

Chemistry
Analytical Chemistry fields

Okayama University

Year 2003

Ultratrace determination of phosphorus
in ultrapurified water by a slope
comparison method

Akhmad Sabarudin*

Mitsuko Oshima[†]

Shoji Motomizu[‡]

*Department of Chemistry, Faculty of Science, Okayama University

[†]Department of Chemistry, Faculty of Science, Okayama University, oshimam@cc.okayama-u.ac.jp

[‡]Department of Chemistry, Faculty of Science, Okayama University, motomizu@cc.okayama-u.ac.jp

This paper is posted at eScholarship@OUDIR : Okayama University Digital Information Repository.

http://escholarship.lib.okayama-u.ac.jp/analytical_chemistry/28

ULTRATRACE DETERMINATION OF PHOSPHORUS IN ULTRAPURIFIED WATER BY A SLOPE COMPARISON METHOD

Akhmad Sabarudin, Mitsuko Oshima[†] and Shoji Motomizu

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

ABSTRACT

The analytical method for the determination of phosphorus in ultrapurified water was developed. Ultrapurified water was evaporated to concentrate phosphorus and the final sample volume for analysis was 10 ml. In 0.55 mol l⁻¹ HCl, orthophosphate forms a molybdophosphate, and then the molybdophosphate forms ion associate with Malachite Green (MG), which can be collected on a tiny membrane filter (diameter : 5 mm, and effective filtering diameter : 2 mm). After the ion associate on the membrane filter is dissolved together with the membrane filter in 1 ml of methyl cellosolve (MC), the absorbance of MC solution is measured at 627 nm by a flow injection-spectrophotometric detection technique. When 10 ml of the sample solution was used for the procedures and absorbance measurement, the calibration graph is linear up to about 500 ng l⁻¹ of phosphorus and the detection limit was 8 ng l⁻¹ (S/N = 3). For the determination of phosphorus in an ultrapurified water, 10 to 40 ml of sample solutions were transferred into PTFE beaker and evaporated to 5 ml or to dryness. To them, 0.003 mol l⁻¹ HCl was added to get 10 ml of final solutions, which was used as samples. Phosphate is determined by comparing the slope of the varied sample volume after evaporation/concentration with a slope of the standard calibration graph (a slope comparison method : SCM). The SCM enables to evaluate the concentration of phosphate in ultrapurified waters more sensitively and accurately.

Keyword : *ultrapurified water, evaporation/concentration, ion associate, molybdophosphate, malachite green, slope comparison method.*

[†]To whom correspondence should be addressed.

Email : oshimam@cc.okayama-u.ac.jp (Mitsuko Oshima)

Telp/Fax : (81)-86-251-7847

Introduction

Nowadays, especially in semiconductor industries, a very large bulk of ultrapurified water is required for manufacturing high-quality semiconductors along with maximized yields. Therefore, there have been growing demand for sensitive and accurate determination of trace- and ultra-trace amounts of impurities in ultrapurified water. Phosphorus is one of the impurities that must be analyzed in ultrapurified waters. The ultratrace determination of phosphorus at around ng l^{-1} levels has been playing a synergistic role in improving and evaluating the quality of the ultrapurified water.

Phosphomolybdenum blue method, either with or without solid phase enrichment has been used for the phosphorus and silicate determination [1-2], however the procedure is often troublesome. The sensitive spectrophotometric method based on ion associates with basic dyes deserve attention. Molybdophosphate forms ion association complexes with cationic or basic dyes, which is the basis of sensitive detection methods for determining phosphorus spectrophotometrically. Malachite Green has found the widest application [3-9]. Others proposed include Crystal Violet, Brilliant Green, Ethyl Violet, Safranin, Methylene Blue, Butylrhodamine B, Acridine Orange, etc.[10]. Ion associates formed with such cationic dyes can be collected on a membrane filter [5]

Motomizu *et.al.*[11-13] have reported a highly sensitive spectrophotometric method for determining phosphorus at sub-ppb and ppt levels using relatively small volumes of 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 was measured by a flow injection-spectrophotometric detection method which is relatively simple and shows excellent sensitivity : probably the method gives the highest sensitivity of the chemicals developed so far. However, trace- and ultra-trace amounts of phosphate in ultrapurified waters cannot be determined because “ the standard certified ultrapurified water “ or “the phosphate-free water “ is not available now.

In this paper, we propose a highly sensitive method for the determination of ultratrace amounts of phosphorus in an ultrapurified water by improving the previous method [11] and coupling the improved method with an evaporation of ultrapurified water under flowing nitrogen gas. More sensitive and accurate results have been achieved by the slope comparison method (SCM) developed in the present study. In the SCM, the influence of the trace amount of phosphorus possibly present in the chemicals, reagent solutions and the solvent can be compensated for the first time.

Experimental

Reagents. Ultrapurified water prepared by ELIX 3 / Milli Q element (Nihon Millipore, Tokyo) was used as a sample solution and used for preparing the reagent solutions.

A stock standard solution of phosphorus was prepared by dissolving 0.2722 g of potassium dihydrogenphosphate dried at 110°C in 100 ml ultrapurified water to give a $2 \times 10^{-2} \text{ mol l}^{-1}$ solution. Working solutions were daily prepared by accurate dilution of the stock solution with 0.003 mol l^{-1} hydrochloric acid.

A molybdate (Mo)-Malachite Green (MG) mixed reagent solution was prepared as follows : Ammonium heptamolybdate tetrahydrate (2.13 g, Wako Pure Chemicals, Osaka) was transferred into a plastic beaker, dissolved in 30 ml of the ultrapurified water, and 24 ml of concentrated hydrochloric acid (Kanto Chemicals, Tokyo) was added to this solution. Then, 10 ml of Malachite Green aqueous solution containing 0.0028 g of Malachite Green Oxalate (Tokyo Kasei Kogyo, Tokyo) was added to the solution and mixed. The mixed solution was diluted to a 100 ml with the ultrapurified water. After stirring this solution for 12 h, it was filtered through a cellulose nitrate membrane filter (pore size : $0.45 \mu\text{m}$ and diameter : 25 mm) under suction in order to remove trace amounts of molybdophosphate formed from orthophosphate which is present as a contaminant in the chemicals used. The final concentrations in the mixed solution were $6 \times 10^{-5} \text{ mol l}^{-1}$ of MG, 0.12 mol l^{-1} of Mo and

2.75 mol l⁻¹ of HCl.

A silicate solution used for examining the effect of diverse ion was a commercially available standard solution for AAS (Wako Pure Chemicals, Osaka).

Apparatus. A simple schematic diagram of flow injection system was the same with the previous work [11]. A double-plunger micropump (Sanuki Kogyo, DMX-2000) was used for propelling carrier of MC at a flow rate of 0.5 ml min⁻¹. A six-way valve (Sanuki Kogyo, SVM-6M2) connected with PTFE tubing (0.5 mm i.d.) was used for injecting sample of 0.2 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 Ross B-1278 recorder.

The filtration-preconcentration apparatus was the same as those used in the previous work [12]. A membrane filter, which has a diameter of 5 mm and an effective filtering diameter of 2 mm, was prepared by punching the commercially available cellulose nitrate membrane (45 mm diameter ; Advantec Toyo, Tokyo) with a steel puch (5 mm diameter). Then it was put on the filtration apparatus. The diameter of membrane filter was much smaller than those used in common works, resulting in more effective enrichment and a lower reagent blank.

Poly(tetrafluoroethylene), PTFE beakers (100 ml) were used for evaporating ultrapurified water samples.

Sample preparation. Aliquots, 10-40 ml of water samples, were transferred into the PTFE beakers, put them in a evaporation chamber (Sanai Kagaku, Nagoya), and then evaporated to about 5 ml or to dryness. While the evaporation was taking place, nitrogen gas from a cylinder was delivered into the chamber. The evaporation chamber used in this work was an almost closed system, which had only 2 small holes for flowing N₂ in and out as shown

in Fig.1. All the procedures were carried out in a clean room. By using this system, the contamination from the atmosphere can be avoided. After the evaporation, they were transferred to the filtration apparatuses. The PTFE beakers used were washed with 5 ml of 0.003 mol l⁻¹ HCl, and the washing solution was also transferred to the filtration apparatuses. Finally, the solutions were diluted to 10 ml, followed by the standard procedure described later.

Standard procedure. Water samples, 10-40 ml, containing 0-250 ng l⁻¹ of phosphorus were transferred into the filtration apparatuses, and mixed with the mixed reagent solution of the molybdate (Mo)-Malachite Green (MG), whose volume ratio to the sample volume was identical (1 : 5) ; in this work, 2 ml of the reagent solution was added to the 10 ml of the sample. The solutions were left to stand for 5 min to complete the formation of the ion associate and filtered through the tiny membrane filter under suction. The ion associate collected on the membrane filter was dissolved together with the membrane filter in 1 ml of MC. The filtrate obtained from the first filtration of the sample solution and the mixed reagent solution was filtered again in the same manner as the above-mentioned procedure, and the ion associate was also dissolved in the MC. The absorbances of the MC solutions were measured at 627 nm by a flow injection technique. Re-filtering procedure for the filtrate was aimed at ascertaining a cause of the absorbance of the reagent blank.

Results and Discussion

Contamination of phosphorus from water, reagents and containers

Although the highest quality reagents now available were used in the present study, it was very difficult to obtain analytical results completely free from the contamination of phosphorus. Its contamination can be attributed to the reagents used, as well as the solvent (ultrapurified water) and containers : all chemicals were dissolved in the ultrapurified water

prepared by ELIX 3/Milli Q Element, which was also used as a sample solution. The contamination of phosphorus from the PTFE beakers, which were used as a container for evaporating samples, was almost neglected by soaking the beakers in 1 mol l⁻¹ nitric acid during 24 h, and washing them with ultrapurified water. To reduce a contamination of phosphorus from the reagents and the solvent, the mixed reagent solution was prepared and treated as described at the reagent section. In this case, the mixed reagent solution was filtered with cellulose nitrate membrane after stirring 12 h, and the filtrate was used for further experiment. By those procedures, the absorbance of the reagent blank was minimized to about 0.028. The reagent blank value seems to be attributed to the ion associate of such anions as isopolymolybdate and chloride with Malachite Green. The explanation of the content of the reagent blank is very complicated and will be done in a later section. In addition to the complexity of the reagent blank, the standard certified ultrapurified water, whose certified phosphate concentration or the phosphate-free water, is not available now in whole the world. The limit of the detection of the present filtration/concentration method is enough to detect phosphate in ultrapurified water. To overcome such problems, we must use the procedure for enriching phosphate in water without the addition of chemicals. For that reason, the determination of phosphorus in ultrapurified water was required to concentrate by two or more, and we developed the slope comparison method (SCM) for the first time. By using the SCM proposed in this study, the influence of the phosphorus present in the chemicals, reagent solutions and the solvent can be neglected, and the reagent blank can be compensated.

Effect of experimental variables

Optimum conditions for the concentrations of MG, molybdate and hydrochloric acid, which were obtained in the previous work [12], were adopted in the present study, except a kind of acid. In many studies for phosphorus determination based on the formation of the

ion associate between heteropolyacid and MG, a diluted sulfuric acid was used to facilitate MG in the protonated yellow form and to decrease of reagent blanks. In this work, a diluted hydrochloric acid was selected because the absorbances of the reagent blank was lower than a diluted sulfuric acid.

The effect of a sample volume was examined by varying the volume from 10 to 40 ml in three kinds of methods: non-evaporation, evaporation to 5 ml and evaporation to dryness. The ultrapurified waters prepared by ELIX 3 / Milli Q element and ELIX 10 /Milli Q Element were used as sample solutions. The absorbances of the sample, which correspond to the reagent blanks, increased linearly with increasing sample volumes. This result indicates that the ion associate of molybdophosphate-MG can be collected completely/quantitatively on the tiny membrane filter as shown in Fig.2. In case of an ultrapurified water prepared by ELIX 10 / Milli Q element, the absorbances tended to constant even with increasing sample volume when the samples were evaporated to 5 ml. This result showed that the ultrapurified water prepared by ELIX 10 / Milli Q element was almost free from phosphorus. The increasing of the absorbance in the non-evaporation method (line B,1 in Fig.2) was due to the increase in the volume of the mixed reagent solution because the slope of the line B,2 is almost 0 (zero). However, the relatively large identical absorbances obtained by the evaporation method (line B,2 in Fig.2) cannot be elucidated at present. In Fig.2, the increase in the absorbance of lines A,2 and A,3 are caused by the phosphate in the ultrapurified water, whereas in the line (A,1), the increase in the absorbance is caused by the sum of the phosphate present in the mixed reagent solution and the ultrapurified water. From these results, It is cleared that the phosphate present in the ultrapurified waters cannot be determined by a common calibration graph method because the reagent blank values are easy to deviate in the sample, and the mixed reagent solution still contains trace amounts of phosphate. This is the reason why the slope comparison method is developed in this study. The absorbances obtained by the re-filtration of the fist filtrate of the sample

solutions were almost equal in each series of the varied sample volumes, even though the sample volumes were increased. It means that the collection of the ion associate of the molybdophosphate-MG in the first filtration was almost 100%.

The contents of the reagent blank and the adsorption mechanism on the filter

In order to clarify the contents of the reagent blank, the effect of chloride ion on the absorbance of the reagent blank was studied by varying its concentration from 0 to 0.015 mol l⁻¹ in the absence and the presence of molybdate. The results showed that the absorbances of the reagent blank increased linearly with increasing the concentration of chloride in the absence of molybdate, and the absorbances were identical in the presence of molybdate even the chloride concentration was increased as shown in Fig.3. These results indicate that chloride ion can form an ion associates with MG and can adsorb on the filter. However, the ion associate of the chloride-MG was less adsorptive on the membrane filter when the molybdate is present in the solution. These results can suggest that the absorbance of the reagent blank is caused not only by the ion associate formed between isopolymolybdate and MG, but also caused by the ion associate of chloride with MG. Furthermore, the adsorptivity of the ion associates with MG can be considered to be : Cl⁻ < isopolymolybdate < molybdophosphate.

From the results obtained in the present study, the adsorption mechanism of the ion associates on the membrane filter can be described as in Fig.4. As mentioned in the previous work for the determination of silicate [13], the membrane filter used in this study can be assumed to possess two kinds of adsorptive sites, a strong site (SS) and a weak site (WS). The adsorption mechanism can be explained as follows : less adsorptive ion associates (MG with chloride or isopolymolybdate) can adsorb only on SS (Fig.4 (b) and (c)), and will be replaced gradually by the more adsorptive ion associates (MG with molybdophosphate, MG-HPM), which can adsorb on both sides, WS and SS (Fig.4 (d)-(f)).

Finally, MG-HPM can occupy all of SSs and some WSs (Fig.4 (f)).

The detectable absorbances of the ion associates are illustrated in Fig.5. The components of the reagent blank can vary with increasing molybdophosphate. At the beginning (region (a)), only the ion associate of isopolymolybdate (MG-IPM) will adsorb on the membrane filter. At the horizontal line (region (b)), MG-IPM will begin to be replaced gradually by the ion associate of molybdophosphate (MG-HPM). The absorbances remain identical while MG-IPM is replaced by MG-HPM. Finally, at the region of the straight line corresponding to the calibration graph (region (c)), the MG-HPM formed is adsorbed on the membrane. This mechanism means that the extrapolated calibration graph must go through the origin (Fig.5 A), if the mixed reagent solution added to the sample solution and the solvent (water) used for the preparation of the standard working solutions are not contaminated by phosphate. Such an adsorptive mechanism indicates that the determination of phosphate by both a common calibration method and a standard addition method are impossible, if we cannot get phosphate-free reagent solution and water, where the reagent blank can play an important role on the accurate determination of phosphorus in ultrapurified water.

Evaporation/concentration of ultrapurified water

The evaporation method was selected as the enrichment of phosphorus in ultrapurified water samples, because “a standard reference ultrapurified water” ,which has a certified value for phosphate, is not available now. Furthermore, it is very difficult or is impossible to obtain chemicals, reagents, and solvents which are completely free from phosphorus. Therefore, the several fold enrichment of phosphorus in ultrapurified water samples without the addition of any reagents is required. This is why the evaporation/concentration method is adopted in this study.

Effect of silicate on phosphate determination

Normally, the amounts of interfering ions present in ultrapurified water are very small and generally tolerable [14]. However, silicate can form molybdosilicate in the presence of molybdate. Then, the molybdosilicate reacts with Malachite Green to form an ion associate, resulting in positive interference. In this study, the effect of silicate was examined at concentrations up to 1000 ng l^{-1} ($= 1 \text{ } \mu\text{g l}^{-1}$), and no interference was found (as an information, the concentration range of silicate in ultrapurified water is about $0.4\text{-}0.9 \text{ } \mu\text{g l}^{-1}$). This is because the acidity of the reaction solution for phosphate determination optimized in this study is stronger than that for silicate, and the formation rate of molybdosilicate is much slower than that of molybdophosphate [13].

Calibration graph

The calibration graph was constructed from $0\text{-}250 \text{ ng l}^{-1}$ of phosphorus using 40 ml of standard phosphate samples. As shown in Fig.6, the calibration graph showed a good linearity in the first filtration, whereas the absorbances obtained from the second filtration were almost equal. The reagent blank obtained in the first filtration correspond to the phosphate present both in the sample solution (ultrapurified water) and in 8 ml of the mixed reagent solution, while the absorbances obtained in the second filtration correspond to the ion associate of isopolymolybdate with Malachite Green.

The detection limit corresponding to three times of the standard deviations of the reagent blank was 8 ng l^{-1} when 40 ml sample was used. The detection limit obtained in the present procedure is the best of all the spectrophotometric methods reported so far. The standard deviation and the relative standard deviation from six measurements of the reagent blank were 0.0008 and 2.8%, respectively.

Slope comparison method (SCM)

The principle of the SCM was illustrated in Fig.7. In this method, the ion associates formed from both the phosphate in the original sample and the phosphate contaminating the reagents are concentrated into small volume to get sufficient sensitivity. The original sample volume (ultrapurified water) is also varied while the reagent volume is fixed. The absorbance increase with increasing the original sample volume is due only to the phosphate in ultrapurified water. Then, the resulting slope from the varied sample volume can be compared with the slope of the calibration graph.

From the effect of sample volume in Fig.2 and the detectable absorbances of the ion associate in Fig.5, the results indicate that the determination of ultratrace and trace amount of phosphate can not be performed by using a common calibration method (CCM, the absorbance of sample is directly plotted against the concentration of analyte) and a standard addition method (SAM), because the reagent blank values are easy to deviate in the sample, and trace amounts of phosphate still remained in the mixed reagent solution.

Since the CCM is applied, the phosphate found in the original sample is lower than the real value because there is some trace amounts of phosphate present in the reagent blank. However, if the SAM is used, the phosphate found will be higher than the real value because the reagent blank attributed to the ion associates of isopolymolybdate and chloride with MG, as well as a remaining phosphate in the mixed reagent solution, will be taken into account together with the real phosphate in the original sample. Much more difficulties will be obtained if the concentration of phosphate present in the original sample is much lower than phosphate present in the chemicals and the reagent solution used. In such condition, a requisite for the SAM is to eliminate the interference effect in the sample. However, this is much more difficult to do than to compensate for this effect (as in SCM). Such difficulties can be overcome by the SCM with two important points, such as : (1) the slope obtained by using varied sample volumes is only due to the phosphate in the original sample and (2) the

slope of calibration graph is only attributed to the phosphate added in the solution. Thus, by comparing these slopes, the influence of the trace amounts of phosphate present in the chemicals, reagent solutions, and solvent can be compensated. These are the reasons why the SCM is expected to be more reliable in terms of accuracy than the SAM and CCM if the methods are applied to trace-and ultratrace analysis.

Determination of phosphorus in ultrapurified water

Two kind of samples, ultrapurified waters prepared by ELIX 3 / Milli Q Element and ELIX 10 / Milli Q Element, were examined. By comparing the slopes of the sample solutions obtained by the evaporation/concentration method with the slope of the standard calibration graph, the phosphate concentration can be calculated. As shown in Fig.7, the phosphate amount in 20 ml of the sample solution (line B) corresponds to 1.394 ng of phosphorus ; therefore the concentration of phosphate in the sample solution is 1.394 ng/20 ml (= 0.0697 ng ml⁻¹ ; 69.7 ng l⁻¹). The slopes of the lines B and C are identically parallel each other. That slopes indicate : (1) the contamination or the vaporization of phosphate in the evaporation procedure is negligibly small, and (2) the evaporation to dryness does not affect the contamination and the vaporization of phosphorus. The absorbances of the line C are larger than those of the line B. Those can be due to the phosphate in 5 ml of the ultrapurified water, which is added to dissolve the residue after the evaporation to dryness. The phosphorus concentrations found were summarized in Table 1. The phosphorus contents obtained by the non-evaporation method is a little larger than those in the evaporation and/or dryness method. The difference can be attributed to the phosphorus amount in the mixed reagent solution. From this difference, we can estimate the phosphorus content remained in the mixed reagent solution after the filtration to be about 89.5 ng l⁻¹. Unavailability of any standard references of ultrapurified water, which has certified concentration of phosphate, cause a difficulty to check the accuracy of this method.

However, the repeatability and the analytical results obtained both by evaporation to 5 ml and the evaporation to dryness, showed excellent agreement of each sample. This result indicates that the proposed method, the slope comparison method (SCM) coupled with the evaporation procedure, is very reliable.

Acknowledgement

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

References

- [1] H.J. Heckemann, *Anal. Chim. Acta*, 410 (2000) 177.
- [2] C.X. Galhardo and J.C. Masini, *Anal. Chim. Acta*, 417 (2000) 191.
- [3] K. Itaya and M. Ui, *Anal. Chim. Acta*, 14 (1966) 361.
- [4] S. Motomizu, T. Wakimoto and K. Toei, *Analyst*, 108 (1983) 361.
- [5] C. Matsubara, Y. Yamamoto and K. Takamura, *Analyst*, 112 (1987) 1257.
- [6] S. Motomizu, M. Oshima and K. Araki, *Analyst*, 115 (1990) 1627
- [7] A. Muñoz, F.M. Torres, J.M. Estela and V. Cerda, *Anal. Chim. Acta*, 350 (1997) 21.
- [8] N. Goto, S. Motomizu and M. Oshima, *Bunseki Kagaku*, 42 (1993) 151.
- [9] Kathryn L.L. and Carolyn E.O., *Anal. Chim. Acta*, 450 (2001), 247.
- [10] Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Wiley, New York, 1986, p. 452.
- [11] J.P. Susanto, M. Oshima and S. Motomizu, *Analyst*, 120 (1995) 187.
- [12] S. Motomizu, J.P. Susanto, M. Oshima, H. Mikasa and H. Hori, *Anal. Sci.*, 11 (1995) 155.
- [13] J.P. Susanto, M. Oshima and S. Motomizu *Analyst*, 120 (1995) 2605.
- [14] K. Yoshimura and U. Hase, *Analyst*, 116 (1991) 835.

Figure and table captions

Fig.1 Evaporation chamber for ultrapurified water

A : evaporation system

B : electric heater (120°C)

Fig.2 Effect of sample volume on the absorbance of reagent blank

A : ultrapurified water (prepared by ELIX 3/ Milli Q Element at Okayama University);

B : ultrapurified water (prepared by ELIX 10/ Milli Q Element at Nihon Millipore Ltd, Tokyo);

1 : non-evaporation method, the ratio of the sample volume to the mixed reagent solution was 5 : 1 ;

2 : non-dryness evaporation method, 5 ml of 0.003 mol l⁻¹ HCl and 2 ml of the mixed reagent solution were added to the 5 ml of residual evaporated sample.

3 : dryness evaporation method, 5 ml of 0.003 mol l⁻¹ HCl, 5 ml of ultrapurified water, and 2 ml of the mixed reagent solution were added to the dried sample.

Fig.3 Effect of chloride ion on the absorbance of the reagent blank

● in the absence of molybdate ; ■ in the presence of molybdate ;

sample : ultrapurified water prepared by ELIX 3/ Milli Q Element.

Fig. 4 Adsorption mechanism of the ion associates between Malachite Green and anions on the membrane filter

□ Strong site (SS) of membrane filter ;

○ Weak site (WS) of membrane filter ;

◐ Strong site occupied by ion associate of isopolymolybdate-Malachite Green (MG-IPM) ;

◑ Strong site occupied by ion associate of molybdophosphate-Malachite Green (MG-HPM) ;

◒ Weak site occupied by ion associate of molybdophosphate-Malachite Green (MG-HPM).

Fig.5 Detectable absorbances of ion associates

MG-IPM : ion associate of isopolymobdate-Malachite Green ;

MG-HPM : ion associate of molybdophosphate-Malachite Green ;

A : the origin of the graph of the absorbance against the concentration of phosphorus.

Fig.6 Calibration graph of phosphorus determination

Sample volume : 40 ml ;

sample : ultrapurified water (prepared by ELIX 3 / Milli Q Element) ;

second filtration means that the filtrates of the first filtration are filtered again and the absorbances of the dissolved filters are measured.

Fig.7 Slope comparison method for the determination of phosphorus

A : calibration graph (sample volume : 10 ml); B : evaporation to 5 ml and dilution to 10 ml with 0.003 mol l^{-1} HCl , C : evaporation to dryness and dilution to 10 ml with each 5 ml of 0.003 mol l^{-1} HCl and ultrapurified water.

Sample : ultrapurified water (prepared by ELIX 3 / Milli Q Element).

Table 1 Determination of phosphorus present as phosphate in ultrapurified water samples by the slope comparison method.

*1 Sample : ultrapurified water prepared by ELIX 3 / Milli Q Element at Okayama University on May 17th, and May 29th, 2001.

*2 Sample : utrapurified water prepared by ELIX 3 / Milli Q Element at Nihon Millipore Ltd, Tokyo on May 23rd, 2001.

*3 Sample were evaporated to dryness.

*4 Sample were evaporated to 5 ml.

*5 Sample were not evaporated; therefore the value of 87.6 ng l^{-1} can include the phosphate in the mixed reagent solution.

Figures and table

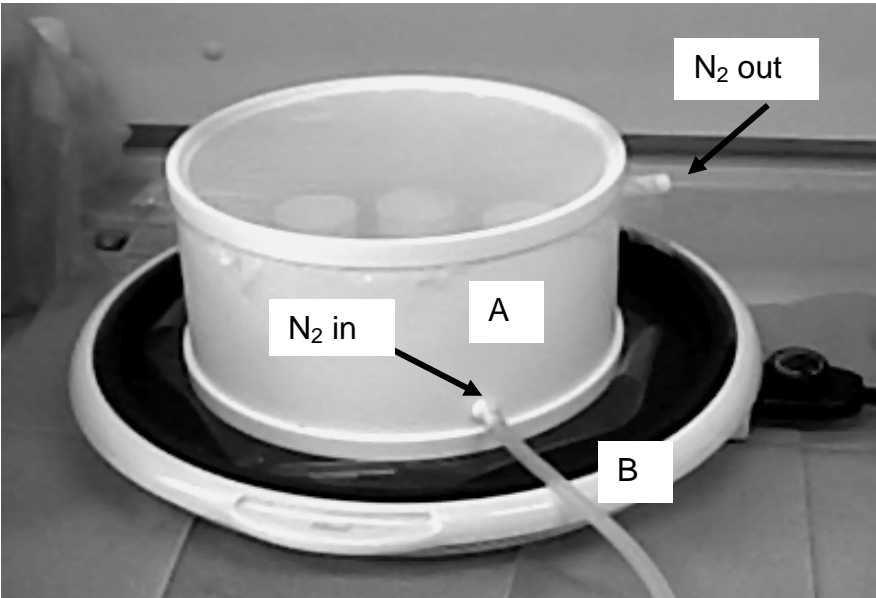


Fig.1 Evaporation chamber for ultrapurified water

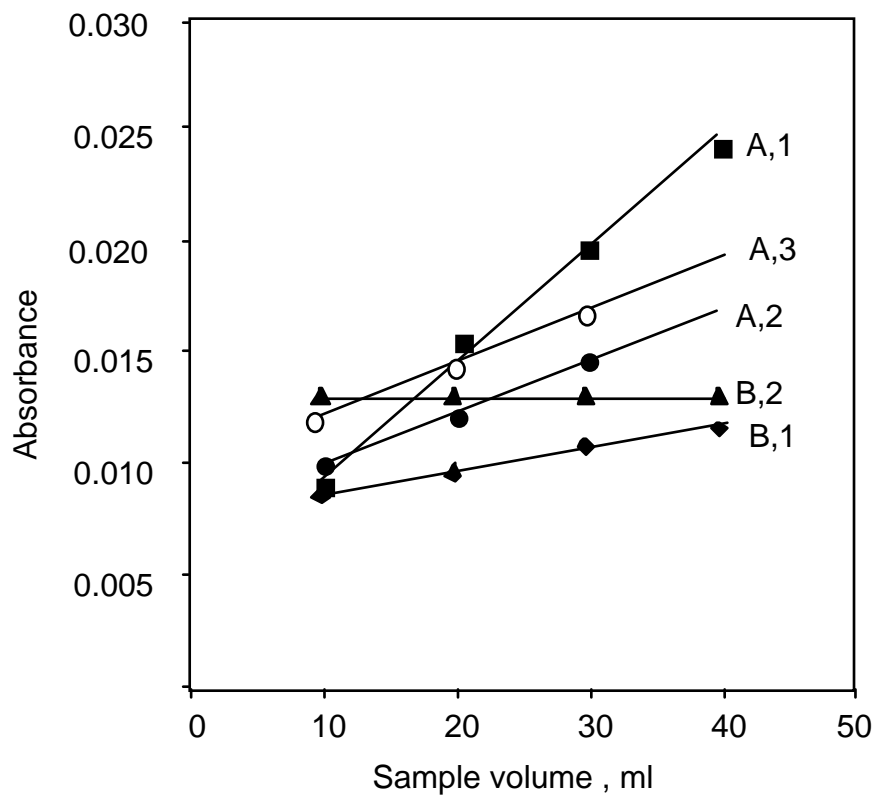


Fig.2 Effect of sample volume on the absorbance of the reagent blank

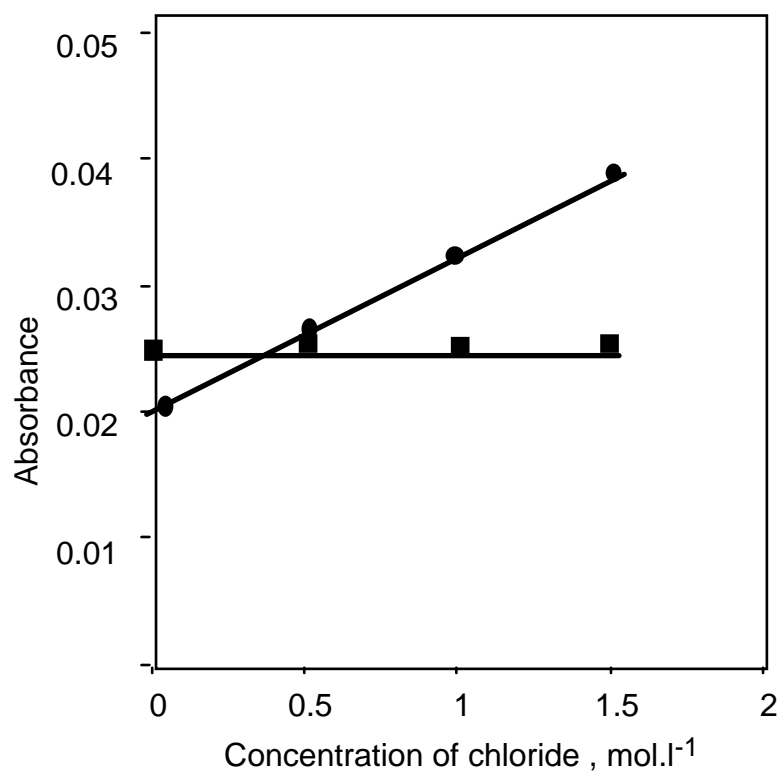


Fig.3 Effect of chloride concentration on the absorbance of a reagent blank

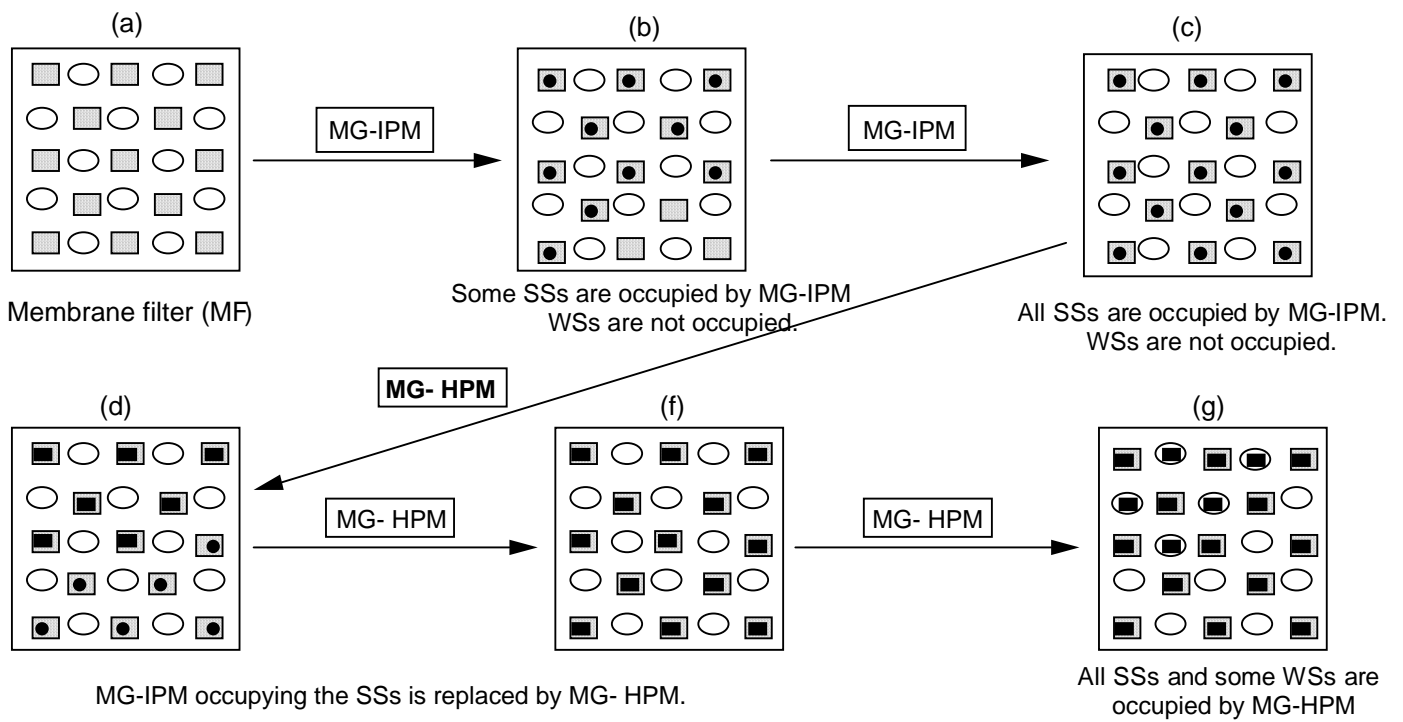


Fig. 4 Adsorption mechanism of the ion associates between Malachite Green and anions on the membrane filter

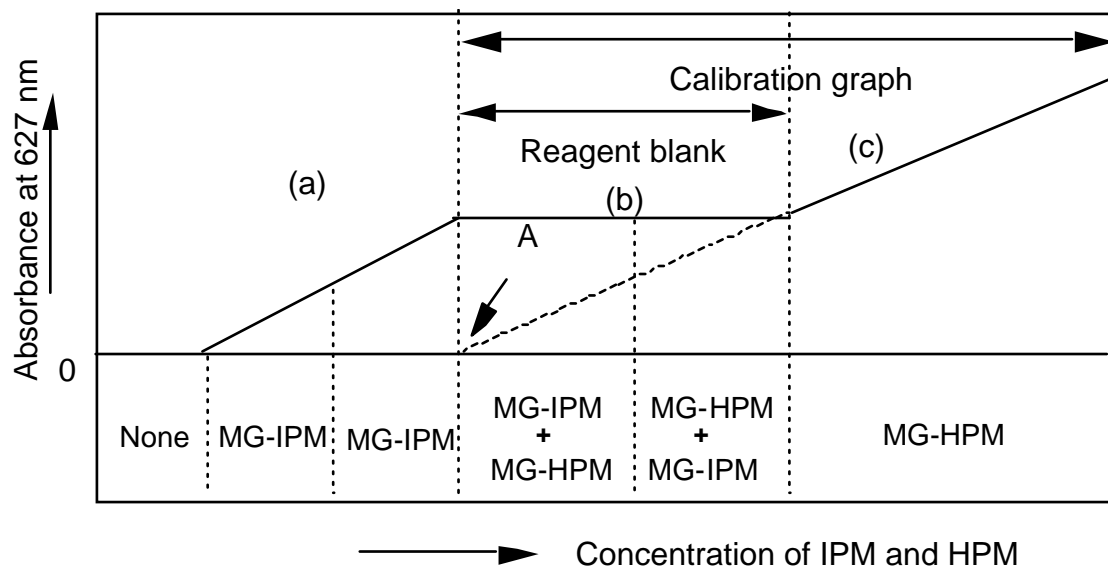


Fig.5 Detectable absorbances of ion associates

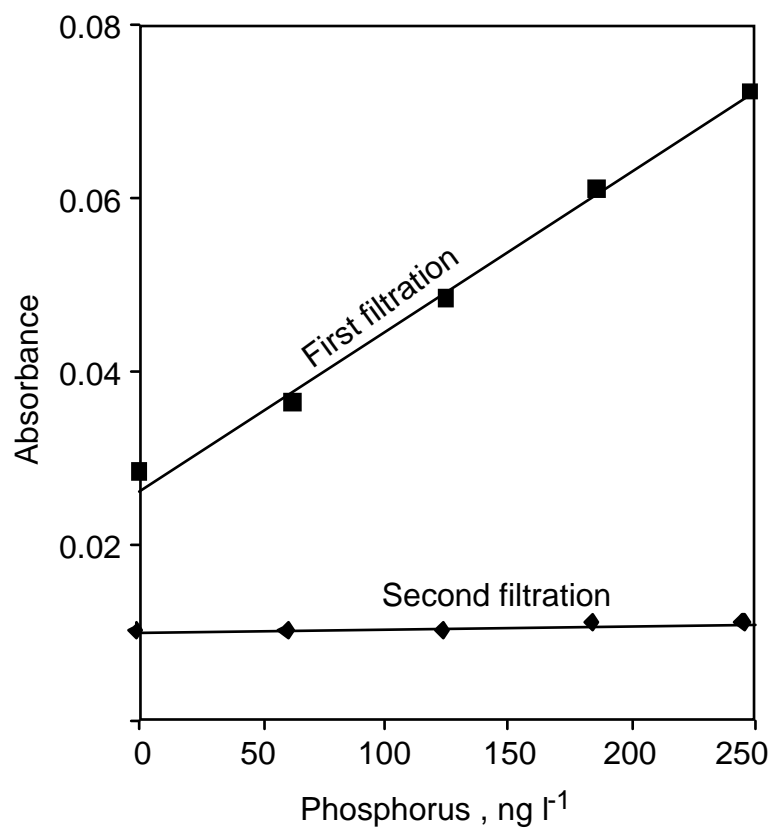


Fig.6 Calibration graph of phosphorus determination

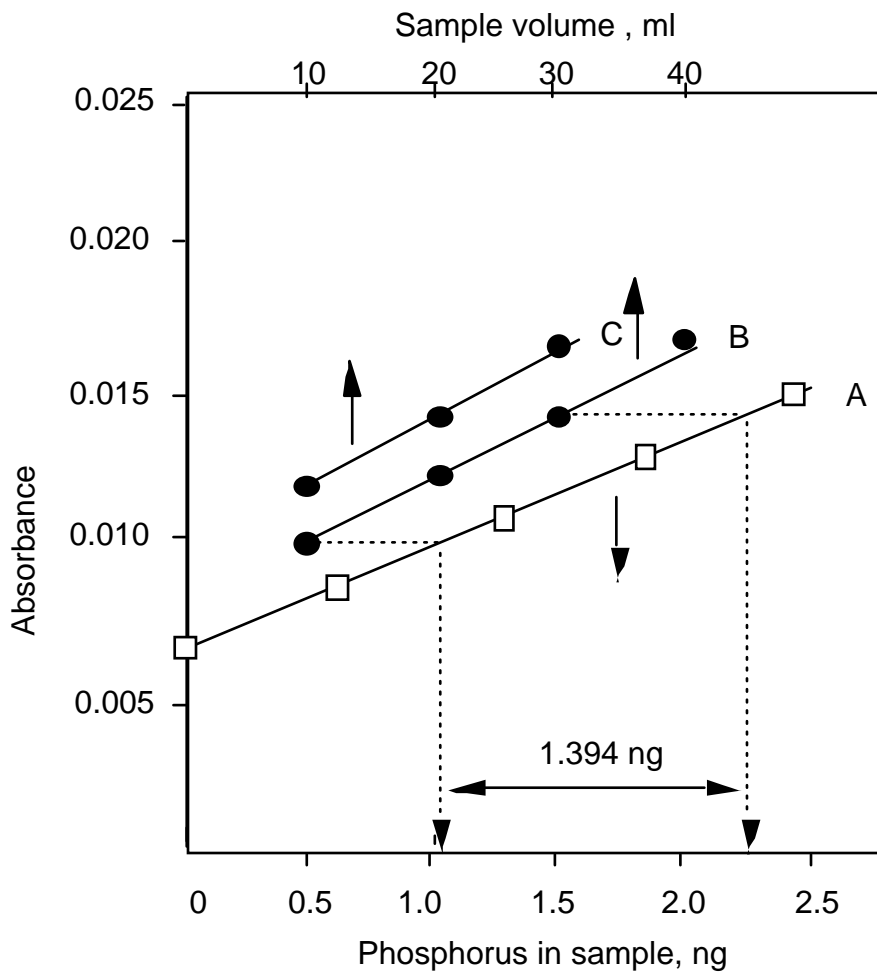


Fig.7 Slope comparison method for the determination of phosphorus

Table 1 Determination of phosphorus present as phosphate in ultrapurified water samples by the slope comparison method.

Sample	Sample volume (ml)	Slope		Phosphorus (ng l ⁻¹)
		Sample Δ abs./10 ml	Calibration graph Δ abs./10 ⁻⁹ mol l ⁻¹	
A ^{*1} (May 17)	10 - 30 ^{*3}	2.25 x 10 ⁻³	1.00 x 10 ⁻³	69.7
B ^{*1} (May 17)	10 - 30 ^{*4}	2.25 x 10 ⁻³	1.00 x 10 ⁻³	69.7
C ^{*1} (May 17)	10 - 40 ^{*5}	4.21 x 10 ⁻³	5.96 x 10 ⁻³	87.6
D ^{*2} (May 17)	10 - 30 ^{*3}	~ 0	1.05 x 10 ⁻³	~ 0
E ^{*2} (May 17)	10 - 30 ^{*4}	~ 0	1.05 x 10 ⁻³	~ 0