

SEPARATION OF SOME LOWER OXY-ACIDS OF PHOSPHORUS BY ANION-EXCHANGE CHROMATOGRAPHY

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In a previous communication¹, the authors have reported the separation of hypophosphite, phosphite and phosphate using gradient elution anion-exchange chromatography. This scheme has been extended to include the following lower oxy-anions of phosphorus, hypophosphate, diphosphite, pyrophosphite, isohypophosphate, an acid containing three phosphorus atoms and the condensed phosphate, pyrophosphate.

EXPERIMENTAL

Materials

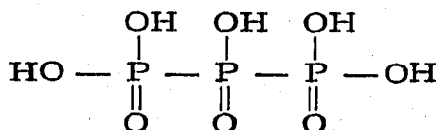
B.D.H. reagent grade sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and disodium phosphite, $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$, were twice recrystallised from aqueous solution. AnalaR grade disodium hydrogen orthophosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was used without further purification. Disodium hypophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ was prepared by the method of LEININGER AND CHULSKI² and three times crystallised from hot water.

Trisodium diphosphite, $\text{Na}_3\text{HP}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ was prepared by the hydrolysis of phosphorus trichloride^{3,4}.

Disodium pyrophosphite $\text{Na}_2\text{H}_2\text{P}_2\text{O}_5$ was prepared by heating monosodium phosphite $\text{NaH}_2\text{PO}_3 \cdot 2.5\text{H}_2\text{O}$ at 120° under vacuum for 6 h⁵. Iodometric titration of the resultant product showed that a small quantity of phosphite remained⁵. Due to the ease of hydrolysis of pyrophosphite in aqueous solution⁶, this solid was used without further purification.

Samples of trisodium isohypophosphate $\text{Na}_3\text{HP}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ and tetrasodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ were kindly donated by Albright and Wilson (Mfg.) Ltd. and were used without further purification. The isohypophosphate contained traces of orthophosphate and orthophosphite as impurities and this salt, like pyrophosphite, hydrolyses in aqueous solution⁷.

The acid containing three atoms of phosphorus and having the structure⁸:



was isolated as $\text{Na}_5\text{P}_3\text{O}_8 \cdot 14\text{H}_2\text{O}$ from the oxidation products of red phosphorus by

sodium chlorite solution. This acid will be referred to as ($\overset{4}{\text{P}}-\overset{3}{\text{P}}-\overset{4}{\text{P}}$) following the nomenclature proposed by BLASER⁹.

B.D.H. reagent grade potassium chloride.

Preparation and use of the chromatographic columns

The anion-exchange columns were prepared and used in an identical manner to that described in the previous communication¹. The conditions are given in Table I. 10 ml fractions of the column effluent were collected, transferred to conical flasks and boiled with 5 ml of bromine water for 30 min and then for a further 30 min after adding 10 ml of concentrated nitric acid. The phosphorus content of each fraction was then determined spectrophotometrically by the phosphovanadomolybdate method¹⁰.

TABLE I
CONDITIONS FOR THE CHROMATOGRAPHIC SEPARATION

Column dimensions (cm × cm)	KCl concentration in mixing vessel (ml/M)	KCl concentration in reservoir (M)	Temperature (°C)	pH	Flow rate (ml/h)
50 × 1.5	750/0.05	0.20	18	6.8	60

Buffer solution: pH 6.8; 25 ml of 2 M ammonium acetate solution per litre of potassium chloride. This pH was selected in order to keep the hydrolysis of pyrophosphite and isohypophosphate at a minimum during the chromatographic separation.

RESULTS AND DISCUSSION

An examination of Fig. 1 and Table II shows that good separations were obtained with the exception of that between diphosphite and pyrophosphite. Elution schemes using more dilute potassium chloride solutions were investigated to try and improve this separation, but without success. Neither could the separation be improved by using eluant solutions buffered at a pH of 9, nor by reducing the column temperature to 2°.

TABLE II
RETENTION VOLUMES OF PHOSPHORUS OXY-ANIONS*

Species	Retention volume (ml)
Hypophosphite	150
Phosphate	260
Phosphite	330
Hypophosphate	590
Diphosphite	680
Pyrophosphite	720
Isohypophosphate	890
Pyrophosphate	990
($\overset{4}{\text{P}}-\overset{3}{\text{P}}-\overset{4}{\text{P}}$)	1180

* Total percentage of phosphorus recovered = 97%.

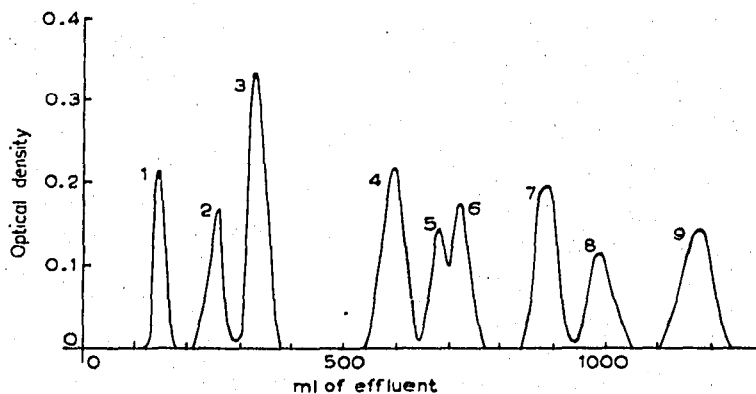


Fig. 1. Elution pattern for the separation of some phosphorus oxy-anions at pH 6.8. (1) Hypophosphite; (2) phosphate; (3) phosphite; (4) hypophosphate; (5) diphosphite; (6) pyrophosphite; (7) isohypophosphate; (8) pyrophosphate; (9) ($\overset{4}{\text{P}}-\overset{3}{\text{P}}-\overset{4}{\text{P}}$).

No appreciable hydrolysis of pyrophosphite or isohypophosphate appeared to occur during the separation. Maximum separations were achieved when the amount of phosphorus per species was less than 2000 μg .

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SUMMARY

Anion-exchange chromatography employing a gradient elution technique has been used to obtain separations of some lower oxy-anions of phosphorus.

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