

THE ISOLATION OF PEROXOMONOPHOSPHORIC ACID BY ANION-EXCHANGE CHROMATOGRAPHY

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Previous attempts to separate peroxomonophosphoric acid from associated orthophosphoric acid have been unsuccessful, partly because no suitable selective precipitant has been found^{1,2} and partly because the strongly oxidizing peroxy-acid is readily decomposed.

In the analogous peroxomonosulphuric acid-sulphuric acid system¹, sulphuric acid can be removed as barium sulphate, leaving the peroxomonosulphuric acid in solution, but it has been confirmed that aqueous peroxomonophosphates decompose in the presence of barium ions and molybdate ions, the commonest precipitants used in mixed phosphate systems.

BOYLAND AND MANSON³ reported that peroxomonophosphoric acid could be separated from its acetone complex and phosphoric acid by paper chromatography, but all the active oxygen was subsequently lost from the chromatograms.

Orthophosphates, pyrophosphates, and the more highly condensed polymetaphosphates can be separated by precipitation techniques^{2,4} but a more effective and more widely applicable method of separation is anion-exchange chromatography⁵⁻⁸. We now report the use of an anion-exchange method for the separation of peroxomonophosphoric acid.

A chloride eluant is normally employed for phosphate separations; the pH of the eluant is varied over a wide range depending on the composition of the phosphate mixture.

Preliminary experiments showed reaction between peroxomonophosphoric acid and polystyrene resins to be very slow below 20°. Peroxomonophosphates decompose rapidly in alkaline solution, but only very slowly in neutral or weakly acid chloride solution or in acetate buffer solution. When aqueous peroxomonophosphoric and orthophosphoric acids were run on to a small column of strong-base anion-exchange resin in its chloride form, orthophosphate ion was eluted by a neutral chloride solution significantly before peroxomonophosphate ion, and a partial separation of the two anions was achieved. Solutions of peroxomonophosphoric acid in aqueous sodium chloride were concentrated by freeze drying, without significant loss of peroxy-oxygen, but neither chloride nor peroxomonophosphate could be precipitated from the solution without loss of oxygen. Peroxomonophosphoric acid rapidly oxidized hydrochloric acid, even at 0°C, when the solution was acidified.

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Peroxomonophosphoric acid decomposes only slowly in dilute acetic acid at 20°C. With the resin column in its acetate form, effective separation of a peroxomonophosphate/orthophosphate mixture is achieved when an acetate buffer solution is used as eluant. The eluate can be concentrated by vacuum distillation and the metal ions removed by passing the solution through a cation-exchange resin in its hydrogen form; only slight (5%) loss of peroxo-oxygen occurs during these operations. Acetic acid can be removed from the solution containing the peroxomonophosphoric acid, by further vacuum distillation and freeze drying, to leave a viscous, involatile residue of peroxomonophosphoric acid.

More than 25% of the peroxo-oxygen was lost during the final concentration of the peroxo-acid. Attempts to precipitate salts of the acid or to obtain crystalline salts from solutions of the acid were unsuccessful.

Although it has not been possible to isolate a pure salt of peroxomonophosphoric acid, the procedure described overcomes several difficulties experienced by other workers. We have shown that it is possible to separate peroxomonophosphoric acid from orthophosphoric acid and to estimate each. Peroxomonophosphoric acid prepared from the acetate eluate is suitable for further study since its passage through both cation and anion-exchange resins removes all ionic impurities, among them the heavy metal ions which are likely to cause catalytic decomposition. Apart from the orthophosphoric acid formed by self-decomposition, the only contaminant is a small amount of involatile organic material.

EXPERIMENTAL

Preparation of peroxomonophosphoric acid

Peroxomonophosphoric acid was prepared by adding hydrogen peroxide (Laporte "80% plus" peroxide) to a suspension of phosphorus pentoxide in acetonitrile, according to the method of TOENNIES⁹. This method gave a mixture of orthophosphoric and peroxomonophosphoric acids; the yield of peroxo-acid (ca. 60%) was lower than previously reported, but in the earlier work the product may have been contaminated by hydrogen peroxide. When the acetonitrile solution was run on to an anion-exchange column the phosphorus acid anions were absorbed whilst the solvent and the excess of hydrogen peroxide could be washed from the column with water.

Analytical methods

Peroxomonophosphoric acid reacted rapidly and quantitatively with neutral potassium iodide solution to give iodine which was estimated spectrophotometrically by the absorption due to the I_3^- ion at 360 m μ ¹⁰. Aliquots of the eluate (0.05 ml) were added to 2 ml of 1% potassium iodide and the light absorption measured using 1 cm cells in a Unicam SP 600 spectrophotometer. The iodine equivalent to H_3PO_5 had a molar extinction coefficient of 23,700.

Phosphoric acid was estimated spectrophotometrically. Aliquots of the eluate (0.05 ml) were added to 2 ml of ammonium vanadomolybdate reagent¹¹ and the absorption measured against a reagent blank at 375 m μ , using the SP 600. Under these conditions the phosphate complex had a molar extinction coefficient of 5,250. In the presence of peroxomonophosphoric acid, orthophosphoric acid readings were too high since the peroxo-acid was catalytically decomposed to orthophosphoric acid by

the reagent. A correction was applied to obtain the actual orthophosphate concentration.

Chromatographic separation

Preliminary experiments were made with a 10 ml column packed with Deacidite FF strong-base (quaternary ammonium) polystyrene resin. Peroxomonophosphate could be recovered from the column in better than 95% yield (chloride elution). Subsequent experiments were carried out using a larger column (80 ml). To reduce the decomposition of the peroxo-anion the resin was maintained at 5°C by the circulation of cold glycol between double walls.

With the column in its acetate form *ca.* 5 ml of the prepared phosphorus acid mixture in acetonitrile was run on to the column and eluted with an acetate buffer solution, pH 5.0, at 3 ml/min. Corrected analysis figures for a typical separation are shown in Table I and the corresponding elution curve in Fig. 1.

TABLE I
THE CHROMATOGRAPHIC SEPARATION OF PEROXOMONOPHOSPHORIC ACID
AND ORTHOPHOSPHORIC ACID

Sample: 6 ml of H_3PO_4/H_3PO_5 prepared solution in acetonitrile. Eluant: 0.5 M KOAc/HOAc buffer solution, pH 5.0. Elution rate: 3 ml/min. Column: 22 cm \times 2.1 cm. Packing: Deacidite FF resin.

Total eluate (ml)	Phosphorus concentration (mmole/l)	
	as H_3PO_4	as H_3PO_5
350	0.16	0.03
450	4.88	0.03
550	10.27	0.28
600	11.75	0.40
650	10.37	0.65
800	3.88	1.27
1,000	0.41	2.02
1,200	0	2.24
1,400	0	1.92
1,600	0	1.33
1,800	0	0.80
2,000	0	0.45

Treatment of eluate

The eluate was collected for peroxo-acid recovery after the phosphorus present in the peroxo-form exceeded 95%. The maximum peroxomonophosphate concentration was about 0.005 M; eluate was collected until the concentration fell to 0.0005 M (total volume 1-2 l). The combined eluate was vacuum distilled below 28°C to reduce its bulk (to *ca.* 150 ml). Some potassium acetate generally crystallized from the solution at this stage and was filtered off. The remaining peroxomonophosphate solution (*ca.* 0.1 M) in concentrated potassium acetate was run through a large column of cation-exchange resin (Amberlite IR 120, hydrogen form) to give a solution of peroxomonophosphoric acid in aqueous acetic acid. This solution was again vacuum distilled to leave a colourless, viscous mass. Peroxomonophosphoric acid was estimated in this residue iodometrically, total acid by a pH titration using sodium hydroxide (equiv-

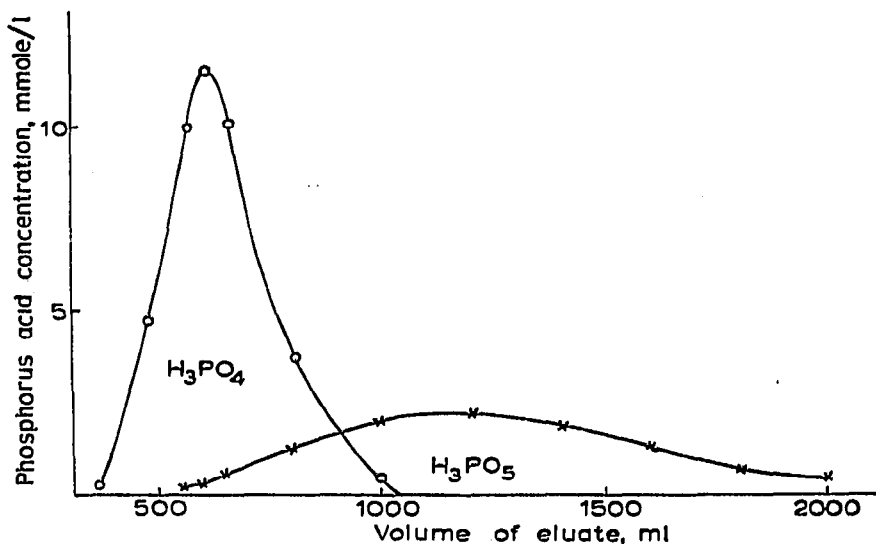


Fig. 1. The chromatographic separation of H_3PO_4 and H_3PO_5 .

alent point pH 5.0, corresponding to $\text{NaH}_2\text{PO}_4 + \text{NaH}_2\text{PO}_5$). When first analysed the mixture contained 80 % peroxomonophosphoric acid but it slowly lost oxygen.

Peroxomonophosphates were obtained by addition of one equivalent of alkali (LiOH, NaOH, KOH) to the cold, concentrated aqueous acid. The solutions so obtained were concentrated *in vacuo* over phosphorus pentoxide; no crystalline salts separated but the solutions slowly yielded deliquescent, amorphous, white solids, which contained up to 70 % of the active oxygen required for a salt of formula MH_2PO_5 . When these salts were stored over phosphorus pentoxide at 0°C , 40 % of their active oxygen was lost in eight weeks.

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SUMMARY

The separation of peroxomonophosphoric acid from orthophosphoric acid by anion-exchange chromatography is described; also the recovery of peroxomonophosphoric acid from the acetate buffer solution used as eluate.

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