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Application of Coagulated Ion-exchanger Colorimetry to the Determination of Trace Amounts of Phosphate in Water

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Synopsis. The combined use of finely divided anion and cation exchange resins reported previously[1)] was partly modified and applied to the determination of trace amounts of phosphate in some environmental water samples, such as rain, snow, lake water and seawater. Both orthophosphate and total phosphate were determined and satisfactory results were obtained.

The ion-exchanger colorimetry developed by Yoshimura *et al.*[2)] is an excellent method for trace analysis, in which a colored metal complex with negative or positive charge is concentrated on the corresponding ion-exchanger and determined spectrophotometrically in a 1-mm cell.

On the other hand, we reported a new type of ion-exchanger colorimetry,[3)] in which a combination of finely divided anion and cation exchange resins was used. One of the characteristics of fine particle ion-exchangers is the coagulation. The coagulated resins are collected on a filter paper as a disk of thin layer, which is directly subjected to spectrophotometric analysis, no cell being required. Therefore, hereafter, we call the method the coagulated ion-exchanger colorimetry.

Experimental

Reagents. Phosphate, molybdate, antimony tartrate, and ascorbic acid solutions were prepared according to the previous report.[1)]

Mixed Reagent: A 100-ml portion of 2.5 M (1 M=1 mol dm^{-3}) sulfuric acid was mixed with 30 ml of the ammonium molybdate solution and 10 ml of the potassium antimony tartrate solution. When a considerable amount of sulfuric acid was already contained in the sample solution, as in the case of hydrolyzable phosphate sample, the acid amount in the mixed reagent was reduced, so that a constant acidity in the final test solution was kept to 0.18 M.

Dipping Solution: The composition was the same as in the previous report.[1)]

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

Ion-Exchange Resin Suspension. The cation exchange resin suspension (CRS) and anion exchange resin suspension (ARS) were freshly prepared according to the method reported.[4)] The exchange capacities were 11.8 μequiv. ml^{-1} for CRS and 7.0 μequiv. ml^{-1} for ARS, respectively. Both suspensions were kept at 25±1 °C.

Apparatus. A Shimadzu UV 140-01 spectrophotometer was used. A Toyo KG 25 filter holder was used with filter papers of No. 5B (Toyo Roshi). A vacuum gauge used was a NRK product, type STV-75. Decomposition vessels of 70-ml capacity (Uniseal) were used.

Procedure. A 50-ml aliquot of the test solution containing less than 0.3 μg of phosphorus as phosphate was taken into a 100-ml beaker and the solution was kept at 25±1 °C in a water bath. A 6.0-ml portion of the mixed reagent and 2.0 ml of the ascorbic acid solutions were added and the solution was stirred by means of a magnetic stirrer for 5 min. Finally, 4.0 ml of ARS and 2.0 ml of CRS were added and the mixture was stirred for 10 min. The coagulated resins were collected on a filter paper strip placed on the holder with suction under *ca.* 160 mmHg by running water. A disk of colored resin, 17 mm in diameter and about 0.3 mm in thickness, was formed. The filter strip was soaked in the dipping solution for 15 min. It was then fixed on a glass plate fitted on the one side of cell holder, which is nearer to the light source, *i.e.*, the light beam goes successively through the thin layer, filter paper, and finally glass plate. The absorbance of the resin phase was measured at 700 nm against a dry filter paper or another white 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 phase was obtained as the difference.

The main differences of the proposed procedure from the previous one[1)] were in the following respects: firstly, 5 min were allowed for the development of the molybdenum blue complex (in the previous procedure, ARS and CRS were successively added immediately after the color developing reagents); secondly, resin suspensions with higher exchange capacities were used, namely, the total exchange capacities were 23.6 μequiv. for cation exchanger and 28.0 μequiv. for anion exchanger (in the previous procedure, the values were 10.4 and 15.2, respectively); thirdly, the suction pressure of *ca.* 4 times higher than that in the previous procedure was applied to collect the mixed resins.

Sample Preparation for Dissolved Orthophosphate (P-D, ortho). The sample water was filtered through No. 5C filter paper.

Sample Pretreatment for Total Phosphate (P, total). A 50-ml portion of sample water was used without filtration. According to the JIS method,[5)] it was digested with hot sulfuric and nitric acids, neutralized, and finally diluted to 50 ml with water. In the case of seawater, a 10-ml portion of sample was digested. A large amount of precipitate was formed, which was removed by filtration. The filtrate together with washings were neutralized and diluted to 100 ml with water. The solution for the blank test was prepared according to the same procedure with deionized water, instead of sample solution.

Pretreatment of Seawater for Hydrolyzable Phosphate (P, hydro). Familiar Harvey's method[6)] being partly modified, a 10-ml portion of seawater was taken into a Teflon crucible and 1.0 ml of 9 M sulfuric acid was added. The crucible was set in the jacket previously kept at 125 °C in an air-bath, and then allowed to stand for ca. 40 min at a room temperature. The sample solution was transferred into a 50-ml volumetric flask and diluted to the mark with water. The 5-ml portions of the solution were subjected to the standard addition method.

Results and Discussion

Stirring Time for Color Development. The thin layer with a constant coloration was obtained by

Table 1. Determination of phosphate

Sample	Date 1981	Amount ml	P-D, ortho ppb[a]	P, total ppb[a]
Snow, fresh	Mar. 16	50.0	$3.0_5\pm0.1_7$	
(Sapporo C.)		10.0		$3.7_8\pm0.2_1$
Snow, old	May 01	50.0	$4.1_4\pm0.0_9$	
(Asari-dake)		10.0		$7.6_3\pm0.5_6$
Lake water	Jun. 04	50.0	$5.1_8\pm0.2_3$	
(Shikotsu-ko)		10.0		$8.3_0\pm1.0_0$
Rain	Jul. 07	50.0	$3.7_6\pm0.6_4$	
(Ebetsu C.)		25.0		$4.7_0\pm1.7_1$
Rain	Jul. 10	50.0	$5.3_7\pm0.6_3$	
(Sapporo C.)		25.0		$7.5_4\pm1.4_5$

a) The 95% confidence limits (n=3).

Table 2. Determination of phosphate in seawater[a]

Date 1981	Sample amount ml	P-D, ortho ppb[b]	P, total ppb[b]	Sum of (P, hydro) and (P, ortho) ppb[b]
Jun. 25	4.0	26.2±1.2		
	2.0		31.1±9.5	
Jun. 29	4.0	24.8±5.8		
	2.0		37.0±13.0	
Aug. 10	4.0	23.3±2.7		
Aug. 15	4.0	21.5±5.0		
Sep. 08	4.0	17.4±5.0		
	1.0			41.1±6.7[c]
	1.0			41.8±6.0[d]
Sep. 16	2.0	17.7±1.1		
	1.0			40.0±1.1[c]

a) Surface seawater at Ishikari bay. b) The standard addition method was applied and the 90% confidence limits (n=4) were calculated. c) 90-min heating. d) 250-min heating.

stirring the test solution in the range 5—30 min before the addition of CRS and ARS. When the resins were added immediately after the addition of the mixed reagent and ascorbic acid solution, a lower absorbance was observed.

Calibration Graph. The calibration graph was linear over the concentration range 1.0—6.0 ng P ml^{-1}. The mean absorbance with the standard deviation was 0.148±0.005 (n=3) for 1.0 ppb P and 0.833±0.012 (n=5) for 6.0 ppb P. The modified procedure having an improved sensitivity was advantageous in comparison with the previous one.[1]

Determination of Phosphate. The results are summarized in Tables 1 and 2. The amount of orthophosphate is determined much more precisely than that of total phosphate, since no pretreatment except filtration is required. The application of the JIS method[5] to the determination of total phosphate has been reported to be difficult.[7] A large amount of precipitate formed in the course of acid digestion will cause the loss of phosphorus and poor reproducibility (Table 2).

On the other hand, the sum of hydrolyzable phosphate and orthophosphate (P, ortho)[8] in seawater is fairly precisely determined (Table 2). Sample seawater was heated in the presence of sulfuric acid at 125 °C in a Uniseal decomposition vessel. A 90-min heating was enough to hydrolyze any phosphate present in seawater. The combined use of sulfuric acid and potassium peroxodisulfate for the determination of total phosphate was also examined, but no reliable result was obtained.

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