September, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2675—2677 (1981) 2675

An Improved Ion-exchanger Colorimetry for the Determination of a Trace Amount of Phosphate

Kiichi Matsuhisa,** Kunio Ohzeki, and Tomihito Kambara*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060
** *Division of Environmental Conservation, Graduate School of Environmental Science, Hokkaido University, Sapporo 060*

(Received March 3, 1981)

A highly sensitive and selective method has been developed for the determination of a trace amount of phosphate. It is based on the concentration of phosphate as the familiar molybdenum blue complex on the coagulated material prepared from finely divided anion and cation exchangers, collection of the mixed resin on a filter paper, and the subsequent measurement of the absorbance of the complex on the resulting thin layer of resin phase. The calibration curve shows a good proportionality in the concentration range of 1 to 6 μg P l^{-1}. The absorbance corresponding to 1 μg P l^{-1} is 0.095. The method is successfully applied to the determination of phosphate in a tap water and a river water.

Ion-exchanger colorimetry[1,2] was developed by Yoshimura *et al.* A colored metal complex is collected by batch method on the ion-exchanger, the size of which is ranging from 200 to 400 mesh. A part of the resin is then transferred into a cell of 0.1 cm in thickness, and the complex on the resin phase is determined colorimetrically. Trace amounts of chromiun(VI)[3] and zinc[4] were determined. The method was also applied to the determination of phosphate.[5] Phosphate was concentrated on the molybdate-loaded ion-exchanger and determined as the molybdenum blue complex.

An improved ion-exchanger colorimetry[6] was reported for the determination of chromium(VI). The method utilizes a mixture of finely divided anion and cation exchangers. Finely divided cation exchanger collects chromium(VI)–diphenylcarbazide complex rapidly by batch method in combination with anion exchanger to form bulky material. The coagulated resin is then separated by filtration and the resulting thin layer of the colored resin on a filter paper is directly subjected to spectrophotometric measurement.

In the present paper, an improved ion-exchanger colorimetry is reported for the determination of phosphate. The molybdenum blue complex is insistently fixed to the coagulated ion-exchangers. A highly sensitive and selective method is developed.

Experimental

Reagents. All reagents used were of analytical reagent grade. Freshly dried potassium dihydrogenphosphate was dissolved into deionized water to give a solution of 50 mg P l^{-1} (1 l = 1 dm^3). A solution containing 0.05 μg P ml^{-1} (1 ml = 1 cm^3) was prepared fresh daily by dilution of the stock solution. Twenty grams of hexaammonium heptamolybdate tetrahydrate were dissolved and diluted to 500 ml with water. Ascorbic acid solution of 0.1 mol dm^{-3} was made fresh dialy. Potassium antimony tartrate was dissolved into water to give a solution of 1 mg Sb ml^{-1}.

Mixed Reagent A: A 100-ml portion of 2.5 mol dm^{-3} sulfuric acid was mixed with 30 ml of the ammonium molybdata solution.

Mixed Reagent B: A 60-ml portion of 0.1 mol dm^{-3} ascorbic acid was mixed with 10 ml of the potassium antimony tartrate solution.

Dipping Solution: A 5-ml portion of 2.5 mol dm^{-3} sulfuric acid, 6 ml of 0.1 mol dm^{-3} ascorbic acid and 1 ml of potassium antimony tartrate solutions were mixed and diluted to 50 ml with water.

Mixed reagents and the dipping solution were prepared fresh daily and stored in a thermostat kept at 25±1 °C.

Ion-exchange Resins. Macroreticular type Amberlyst 15 and A-27 (both Rohm and Haas Co.) in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively, were used. Suspension of the respective resins was prepared according to the method reported.[7] The stock suspension was stored as required in the thermostat kept at 25±1 °C. The solution was well shaken before being pipetted out. The mutual coagulation of the finely divided anion and cation exchangers was examined as follows. The varying amounts of the anionic resin suspension (ARS) up to 20 ml were separately taken into a 50-ml beaker and diluted to 30 ml with water. A 10-ml portion of 0.25 mol dm^{-3} potassium chloride solution was added to keep the constant ionic strength. A 2.0-ml aliquot of the cationic resin suspension (CRS) was then added and the final volume of the solution was adjusted to 50 ml with water. The mixture was stirred magnetically for 10 min and filtered. The absorbance of filtrate was determined at 500 nm against water.

Apparatus. A Shimadzu UV-140-01 spectrophotometer was used. Filter papers (Toyo Roshi No. 5 A) were cut in 3 cm × 6 cm wide strips. A Toyo KG 25 filter holder (Toyo Roshi Co.) was used.

General Procedure. A 50-ml aliquot of the solution containing less than 0.3 μg phosphorus as phosphate was placed in a 100-ml beaker set in a water bath kept at 25±1 °C. A 6.0-ml portion of the mixed reagent A, 3.0-ml of the mixed reagent B, 6.0 ml of ARS and finally 2.0 ml of CRS were added to the sample solution. The mixture was stirred by means of a magnetic stirrer for 10 min. The resulting coagulated material was collected on one end of the filter strip placed on a holder. A disk of colored resin of the 17-mm diameter and about 0.3 mm in thickness was formed. The filter strip was dipped in the dipping solution for 20 min. It was then fixed on a glass plate fitted to the cell holder. The absorbance of the resin phase was measured at 700 nm against the other end of filter paper.

Another disk of resin was prepared without addition of phosphate. The absorbance corresponding to the reagent blank including the resins was also measured. The net absorbance of the complex on the resin was obtained by the difference.

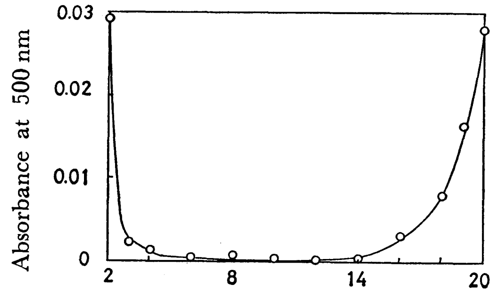

Fig. 1. Coagulation of the suspensions of finely divided cation and anion exchangers (CRS and ARS). A 2-ml portion of CRS was mixed with ARS in 50 ml of 0.05 mol dm^{-3} potassium chloride solution.

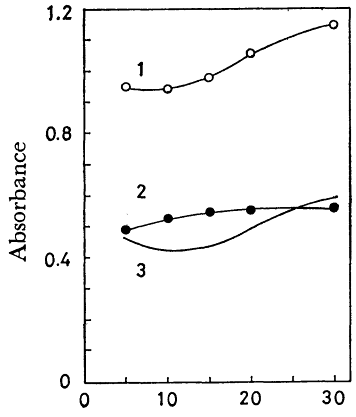

Fig. 2. Effects of shaking time on the fixation of the molybdenum blue compound on the mixed resin from the 50-ml solution containing 0.25 μg P (1), and without addition of P (2). Curve 3 indicates the net absorbance at 700 nm.

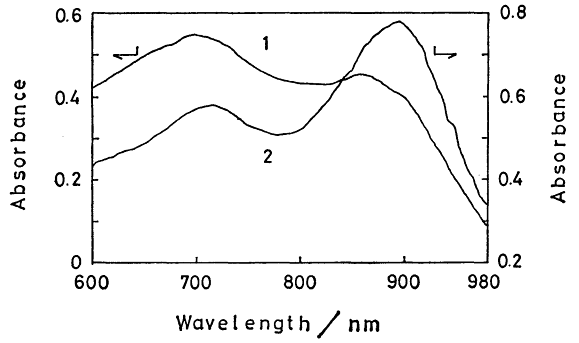

Fig. 3. Absorption curves of the molybdenum blue compound; (1) on the thin layer of mixed resin prepared from 50 ml of solution containing 0.3 μg P as phosphate, and (2) in aqueous solution containing 1 μg P ml^{-1} (1-cm cell).

Results and Discussion

Ion-exchanger. In the previous works[6—8] Amberlyst 15 and A-26 were used. In this work A-27 was used in place of A-26. The ion-exchange capacities of A-26 and A-27[9] have been reported as 4.4 and 2.6 meq g^{-1}, respectively. The pore radius range of A-26 is 14—22 nm and that of A-27 is 21—120 nm. Amberlyst A-27 is well suited for fixing the bulky anions.

Suspension. The suspension of Amberlyst 15 is slightly brown while that of A-27 is white. The ion-exchange capacities of ARS and CRS were determined by conductometric titration with the standard silver nitrate and sodium hydroxide solutions, respectively. The exchange capacities were 2.54×10^{-3} meq ml^{-1} for ARS and 5.21×10^{-3} meq ml^{-1} for CRS. The anion exchanger is 4—16 ml of ARS was almost completely coagulated with the cation exchanger in 2 ml of CRS (Fig. 1). The resulting mixed resin was easily separated by filtration from the solution. The combination of 2.0 ml of CRS and 6.0 ml of ARS was used throughout the following experiments.

Effect of Temperature. The preliminary experiments revealed that the development of coloration was seriously affected by the temperature of reaction solution. Hence, all experiments were carried out at a constant temperature of 25 °C.

Shaking Time. During the course of shaking, the anionic molybdenum blue complex is fixed on the anion exchanger, which combines with cation exchanger to form the coagulated material. The effect of shaking time was examined (Fig. 2). The absorbance of sample disk was almost constant in the shaking period of 5—10 min. With a prolonged shaking, the absorbance increased gradually. On the other hand, the blank value increased slowly with increasing shaking time. The net absorbance showed a constant value between 10 to 15 min.

Standing Time. The coagulated resin was filtered with a gentle suction. The resulting thin layer was stored wet in the dipping solution, the composition being determined after many trials. Almost a constant coloration was kept for 10—60 min.

Absorption Curve. The absorption curve of the molybdenum blue in the resin phase was different from that of in the solution (Fig. 3). The maximum at 890 nm in the solution[10] disappered when the complex was fixed on the ion-exchange resin. The complex on the resin has an absorption maximum at 700 nm.[5]

Calibration Curve. A calibration curve showed a proportionality in the concentration range of 1 to 6 ppb (μg l^{-1}) P as phosphate. The mean absorbance of blank value with the standard deviation was 0.535 ± 0.024 ($n=7$). The net absorbance for 6 ppb P were 0.550 ± 0.038 ($n=8$). The variation would be reduced if a temperature could be much more exactly controlled.

Effects of Forein Ions. The effects of arsenate and silicate were examined. The duplicate determinations of 0.2 μg P were carried out in the presence of one of them. The equal amount of As as arsenate gave a relative error of +8.1% and a 5000-fold amount of SiO_2 as silicate showed the deviation of +3.9%.

Analysis. The method was applied to the determination of phosphate in a tap water and a river water (Table 1). The standard addition method together with the original calibration method was applied to the analysis of a tap water. Both plots show-

Table 1. Results of analysis of a tap water for phosphate

Date 1980	Sample volume (ml)	P found (μg)	P in tap water (μg l^{-1})
05/11	5.0	0.088	17.6
	5.0	0.199[a)]	19.8
	5.0	0.294[b)]	18.8
10/11	5.0	0.099	19.8
	5.0	0.102	20.4
11/11	10.0	0.201	20.1
	10.0	0.203	20.3
14/11	10.0	0.156	15.6
	10.0	0.165	16.5

a) 0.100-μg P was added. b) 0.200-μg P was added.

ed good linearity with the same slope (Fig. 4). This result indicated that the recovery of phosphate as the molybdenum blue complex was quantitative from the sample solution to the mixed resin, although there were many competing ions for the ion-exchange sites. The variation of the phosphate content in the tap water supplied to our laboratory was examined. The water sample was taken freshly each day. As shown in Table 1, no significant variation was found in the period studied.

A river water was filtered through a filter paper (Toyo Roshi No. 5C) as soon as possible. The concentration was found to be 12 ppb P as phosphate. The value increased to 50 ppb P when the filtrate was treated with sulfuric and nitric acids to decompose the organic substances according to JIS method.[11] The considerable amounts of phosphate were found to originate from the organic substances in the river water.

The method was ascertained to be highly selective and sensitive for the determination of phosphate in water samples. Only small amount of sample water was required.

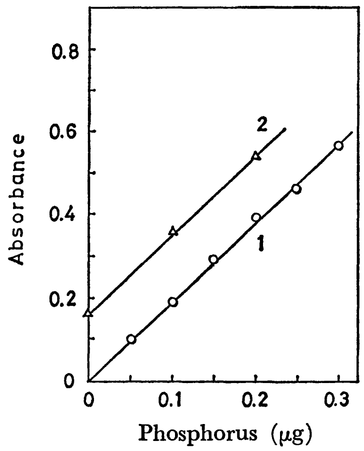

Fig. 4. Calibration curve (1) and the result of the standard addition method (2). Sample amount: 50 ml.

References

1) K. Yoshimura, H. Waki, and S. Ohashi, *Talanta*, **23**, 449 (1976).

2) K. Yoshimura, H. Waki, and S. Ohashi, *Kagaku Zokan*, **78**, 95 (1978).

3) K. Yoshimura and S. Ohashi, *Talanta*, **25**, 103 (1978).

4) K. Yoshimura, H. Waki, and S. Ohashi, *Talanta*, **25**, 579 (1978).

5) T. Tanaka, K. Hiiro, and A. Kawahara, *Bunseki Kagaku*, **28**, 43 (1979).

6) K. Ohzeki, T. Sakuma, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **53**, 2878 (1980).

7) M. Abe, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **51**, 1090 (1978).

8) M. Abe, N. Takei, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **52**, 2574 (1979).

9) K. A. Kun and R. Kunin, *J. Polym. Sci.*, *Part C*, 1457 (1976).

10) J. Murphy and J. P. Riley, *Anal. Chim. Acta*, **27**, 31 (1962).

11) JIS K 0101-1979, "Testing Method for Industrial Water."