

Note

Separation of orthophosphoric, phosphorous and hypophosphorous acids using single-column ion chromatography with conductivity detection

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The chromatographic separation of the lower oxo acids of phosphorus, *i.e.* hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3) and orthophosphoric acid (H_3PO_4), either as acids or as salts, and particularly in the presence of other organophosphorus compounds, has rarely been reported. The three acids have been eluted from a cation-exchange column¹ but no resolution was observed. The anions as orthophosphate, phosphonate and phosphinate were separated² on an anion-exchange column and detected using a flow injection system as a post-column detector employing oxidation to orthophosphate followed by chromogenesis with molybdenum reagent. Classical suppressed ion chromatography³ was used to determine the three acids in nickel plating baths although limits of detection are not quoted. However, in this work the more flexible single-column system was chosen for further investigation.

Initially the "standard" potassium hydrogen phthalate eluent was used but it produced poor peak shapes and insufficient resolution. It has been shown⁴ that weak organic acids are useful eluents for resin-based anion exchangers giving increased sensitivity due to low dissociation, while retaining sufficient eluting power for early eluting analytes.

In this work, therefore, succinic acid was investigated as the eluent, and after optimisation a quantitative method was developed which enabled the determination of all three oxo phosphorus anions at ppm levels and in the presence of polyorgano-phosphorus compounds.

EXPERIMENTAL

A Waters Assoc. Model 6000A solvent pump incorporating a Rheodyne 7125 injector with a 100- μl loop was used to deliver the eluent, an 0.02 *M* aqueous solution of succinic acid degassed with helium. The separation was carried out at a flow-rate of 4 ml/min with a 25 \times 0.45 cm Vydac 302 silica-based anion-exchange column. The anions were detected using an LDC Conductomonitor III thermostatically controlled conductivity detector, and the chromatograms were recorded on a Spectra-Physics Model 4270 integrator.

The phosphorus acids, their potassium salts and the succinic acid were obtained from BDH, Poole, U.K.

RESULTS AND DISCUSSION

When succinic acid was used at its natural pH of 3.0, the three oxo phosphorus anions were eluted in order of decreasing ionic size, *i.e.* H_2PO_4^- , H_2PO_3^- , and H_2PO_2^- . According to Ujimoto *et al.*⁵ the average negative charge on each of these species within the pH range of 3–5 is close to one. The effect of varying ion concentration and pH was investigated. As may be seen from Fig. 1, decreasing succinic acid concentration in the eluent resulted in increased retention of H_2PO_4^- , although the effect was only marked at very low concentrations where H_2PO_3^- and H_2PO_2^- were excessively retained. On increasing the pH of the eluent by addition of sodium hydroxide, retention and resolution were reduced (Fig. 2). As the first pK_a value of succinic acid at pH 4.2 was approached with a consequent increase in dissociation, which led to a higher eluent conductance, the peak shape was adversely affected and the sensitivity dramatically reduced. The area response to H_2PO_4^- on the conductivity detector was reduced by a factor of 25 on changing the pH from 3.0 to 3.8.

Maleic acid and phthalic acid proved unsuccessful as eluents for this system, showing poor sensitivity and peak shape. The separation was optimised at 0.02 *M*

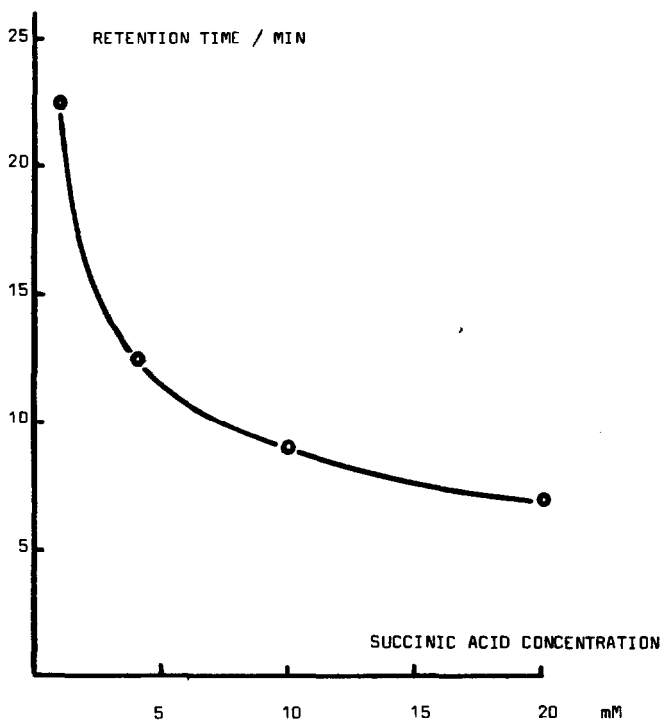


Fig. 1. Plot of variation in retention of H_2PO_4^- with change in the succinic acid eluent concentration.

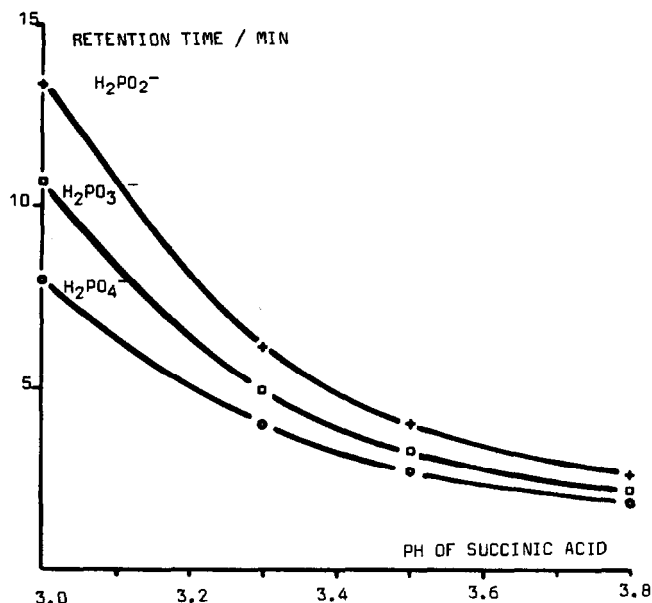


Fig. 2. Plot of variation in retention times of oxo phosphorus acids with change in pH of 0.02 *M* succinic acid eluent, adjusted with sodium hydroxide.

succinic acid without pH adjustment and with a flow-rate of 4 ml/min; this allowed separation to be completed within 20 min (Fig. 3). No system peak interference has been experienced. Despite the high flow-rate an efficiency of approximately 20 000 plates/m was obtained on the last eluted acid, $H_2PO_2^-$.

The limits of detection using these conditions were found to be 0.2 ppm for a 100- μ l injection, with a response of three times the average noise level. The linearity for each acid was tested from 5 ppm to 50 ppm using peak area integration (Fig.4).

The method has been used for the determination of residual oxo phosphorus acids in a range of polycarboxyphosphinates and phosphonates over a period of six months. After more than 400 injections on to the same column the efficiency and resolution are still good even though the retention times have become progressively shorter. Duplicate columns of these same type give very similar separations and relative retention times but somewhat different absolute retention times.

CONCLUSION

Single-column ion chromatography using succinic acid as eluent and conductivity detection was found to provide a suitable and sensitive method for the separation of hypophosphorous, phosphorous and phosphoric acids down to the sub-ppm level. The method is robust and has been used for the quantitative determination of the acids in polycarboxyphosphorus compounds.

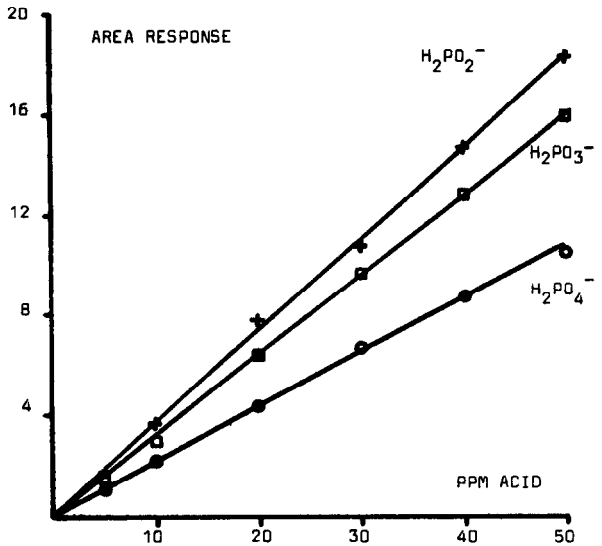
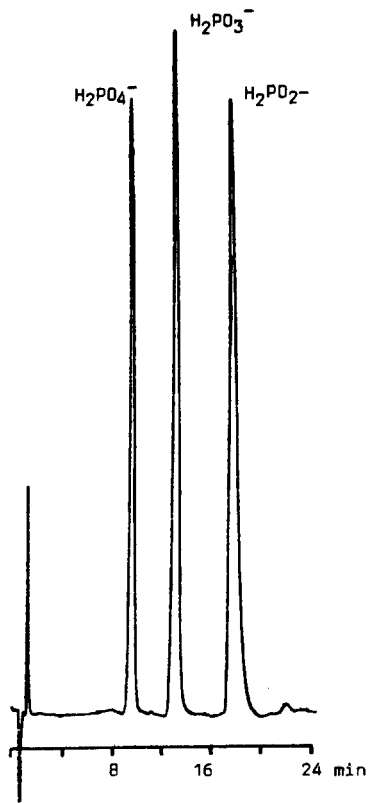


Fig. 3. Separation of oxo phosphorus acids on a Vydac 302, 25×0.45 cm I.D. column with 0.02 M succinic acid. LDC conductometer at $3\mu S$, 100- μl injection containing 50 ppm of each acid.

Fig. 4. Calibration plots of oxo phosphorus acids using 100- μl injections.

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