. By using the SCM proposed in this study, the influence of the silicate present in the chemicals, the reagent solutions, and the solvent can be neglected, and the reagent blank can be compensated.

Principle of SCM for the determination of silicate in ultrapurified water

The principle of the SCM is illustrated in Fig.2. In this method, the ion associate formed from both the silicate in the original sample (ultrapurified water) and the silicate contained in the reagents used are concentrated into a small volume to get sufficient sensitivity. In the SCM, the original sample volumes are varied, while the reagent added is fixed to the constant volume. Under this condition, the increase in absorbance with the increase in original sample volumes will only be due to the amounts of silicate in ultrapurified water samples. The resulting slope obtained by varying the sample volume is compared with the slope of the calibration graph, and hence, named as the slope comparison method (SCM).

Detailed explanation of SCM is as follows: a series of the volumes of ultrapurified water samples such as V_1, V_2, V_3, and V_4 (the number 1, 2, 3, and 4 show the increase in sample volume in this order) are evaporated/concentrated to the identical final volume, so that the reagents added to each sample volume are of the same amounts.

It is therefore assumed that the contamination level from the reagents is identical with one another. If the contamination level from reagents is denoted by constant concentration, C_0, the corresponding concentrations of silicate detected in increasing sample volume become C_1+C_0, C_2+C_0, C_3+C_0 and C_4+C_0, where C_1, C_2, C_3 and C_4 are concentrations of silicate corresponding to V_1, V_2, V_3, and V_4. A plot of absorbance against volume yields a linear graph (see B, C in Fig.2). Let α_B and α_C be the calculated slope of the line B and the line C, respectively. These slopes show Δabsorbance per unit volume. From the calibration graph (A), the slope of α_A, which shows Δabsorbance per unit concentration, is obtained. By comparing the slope of the calibration graph with the slope of the samples, the accurate amount of silicate as silicon (C_B and C_C, mass per unit volume) in the samples can be obtained and the effect of C_0 (content of the reagent blank) can be compensated. More detail of the principle of SCM is explained in the latest section

In our previous work [19] for the determination of ultratrace amounts of phosphorus in ultrapurified water based on the formation of the ion associate of Malachite Green with molybdophosphate, it was found that the reagent blank can deviate to samples and the reagent used, and trace amounts of phosphate still remained in the mixed reagent solution. It implies that in the determination of ultratrace and trace amounts of phosphate as well as silicate, conventional calibration method (CCM, the absorbance of sample is directly plotted against the concentration of analyte) and standard addition method (SAM) can not be applied because some parts of actual amount of silicate present in the original sample will be taken into account together with the blank value as well as trace contamination of silicate containing in the reagents and solvent used. More difficulties will be encountered if the concentration of silicate present in the original sample is much lower than silicate present in the chemicals and the reagent solutions used. Under such conditions, a prerequisite for the SAM is the elimination of interference effects in the samples. However, it is much more difficult to eliminate than to compensate for such effects. To overcome these difficulties, SCM can be applied. The method incorporates two important intrinsic features, viz.; (1) the slope obtained by varying the sample volumes is only due to the silicate in the original samples and (2) the slope of the calibration graph is only attributed to the silicate added in the standard solution. Thus, by comparing these slopes, the influence of the trace amounts of silicate present in the chemicals, the reagent solutions, the solvent can be compensated. Consequently, SCM enables the evaluation of concentration of silicate in ultrapurified water samples more sensitively and accurately than either the conventional calibration method (CCM) or the standard addition method (SAM). From the foregoing reasons, SCM is more reliable in terms of accuracy and sensitivity than the conventional SAM and CCM, especially when the method is applied to trace-and ultratrace analysis.

Reaction conditions for the formation of ion associates

Similar optimum conditions as those used in the previous work [17] were adopted in the present work for the concentration of MG, molybdate and sulfuric acid, except for the acidic medium and the standing time for the formation of molybdosilicate and ion associate.

Optimum conditions for the standing times were examined; the results are shown in Fig. 3. The formation of molybdosilicate was studied by varying the standing time from 5 to 40 min at room temperature. The absorbance of the reagent blank tended to be constant after 20 min, which indicates that the heteropolyacid of molybdosilicate exists as stable species and the formation reaction is completed. The color development of the ion associate formed between molybdosilicate and MG was examined in a similar manner as the formation of molybdosilicate. The absorbance of the reagent blank decreased during the standing time of 5-20 min, and tended to a constant value during the standing time of 20-40 min. The molybdosilicic acid ($H_4SiMoO_{12}O_{40}$) reacts stepwise with MG to form the final product of 1:4 ion associates, where the proton of molybdosilicic acid can be replaced stepwise with MG. During the first 20 min, some MG do not react with molybdosilicate, as they exist as an ion associate with molybdate, which results in a higher absorbance of the reagent blank. According to the acid-base equilibrium of MG as described in Fig. 4, MG can be present as its main and protonated species [20]. The species represented as **II** is a reactive species, which can reacts with molybdate as well as molybdosilicate to form ion associates. The protonation and deprotonation reactions of species **II** is very fast, while the hydration and dehydration reactions between the species **II** and **III** are very slow. Such kinetics influences the rate of the ion associate formation, which is apparently faster when species **II** predominates. In order to maintain low absorbance of reagent blank, 25 min and 30 min were selected as the optimum conditions for the formation of molybdosilicate and ion associate molybdosilicate with MG, respectively.

Effect of sample volume was examined by varying the volume from 15 to 60 ml with various treatments, such as non-evaporation, evaporation to 5 ml and evaporation to dryness. In this work, sulfuric acid and hydrochloric acid were examined as acidic medium for the formation of molybdosilicate. The absorbances increased with increasing sample volume for non-evaporation and non-dryness evaporation method, which indicates the ion associate can be collected completely/quantitatively on the tiny membrane filter. However, in case of the dryness evaporation method, the absorbances tend to constant, which is caused by undissolved silicate remaining at the bottom of vessel after the dissolution with 0.003 mol l^{-1} H_2SO_4. The absorbance of the reagent blank prepared by using hydrochloric acid as an acidic medium were higher than those obtained by sulfuric acid as an acidic medium, indicative of large amounts of silicate in hydrochloric acid. The absorbances obtained by re-filtering of the filtrate (sulfuric acid as an acidic medium) increased slightly with increase in sample volumes, and became a constant when hydrochloric acid used as acidic medium as shown in Fig.5.

Influence of sulfate and chloride ions on the absorbance of reagent blank were studied by varying their concentration from 0 to 0.6 mol l^{-1} in the absence of molybdate in order to further clarify the above phenomena. The results showed that the absorbances of reagent blank increased linearly with increasing concentration of both chloride and sulfate ion which indicated that sulfate and chloride ions can form ion associates with MG. It should be noted that sulfate ion resulted in higher blank than chloride ion as shown in Fig. 6. Based on the result obtained by investigating the effect of chloride, sulfate, and heteropolyacid on the absorbance of reagent blanks, it was concluded that the absorbance of the reagent blank was not only caused by the ion associates of the heteropolyacids of isopolymolybdate with MG, but also by the ion associate between sulfate as well as chloride with MG. Furthermore, the adsorptivity of the ion associate with MG is thought to follow the order: Cl^- < isopolymolybdate < SO_4^- < molybdosilicate.

Effect of the evaporation of sample solutions on the determination of silicate

Generally, silicates in water are present in various monomeric and polymeric forms. However, most of the silicates at the concentration of sub-ppb levels seem to be in the monomeric form. In the reaction with molybdate in acidic mediums, only monomeric silicate (orthosilicate) can be determined. In this work, ultrapurified water samples were pretreated by evaporation of original samples to non-dryness and dryness. As shown in Table 1, the concentrations of silicate obtained by non-dryness evaporation method were twice higher than those obtained by non-evaporation method. These results indicate that unreactive silicate (polymeric species) can be converted to the reactive silicate (monomeric species), which can easily reacts with molybdate to form molybdosilicate. Results from evaporation to 3 and 5 ml are in good agreement showing that this enrichment technique is useful for good accuracy and reproducibility, while in the case of evaporation to dryness, silicate present at the bottom of PTFE beaker was difficult to be completely dissolve in diluted sulfuric acid.

In addition to the advantage of the conversion of unreactive silicate to the reactive silicate, the evaporation without addition of any chemicals was selected as concentration method for ultrapurified water samples, because a standard reference material of ultrapure water, which bears a certified value of silicate is not currently available. Furthermore, at the present, obtaining chemicals, reagents, and solvents, which are completely free from silicate is not possible. Therefore, attaining several-folds enrichment of silicate in ultrapurified water samples without addition of any reagent is required. This explains why the evaporation/concentration method is necessary for the present purpose.

Effect of phosphate and arsenate on silicate determination

In addition to the reaction with silicate, molybdate is also capable of reacting with phosphate (orthophosphate) and arsenate to form heteropolyacids. In the proposed procedure, the effect of phosphorus existing as phosphate was examined by varying its concentration from 0 to 0.3 ng ml^{-1}. The results showed that positive error of 3.22 % was found when the concentration of phosphorus was 0.124 ng ml^{-1}. Since the concentrations of phosphorus in ultrapurified water are in the range of 0.06-0.07 ng ml^{-1} [19], the interference from phosphate can be regarded as negligible.

The effect of arsenate was similarly examined. Various concentrations of arsenate from 0 to 1.67 ng ml^{-1} were added to the ultrapurified water samples to ascertain its effect on the silicate determination. The results showed that no interference from arsenate up to 1.33 ng ml^{-1}, but a positive error of 6.45% was found when concentration of arsenate was 1.67 ng ml^{-1}. However, the effect of arsenic can be ignored because the concentrations of arsenate in ultrapure water are lower than 0.01 ng ml^{-1} [7].

Calibration graph, detection limit and precision

The calibration graph as given in Fig. 7 showed a good linearity for the range of 0-0.25 ng ml^{-1} of standard Si solutions with the linear equation, $Y = 0.2409X + 0.0338$, where Y is the absorbance of the ion associates of molybdosilicate with MG and X is the concentration of Si (ng ml^{-1}); the correlation coefficient was 0.998. The standard deviation (absorbance unit) and relative standard deviation from six measurements of the reagent blank were 0.0012 and 3.5%, respectively. The detection limit calculated from three times of the standard deviations of the reagent blank was 10 pg ml^{-1} (ppt) when 30 ml sample was used. To our best knowledge, the detection limit obtained in the present procedure is the best of all the spectrophotometric methods reported so far.

The absorbances obtained by the second filtration of the filtrate from the first filtration were almost identical, which means that almost all of the silicates contained in the standard solutions are retained on the tiny membrane filter by the first filtration. By using the straight line and the second filtration line of the reagent blank, it can be assumed that the total amount of the reactive (monomeric) silicate contained in water used for the preparation of the standard solutions, the reagent solution (molybdate solution), and acid (H_2SO_4) added to standard solutions to be about 0.055 ng ml^{-1} (55 ppt).

Determination of silicate in ultrapurified water by the slope comparison method (SCM)

The proposed method (SCM) was applied to the determination of silicon existing as silicate in ultrapurified water samples prepared by ELIX 3/Milli Q element and Milli Q-Labo as shown in Fig. 8, and the results obtained were summarized in Table 1. As given in Fig.8, straight line of A is the calibration graph, which is constructed using standard solution of silicate in the range concentration of 0.0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 ng ml^{-1}. The volume of solution used for calibration curve is 40 ml. Therefore, the mass of silicate (as silicon) are 0, 1.5, 3.0, 4.5, 6.0, 7.5 ng. The mass of silicon is then used as the axis for calculation of silicate in the original samples. From the straight line of samples (eg. solid line B), dotted lines from two points of absorbance (from two different volumes; 20 and 30 ml) were extended to meet the calibration line (solid line A), then, further extrapolated to the axis representing the mass of silicate. The concentration of silicate in the sample obtained by difference of mass is found to be 3.177 ng Si in 10 ml. In other word, the concentration of Si is 3.177 ng/10 ml = 0.32 ng ml^{-1}.

Two data points of absorbance (from two different volumes) as shown in Fig.8 are required to correct the calculation of silicate in the samples. As seen in Fig.7 (calibration graph), the phenomenon of reagent blank will affect the calculation of original concentration of the samples, especially if the conventional calibration graph (CCM, the absorbance of sample is directly plotted against the concentration of analyte) or standard addition methods (SAM) were used. From the first filtration (Fig. 7), the absorbances increase with the increase in silicate concentration. The lowest absorbance value, in the absence of silicate (0 ppb), was 0.034. The second filtration gave the absorbance of about 0.022, showing that a difference in absorbance between first filtration and second filtration exists (0.034-0.022 = 0.012). If such a difference was non existent, then CCM and SAM can be applied. Based on the experiments as shown in Fig 5, Fig.6, and the second filtration of calibration graph (Fig7), the absorbance of 0.022 is not only due to the ion associate of sulfate with Malachite Green (MG), but also ion associate between isopolymolybdate and MG. The difference in absorbance of 0.012 is due to the silicate contained in the solvent (ultrapurified water) used for solution preparation as well as silicate in the reagent used. In this experiment, the solvent used for solution preparation is the sample itself. From these results, it was found that reagent blank easily deviate to the samples as well as reagent used. Therefore, if CCM and SAM are used, the concentration of silicate in the sample will be lower than the original concentration. For example, if we used SAM (extrapolation of the calibratrion graph), the concentration of silicate in the sample will be found to be about 0.14 ng ml^{-1}, and if we use CCM, the concentration of silicate in sample will be found about 0.17 ng ml^{-1} (based on the absorbance of 30 ml of sample after evaporation/concentration, and directly plotted to the calibration graph, Fig.8, line B). Therefore, in this method at least two different data points were needed and extended to the calibration line as shown in Fig.8. By plotting two or more different data points of absorbance of samples, it means that we compare the slope of varying sample volume with the slope of calibration graph. From this method, the silicate in sample was found to be 0.32 ng ml^{-1} (3.18 ng/10 ml = 0.32 ng ml^{-1}). This result is more reliable because the slope obtained by varying volume is only due to the silicate in the original samples, and the slope of the calibration graph is only due to the silicate added in the standard solutions. Therefore, the effect of reagent blank, that will cause an error in calculation, is avoided.

We can also calculate the concentration of silicate by directly comparing the slopes of varying sample volume to the slope of calibration graph as given in Table 1. For example in sample C ;

- Slope of varying sample volume (SV) = 2.55 x 10^{-3} A.U/ml
- Slope of calibration graph (SC) = 2.41 x 10^{-1} A.U/ng ml^{-1} (volume of solutions used for calibration graph is 30 ml)

For sample C, 1 ml of sample volume corresponds to 1.23 x 10^{-3} A.U. Therefore, 30 ml of sample volume correspond to 76.5 x 10^{-3} A.U. (the absorbance increase linearly with increase in sample volume, Fig.5). Thus, by comparing both slopes, the concentration of silicon in the sample C = (76.5 x 10^{-3} A.U x 1 ng ml^{-1})/(2.41 x 10^{-1} A.U) = 0.32 ng ml^{-1}.

The ultrapurified water samples were sampled in our laboratory. Non-dryness evaporation method showed good results on sample pretreatment method as indicated by good reproducibility of silicon concentrations obtained for the same sample of ultrapurified water. The non-evaporation sample pretreatment method, which also utilized slope comparison method, gave a lower value than those obtained by non-dryness evaporation method. Probably, this is caused by non-conversion of unreactive (polymeric) silicates to reactive (monomeric) silicates. However, the dryness-evaporation method cannot be applied to this analysis due to the difficulty of dissolving silicate in the evaporation vessel with the diluted sulfuric acid.

On the basis of the reproducibility test, the proposed method can be said to be highly reliable and precise. Unavailability of the standard reference material for ultrapurified water bearing 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 2, it can be concluded that the proposed method exhibits good accuracy and higher sensitivity than any other method previously reported.

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Figure captions

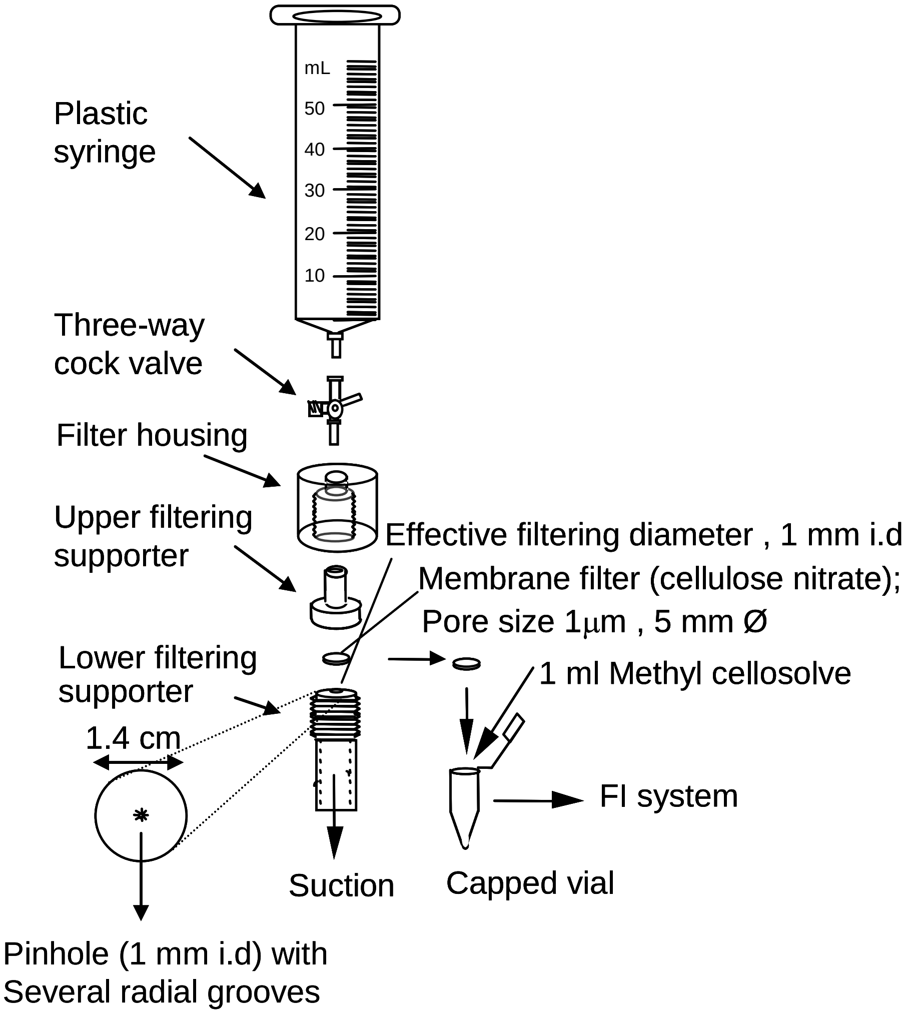

Fig.1 Syringe-type filtration apparatus with tiny membrane filter

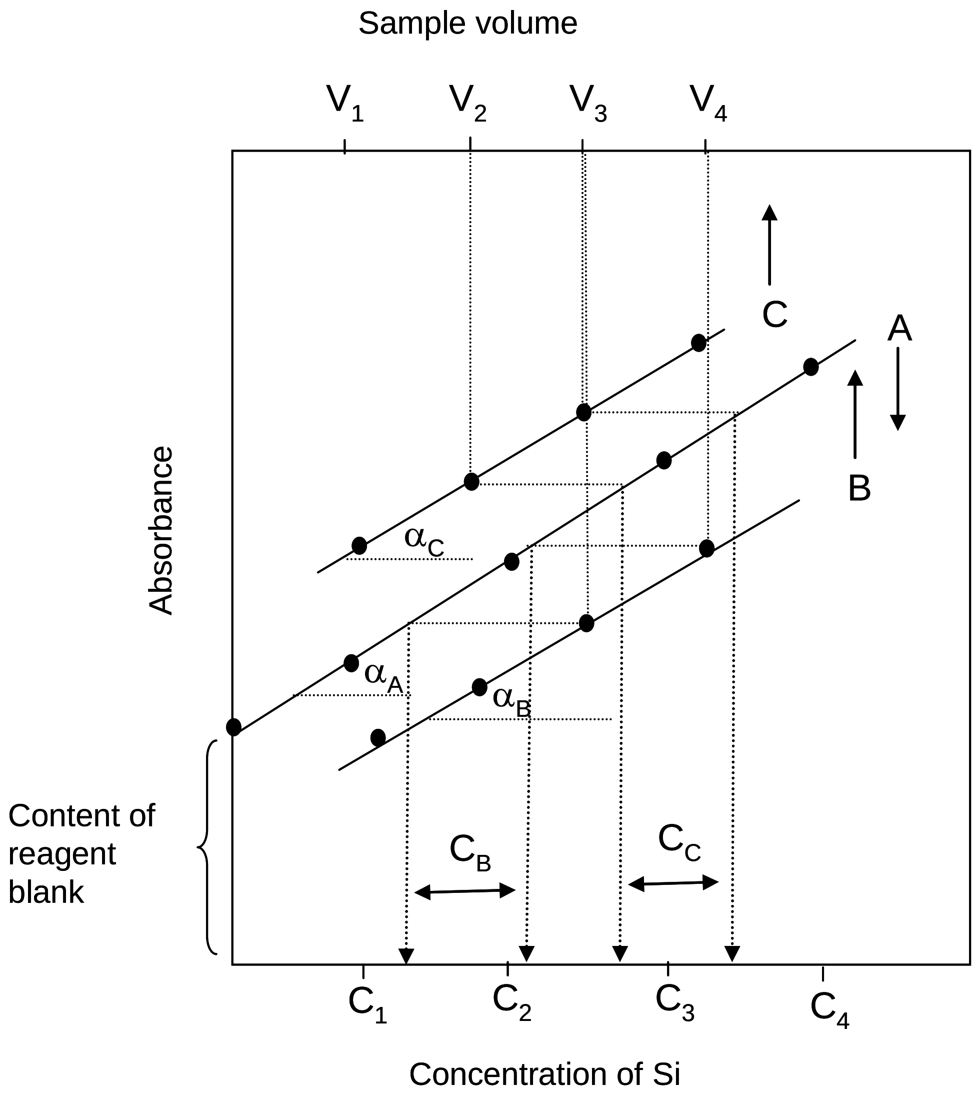

Fig.2 Illustration of the slope comparison method for evaluating silicate in ultrapurified water samples

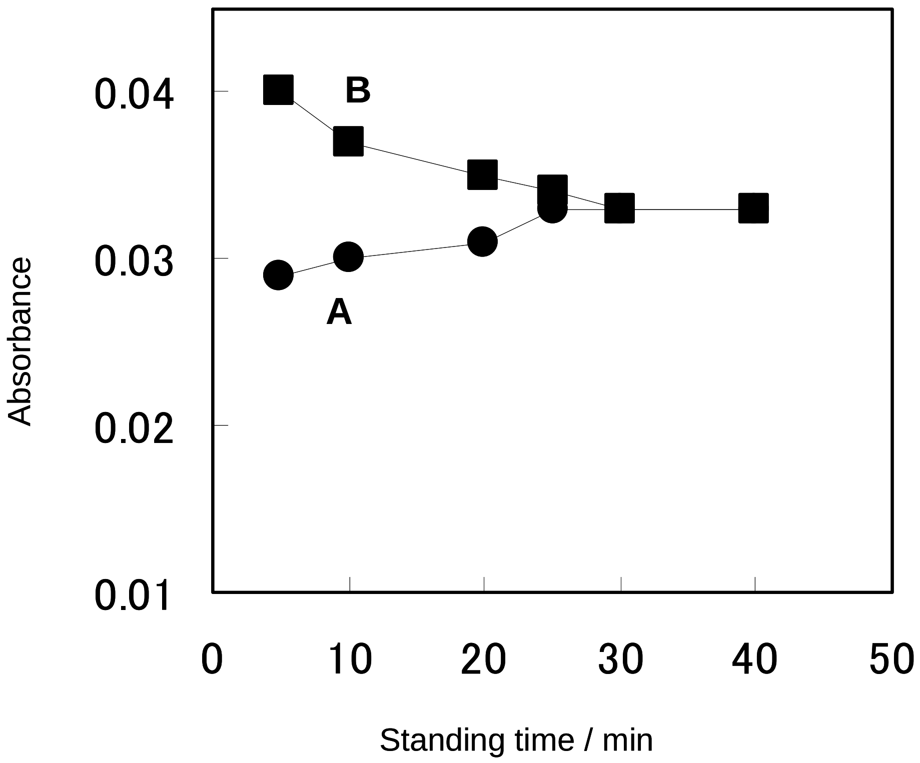

Fig.3 Effect of standing time on the formation of molybdosilicate and ion associate of molybdosilicate with MG

A: Effect of standing time for the formation of molybdosilicate

B: Effect of standing time for the formation of ion associate of molybdosilicate with MG

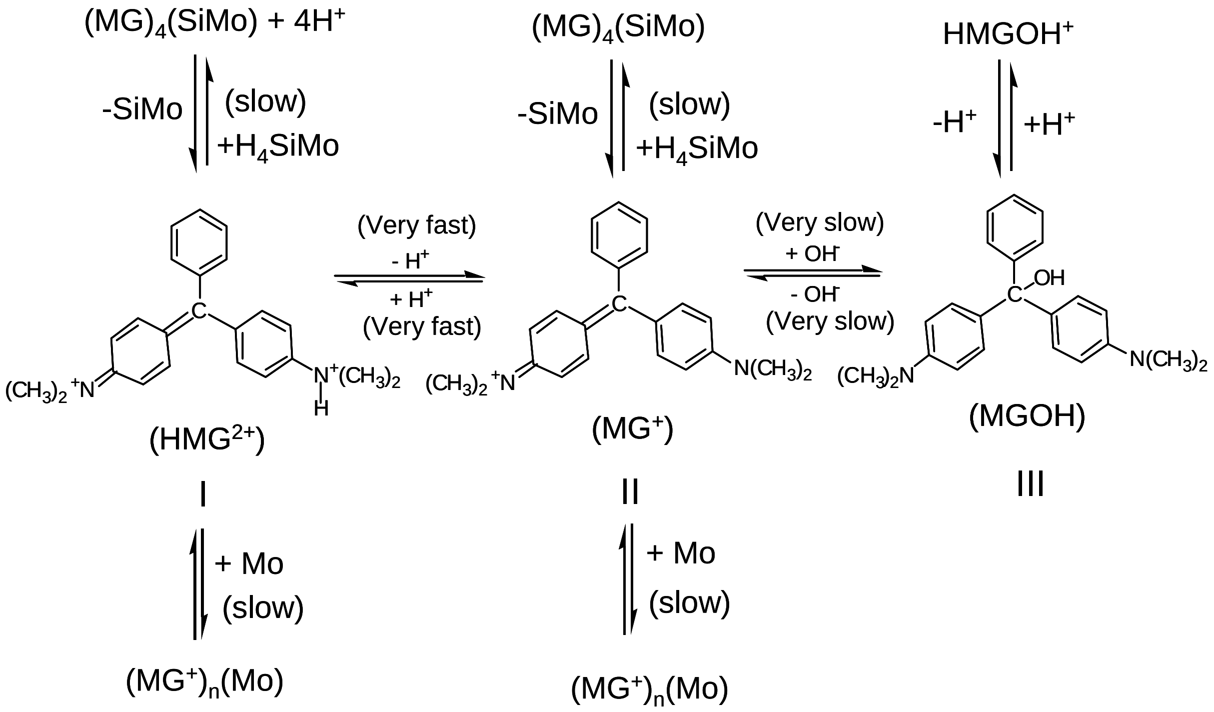

Fig.4 Acid-base and ion associate equilibriums of Malachite Green in aqueous solution

H_4SiMo : $H_4SiMo_{12}O_{40}$; Mo : isopolymolybdate ion

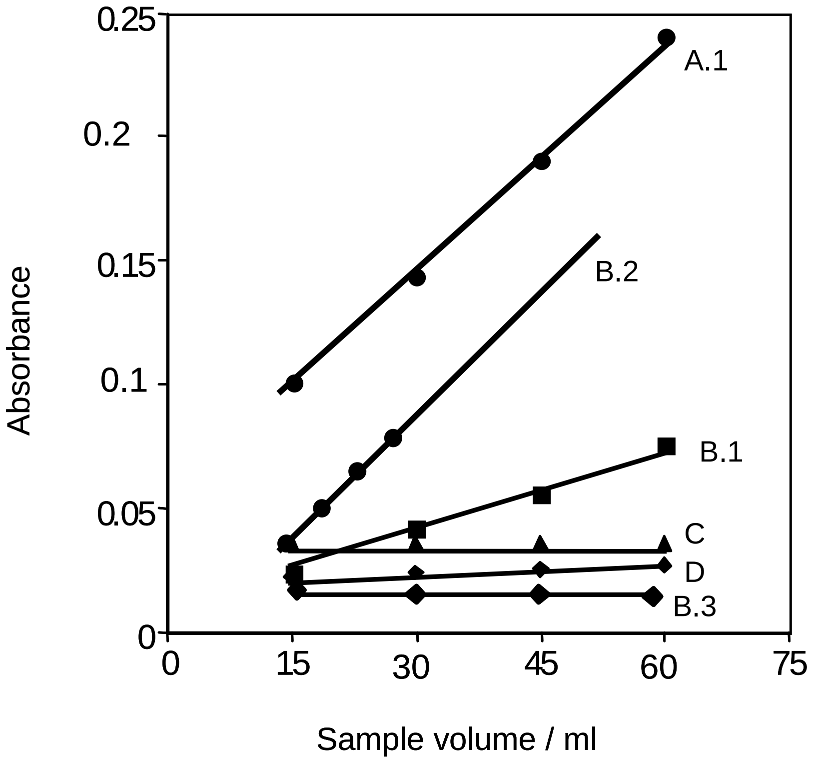

Fig.5 Effect of sample volume and acidic medium on the absorbance of reagent blank
Sample : ultrapurified water prepared by ELIX 3 / Milli Q Element System;
A : HCl as acidic medium; B : H_2SO_4 as acidic medium; C : re-filtration of A; D : re-filtration of B; (1) non-evaporation method, each 0.25 ml of 1.7 mol l^{-1} H_2SO_4 and 0.52 mol l^{-1} Mo solution ,and 1 ml of 3.4 x 10^{-4} mol l^{-1} MG solution were added to per 15 ml of water samples; (2) non-dryness evaporation method, 5 ml of 0.003 mol l^{-1} H_2SO_4, each 0.17 ml of 1.7 mol l^{-1} H_2SO_4 and 0.52 mol l^{-1} Mo solution, and 0.67 ml of 3.4 x 10^{-4} mol l^{-1} MG were added to the 5 ml of residual evaporated sample; (3) dryness evaporation method, 5 ml of 0.003 mol l^{-1} H_2SO_4, 5 ml of ultrapurified water, each 0.17 ml of 1.7 mol l^{-1} H_2SO_4 and 0.52 mol l^{-1} Mo solution, and 0.67 ml of 3.4 x 10^{-4} mol l^{-1} MG were added to the dried sample.

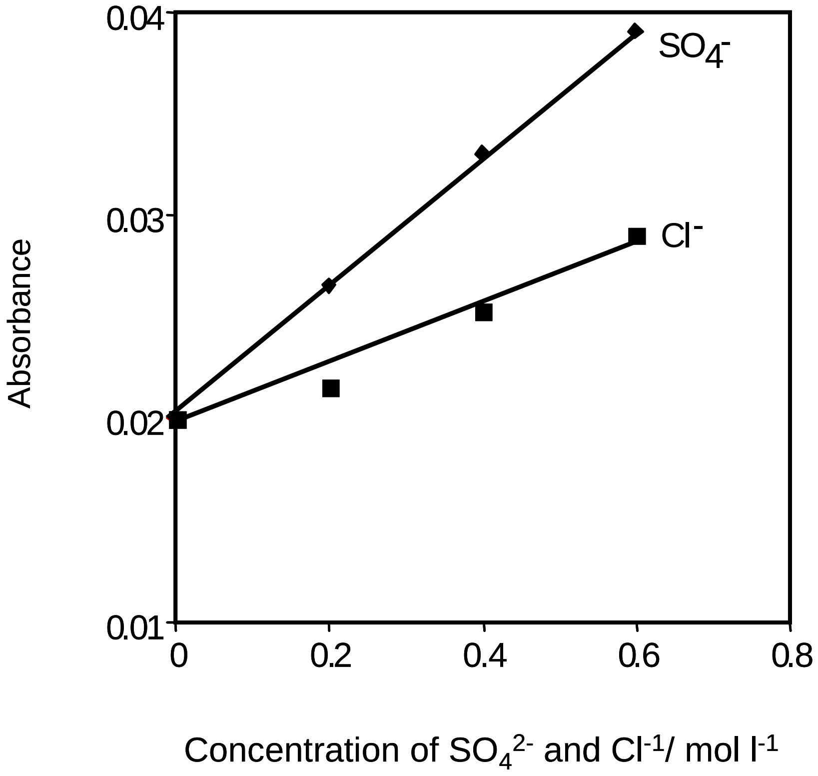

Fig.6 Effect of sulfate and chloride ion on the absorbance of reagent blank

Sample : ultrapurified water prepared by ELIX 3 / Milli Q Element System; sample volume : 30 ml, each 0.5 ml of 1.7 mol l^{-1} H_2SO_4 and 0.52 mol l^{-1} Mo solution ,and 2 ml of 3.4 x 10^{-4} mol l^{-1} MG solution were added to the samples.

The effect of sulfate and chloride were examined in the absence of Molybdate solution.

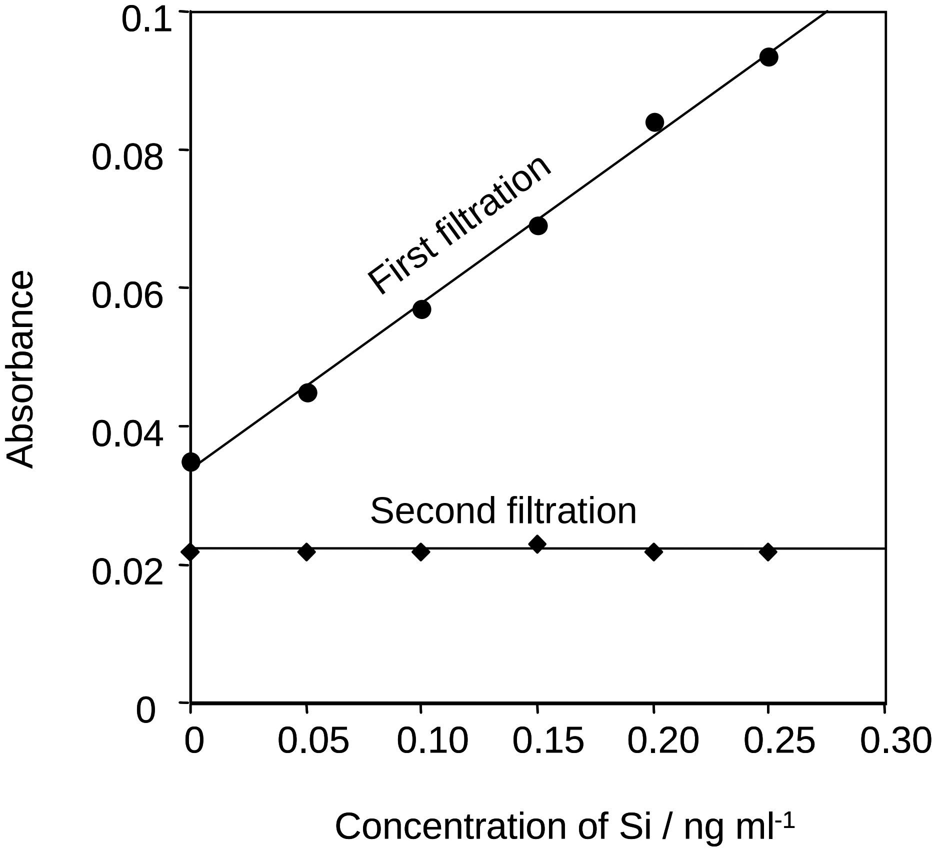

Fig.7 Calibration graph of the silicate determination.

Sample volume: 30 ml; sample: ultrapurified water (prepared by ELIX 3/Milli-Q Element System); second filtration means that the filtrates of the first filtration are filtered again and the absorbances of the dissolved filters are measured.

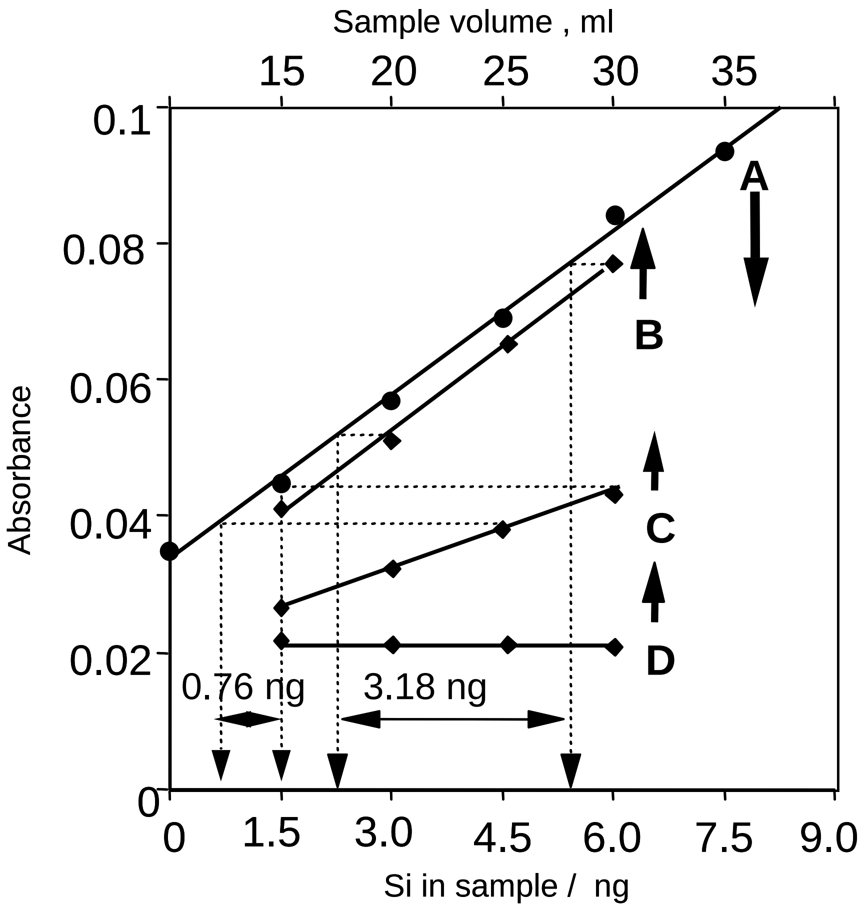

Fig.8 Slope comparison method for the determination of silicate in real samples

(A) Calibration graph (sample volume: 30 ml); (B) evaporation to 5ml and dilution to 10 ml with 0.003 mol l^{-1} H_2SO_4; (C) non-evaporation sample; (D) evaporation to dryness and dilution to 10 ml with each 5 ml of 0.003 mol l^{-1} H_2SO_4 and ultrapurified water; sample: ultrapurified water prepared by ELIX 3/Milli-Q Element System.

Table 1 Determination of silicon as silicate in ultrapurified water samples by the slope comparison method (SCM)

Sample	Sample volume (ml)	Slope		Silicon ($ng\ ml^{-1}$)
		Sample Δ abs./ml	Calibration graph Δ abs./ ng ml^{-1}	
A[*1]	15 - 60[*a]	1.23×10^{-3}	2.41×10^{-1}	0.15
B[*1]	15 - 60[*b]	2.60×10^{-3}	2.41×10^{-1}	0.33
C[*1]	15 - 30[*b]	2.55×10^{-3}	2.41×10^{-1}	0.32
D[*1]	15 - 30[*b]	2.55×10^{-3}	2.41×10^{-1}	0.32
E[*1]	15 - 30[*c]	~ 0	2.41×10^{-1}	~ 0
F[*2]	15 - 30[*b]	7.50×10^{-3}	2.41×10^{-1}	0.93
G[*2]	15 - 30[*b]	8.89×10^{-3}	2.41×10^{-1}	1.10
H[*2]	15 - 30[*b]	7.80×10^{-3}	2.41×10^{-1}	0.98

1 : Ultrapurified water prepared by ELIX 3 / Milli Q Element ; 2 : ultrapurified water prepared by Milli Q labo ; a : samples were not evaporated; b : samples were evaporated to 5 ml; c : samples were evaporated to dryness.

All the ultrapurified waters were sampled at Laboratory of Analytical Chemistry, Okayama University on November, 2001.

Nitrogen gas was introduced into evaporation chamber when evaporation process took place.

Table 2 Comparison of the various analytical methods for the determination of silicate in ultrapurified water.

Method	Sample pretreatment[*a]	Detection limit (ng ml^{-1})	Range of Si concentration found[*b] (ng ml^{-1})	Reference
ICP-AES	E/C	3	0.2-0.9	9
ICP-MS	E/C	1	0.2-0.9	9
Colorimetry	E/C	0.25	0.2-0.9	9
HR-ICP-MS	E/C	-	0.5-1.0	8
Gel-phase absorptiometry	E/C	0.1-0.2	0.3-0.9	10
Flow injection-fluorophotometry	E/C	0.06	0.4-0.9	7
SCM-spectrophotometry	E/C	0.01	0.3-1.1	This work

*a: C/E : evaporation/concentration

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