Determination of Ortho-, Pyro- and Tripolyphosphate by the Use of a Small Column of Ion-exchange Resin

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The determination of ortho-, pyro- and tripolyphosphate in their mixture is usually carried out by paper chromatography[1] or ion-exchange chromatography[2]. In paper chromatographic determination satisfactory separation of the chain phosphates can be obtained only in acid chromatographic solvent mixtures. Therefore, care must be taken about partial hydrolysis of the condensed phosphates during a chromatographic separation. When paper chromatographic separation is performed at room temperature (15~30°C), a correction due to the hydrolysis of the condensed phosphates should be applied, depending on the temperature. When the separation is performed at a lower temperature then 5°C, the correction due to the hydrolysis is negligible, but a long time is consumed for the separation. On the other hand in the ion-exchange chromatographic determination the phosphates adsorbed by a column are successively eluted with a buffered solution of potassium chloride of pH 4~9. Therefore in the process of the elution the condensed phosphates are not hydrolyzed practically, but by the use of a column of the usual scale a long time is consumed for the separation.

The purpose of this paper is to present a rapid method for the determination of mixed ortho-, pyro- and tripolyphosphate by the use of a small column of ion-exchange resin. The continuous-gradient elution method by Jameson[2h] was applied and a paper micro-fraction collector was used.

Experimental

The assembly of apparatus used in this investigation is shown in Fig. 1.

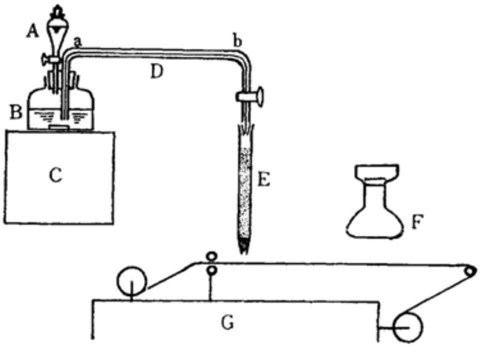

Fig. 1. Apparatus.
A : Stock bottle, B : Mixing bottle,
C : Magnetic stirrer, D : Capillary,
E : Column, F : Infrared lamp,
G : Paper micro-fraction collector.

Ion-exchange Column.—A coarser part of Dowex 1-X 4 (200~400 mesh) of chloride form was filled in a capillary, 2.6 mm. in diameter and 60 mm. in height.

Phosphate Samples.—Disodium hydrogen orthophosphate dodecahydrate, tetrasodium pyrophosphate decahydrate and pentasodium tripolyphosphate hexahydrate were used.

Elution.—Solutions of potassium chloride of various concentrations were buffered with sodium formate and formic acid. The concentrations of sodium formate and formic acid were kept constant (HCOONa 5.1 g./l. and 80% HCOOH 2.5 ml./l.) and the pH of the solution was regulated with aqueous ammonia. The solution of potassium chloride in a stock bottle was continuously added to a mixing bottle which contained 10 ml. of water initially. Then the solution in the mixing bottle was introduced to the ion-exchange column. The flow rate was regulated to be about 30 sec./drop.

Fraction Collector.—By the use of a paper micro-fraction collector[3] manufactured by Mitamura the eluted solution was collected drop by drop on a piece of filter paper and was dried immediately with an infrared lamp.

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Qualitative Observation on the Separation of Phosphates. — After the separation the filter paper containing phosphates was sprayed with a solution which was made by mixing 5 ml. of 60% perchloric acid, 1 ml. of concentrated hydrochloric acid, and 1 g. of ammonium heptamolybdate tetrahydrate and diluting this to 100 ml. with water. The sprayed paper was dried under the infrared lamp, then placed under an ultraviolet lamp and irradiated until blue spots appeared.

Quantitative Analysis of Phosphate Mixtures.— The paper area containing each phosphate species was cut into small pieces and was burned to ashes in a crucible. The ash was digested with nitric acid and the acid solution was evaporated to dryness. The residue was dissolved in a diluted solution of sulfuric acid and the phosphate was determined colorimetrically according to the method of Karl-Kroupa[1c)].

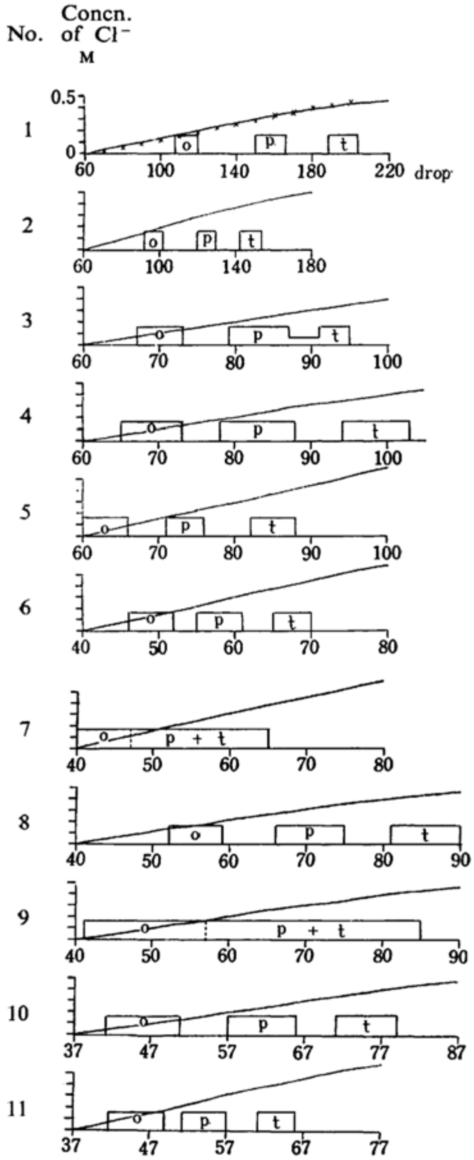

Fig. 2. Separation of phosphate mixtures.
o : Orthophosphate, p : Pyrophosphate,
t : Tripolyphosphate.

Results and Discussion

Experimental results for the dependence of separation of phosphate mixtures on the elution conditions are summarized in Fig. 2 and Table I. The rectangles in Fig. 2 indicate only the positions of phosphate species in the elutions but not their concentrations. The variation of the concentration of chloride ion in the eluant is expressed by the equation,

$$x = a(1 - e^{-ft/v}) \qquad (1)$$

where x (mol./l.) is the concentration of chloride ion in the mixing bottle, a (mol./l.) is the concentration of chloride ion in the stock bottle, f (ml./min.) is the flow rate, v(ml.) is the volume of solution in the mixing bottle and t (min.) is the time from the start of mixing. The curves in Fig. 2 indicate the concentration of chloride ion in the eluant calculated from Eq. 1. The cross marks in Fig. 2-1 indicate the concentration of chloride ion determined experimentally.

TABLE I. CONDITIONS OF EXPERIMENTS SHOWN IN FIG. 2

No.	Amount of phosphate μg.		Concn. of KCl in the stock bottle M	pH of KCl soln.
1	Each	20	0.75	5.5
2	〃	20	1	5.5
3	〃	20	2	5.5
4	〃	20	2	4.5
5	〃	20	3	4.5
6	〃	20	3	4.5
7	〃	100	3	4.5
8	〃	100	2	4.5
9	〃	300	2	4.5
10	〃	100	2	4.5
11	Ortho Pyro Tripoly	100 10 10	3	4.5

The capillary between a and b in Fig. 1 was shortened step by step to promote the efficiency of the elution. In the experiments of Fig. 2-1∼5, 6∼9 and 10∼11, the capillaries of the length 41.5, 24.0 and 20.7 cm. were used, respectively.

Jameson[2h)] used 0.75 M solution of potassium chloride of pH 5.5 as a stock solution to determine the compositions of strong phosphoric acids. Using a potassium chloride solution of the same concentration and pH as those used by Jameson, the authors tested the separation of the phosphate mixture. The separation of 20 μg. as phosphorus of each phosphate species is complete, but too much eluant is consumed

(Fig. 2–1). The same amounts of the phosphate mixture can be separated by the use of 1 M potassium chloride of pH 5.5 (Fig. 2–2), but in the case of 2 M potassium chloride of pH 5.5 the separation of pyro- and tripolyphosphate is incomplete (Fig. 2–3). The use of 2 or 3 M potassium chloride of pH 4.5 can separate 20 μg. as phosphorus of each phosphate species (Fig. 2–4 and 5, and 6). The separation of 100 μg. as phosphorus of each phosphate species can not be achieved by the use of 3 M potassium chloride of pH 4.5 (Fig. 2–7). On the other hand 2 M potassium chloride of pH 4.5 should be used for that purpose (Fig. 2–8 and 10). However, 2 M potassium chloride of pH 4.5 can not separate 300 μg. as phosphorus of each phosphate species (Fig. 2–9).

As shown in Fig. 2–10, 100 μg. as phosphorus of each phosphate species can be separated by letting only 79 drops of the eluant flow. Similarly 100 μg. of orthophosphate, 10 μg. of pyrophosphate and 10 μg. of tripolyphosphate, as phosphorus in all cases, can be separated satisfactorily by letting only 66 drops of the eluant flow (Fig. 2–11).

TABLE II. RESULTS OF ANALYSES OF PHOSPHATE MIXTURES

Sample	Phosphate species	% P		
		Calcd.	Found, this method	Found, paper chromatography[1c]
Pure phosphate mixture	Ortho-	50.1	50.4	50.8
	Pyro-	49.9	49.6	49.2
Pure phosphate mixture	Ortho-	66.8	67.5	—
	Pyro-	33.2	32.5	—
Commercial sodium tripolyphosphate	Ortho-	—	0.0	0.0
	Pyro-	—	7.6	7.2
	Tripoly-	—	92.4	92.8

The results of the quantitative analyses obtained by the precent procedure are shown in Table II. The first and the second sample are synthetic mixtures of pure alkali orthophosphate and pyrophosphate and the third sample is a commercial sodium tripolyphosphate. For comparison, the paper chromatographic analyses were carried out for the first and the third sample by the method of Karl-Kroupa[1c]. The data obtained by the present method were well coincident with the calculated values and the data obtained by paper chromatography.

Summary

The authors presented the new rapid method for the determination of ortho-, pyro- and tripolyphosphate in the mixture by the use of a small column, 2.6 mm. in diameter and 60 mm. in height, of ion-exchange resin, Dowex 1−X4 (200∼400 mesh). The continuous-gradient elution method was applied and the paper micro-fraction collector was used. For example, by the use of 2 M potassium chloride of pH 4.5 as the stock solution, 100 μg. as phosphorus of each phosphate species can be separated by letting only 79 drops of the eluant flow. The quantitative data obtained by the present method were well coincident with the calculated values or the data obtained by the paper chromatography.

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