Studies on Several Phosphates from the View-point of Analytical Chemistry. V. An Electro-Chromatography on Several Meta- and Poly-phosphates labelled with P^{32}

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In the previous paper[1] we reported on the separation by paper chromatography of several meta- and poly-phosphates. In this paper the behaviour of several phosphate ions in electro-chromatography is discussed. The detection of the positions to which several phosphate ions migrated was carried out with active phosphates labelled with P^{32} and was found to be made possible by decolorization caused by the formation of complex metal phosphates.

Material and Apparatus

Samples used were sodium ortho-, pyro-, trimeta-, tripoly-, and hexameta-phosphate[1,2]. Almost all the separations reported here were performed on paper moistened with a single supporting electrolyte, i.e. aqueous acetic acid or ammonium acetate. Filter paper (Toyo Rosi No. 50, size 20 cm. ×20 cm.) was employed in all the experiments described herein. Aqueous solutions permeate this paper exceptionally well and hence it was found useful in the formation of chromatograms which may be developed quickly by flow of solvant.

The control of temperature of the paper during the electrical migration was not necessary because there was no remarkable change of temperature. A dry sheet of filter paper was placed on the glass sheet (the size was equal to that of the paper) and the acetic acid solution was added until an excess was present in the paper. After a few minutes, the excess electrolytic solvent was removed with a piece of blotting paper and the mixed solutions to be investigated were then added by a sharp-pointed capillary to pencilled circles on the paper.

Platinum wire electrodes were placed along both ends of the paper on which a glass sheet of the same size was placed. These two glass plates were firmly pressed together with clamps. Potential (0 to 300 V.) from an electronic rectifier was applied to these electrodes.

Detection and Identification of Several Ions

a) Tracer Method. — The migration of radioactive ions in the moist paper was followed with a thin-window G. M. Counter[1]. When the separation was complete, the moist filter paper was placed in a warm (25°∼30°C) well ventilated hood and dried on a table shielded from radioactive contamination by a thick nonactive paper placed on glass sheets. The filter paper was then cut along pencilled lines and it was found that the ions had migrated parallel to the lines and had been separated. The cut papers were treated by the method reported previously[1] and hence radioactive ions separated in the filter paper were detected directly with a G. M. tube and scaler. Non-radioactive ions and acidic and basic zones in the paper were detected with suitable reagents and acid-base indicators.

b) Chemical Method. — In spot tests of phosphate ions, Feigl[3], Hanes, and Isherwood[4] have already applied the formation of molybdenum blue from complex phosphomolybdate. We were able to detect phosphate ions (0.1 to 0.05 M) simply, by using Fe (III) (0.01 to 0.005 M) and $[Fe(CN)_6]$ (IV) (0.01 to 0.05 M) as reagents. Concentrations of reagents were adjusted so they could correspond with that of the samples. Sample solutions were dropped on the filter paper and dried in air. Then iron alum solution was sprayed on uniformly and again after drying in air, $[Fe(CN)_6]$ (IV) ion solution was sprayed on. Instantly the paper turned prussian blue in colour, but the parts where phosphate ions were present remained unchanged or developed somewhat different colours as compared with the colour of the

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[1] M. Shinagawa, T. Takanaka, Y. Kiso, A. Tsukiji and Y. Matama, This Bulletin, **28**, 565 (1955), Presented at the 7th Annual Meeting of Chem. Soc. of Japan, April 1954.

[2] L. T. Jones, *Ind. Eng. Chem. Anal. Ed.*, **14**, 536 (1942).

[3] F. Feigl, "Qualitative analysis by spot test" 3rd English edition, 1947, p. 251. F. Feigl, *Z. Anal. Chem.*, **61**, 454 (1922): **74**, 386 (1928).

[4] C.S.I. Isherwood, *Nature*, 164, 1107 (1949).

background. If the reagent solution were sprayed in reverse, it was possible to detect and identify phosphate ions by the difference in colours of the discoloured spots and in the widths of spot-rings, as shown in Table I.

TABLE I

SPOT TEST FOR SEVERAL PHOSPHATE IONS

Phophate ion	Colour of spot	Width of ring	Identif. Lim.
PO_4^{3-}	thin violet	narrow	10 γ
$P_2O_7^{4-}$	thin violet	diffuse	
$P_3O_9^{3-}$	deep blue	diffuse	
$P_3O_{10}^{5-}$	thin violet	wide	1.3 γ
$P_6O_{18}^{6-}$	thin blue	narrow	20 γ

Identification limit of tripolyphosphate ion was the smallest among several phosphates. Identification limits shown in Table I are minimum quantities that permit the specific detection of each ion. However when the detection was not restricted to specificity, the detection limits were much smaller.

These methods for detecting phosphate ions proved satisfactory in procedure and in specific detection and were comparable to Feigl's method[4].

This method could be applied to paper chromatography and electro-chromatography.

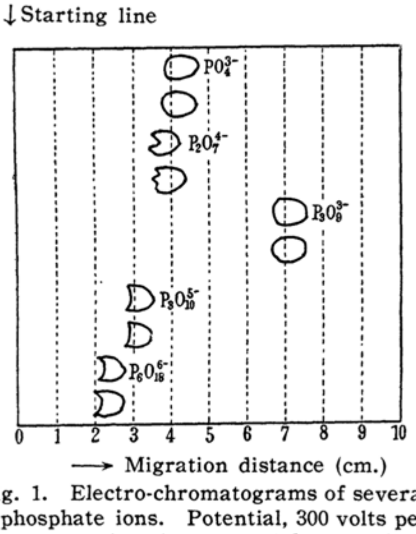

Fig. 1. Electro-chromatograms of several phosphate ions. Potential, 300 volts per 20 cm.; migration time, 2 hours; electrolyte, 0.1 mol. ammonium acetate.

Result

Fig. 1 was obtained by the detection method reported previously[3].

The vertical axis indicates the counting rate per minute and horizontal axis the migration distances of each phosphate ion. Sample concentration was about 0.05 M; the migration time, two hours; and the electrolyte concentration, 0.1 M.

Fig. 2 shows the decolorization patterns of phosphate ions which was gotten from the method of decolorization.

Fig. 1 and Fig. 2 were obtained from same experimental results.

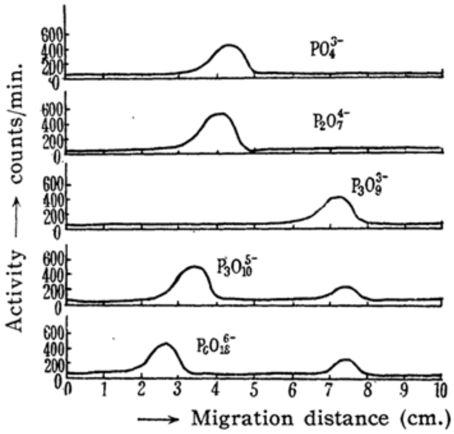

Fig. 2. Electro-chromatograms of several phosphate ions. Potential, 300 volts per 20 cm.; migration time, 2 hours; electrolyte, 0.1 mol. ammonium acetate.

Summary

1) Several phosphate ions can be separated by the present electro-chromatographic method. This method of separation is a vast improvement over the paper chromatography.

2) The smaller the number of phosphorus atoms contained in a phosphate ion, the greater the migration rate of ion in the case of chain ionic structure. Trimetaphosphate ion which has ring ionic structure showed the greatest migration rate among all of them.

3) The test by means of prussian blue was more distinct in electro-chromatography than in paper chromatography.

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