

SEPARATION OF HYPOPHOSPHITE, PHOSPHITE AND PHOSPHATE BY ANION-EXCHANGE CHROMATOGRAPHY

F. H. POLLARD, D. E. ROGERS, M. T. ROTHWELL AND G. NICKLESS

*Department of Physical and Inorganic Chemistry, The University,
Bristol (Great Britain)*

(Received March 5th, 1962)

Iodometric methods for estimating hypophosphite, phosphite and phosphate in a mixture^{1,2} are unsatisfactory when the mixture also contains other lower oxyanions or thioxyanions of phosphorus, since these also react with iodine. A scheme employing gradient elution anion-exchange chromatography similar to that developed by GRANDE AND BEUKENKAMP³ and other investigators⁴⁻⁹ is used to obtain a separation of hypophosphite, phosphite and phosphate. Quantitative separations, using two independently developed schemes, one at pH 6.8 and the other at pH 11.4 are described.

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.

B.D.H. AnalaR disodium hydrogen orthophosphate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was used without further purification.

B.D.H. Reagent Grade potassium chloride.

Preparation of chromatographic columns

Dowex-1 X8 anion-exchange resin (mesh size 100-200; batch number 3246) was made into a slurry with distilled water and poured into a glass column fitted with a tap at the lower end, and surrounded by a water-jacket suitable for the circulation of water from an external source. The resin was allowed to settle until the length of the resin bed was 50 cm. It was then washed with 200 ml 4 N hydrochloric acid, followed by distilled water until the effluent was free of chloride ions. Finally the column was washed with 200 ml of buffered potassium chloride of the same concentration and pH as the initial eluant solutions.

Chromatographic separation

1.0 ml of a solution of a mixture of the anions to be analysed, containing up to 2000 μg of phosphorus per anion per ml, was pipetted on to the column. When the sample solution had almost been completely absorbed in the resin, it was washed into the resin bed by about 2 ml of initial buffered potassium chloride eluant solution.

The anions were eluted from the column using a gradient of potassium chloride concentration obtained by the method described by GRANDE AND BEUKENKAMP³.

TABLE I
CONDITIONS OF THE CHROMATOGRAPHIC SEPARATIONS

Figure number	Column dimensions cm	KCl concentration in mixing vessel ml/M	KCl concentration in reservoir M	Temperatures °C	pH*	Flow rate ml/h
1	50 × 1.5	750/0.05	0.20	18	6.8	60
2	50 × 1.0	750/0.075	0.10	18	11.4	40
3	50 × 1.0	750/0.075	0.10	~ 2**	11.4	25

* Buffer solutions: pH 6.8–25 ml of 2 M ammonium acetate solution per l of potassium chloride solution; pH 11.4–20 ml of 0.880 AnalaR ammonia per l of potassium chloride solution.

** ~ 2° obtained by pumping ice-cold water through the water jacket of the column.

10 ml fractions of effluent were collected by means of a syphon pipette and an automatic fraction collector.

Analysis of the fractions

The phosphorus content of each 10 ml fraction was determined by modification of the phosphovanadomolybdate method¹⁰. The 10 ml fractions were transferred to conical flasks and boiled for one hour with 10 ml of conc. nitric acid (1.42) and 5 ml of bromine water. After cooling, the contents of the conical flasks were transferred to 100 ml graduated flasks. 5 ml of an ammonium vanadate solution (containing 5 g of ammonium vanadate and 20 ml of conc. nitric acid (1.42) per l) were added, followed by 10 ml of 10% w/v ammonium molybdate solution. The solutions were diluted to 100 ml with distilled water.

The absorbance of the solutions was measured in 1 cm cells at 400 m μ employing a Unicam SP 500 spectrophotometer, after allowing not less than 15 min for full development of the coloured complex.

RESULTS AND DISCUSSION

An examination of Figs. 1, 2 and 3, shows that excellent separations were obtained using both schemes. The order of elution of phosphite and phosphate is reversed on changing the pH of the eluant solution from 6.8 to 11.4. This is presumably because

TABLE II
RETENTION VOLUMES AND PHOSPHORUS RECOVERY

Figure number	Hypophosphite		Phosphite		Phosphate	
	Retention volume ml	Recovery %	Retention volume ml	Recovery %	Retention volume ml	Recovery %
1	150	99	330	98	260	97
2	85	—	285	—	410	—
3	70	98	215	99	370	103

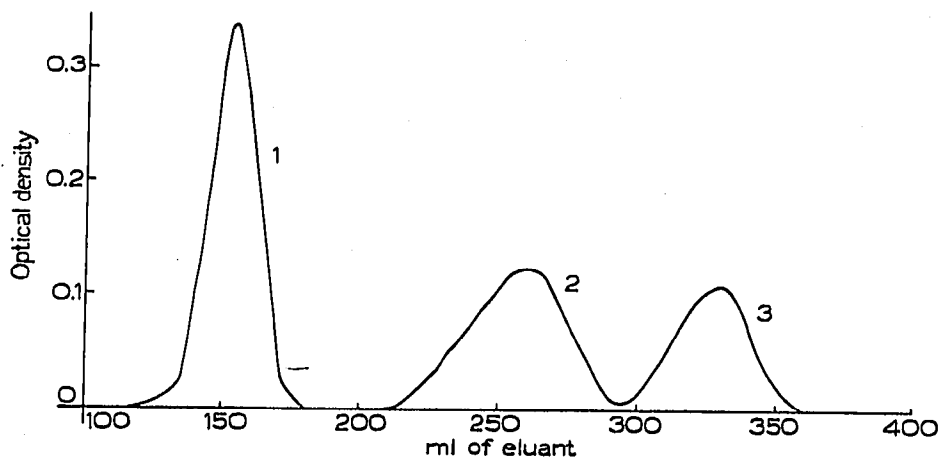
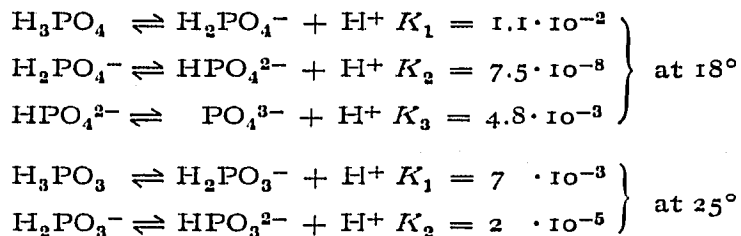


Fig. 1. Separation at a pH of 6.8 at 18°. (1) Hypophosphite; (2) phosphate; (3) phosphite.

the predominant phosphate ion is singly charged in the former solution and doubly charged in the latter case, whilst the predominant phosphite ion is the same in both cases.



Comparison of the separation at room temperature and at 2° indicates that the retention volumes of the three anions are decreased at the lower temperature, and the effect is greatest for phosphite. As a result the separation of phosphate and phosphite is increased at pH 11.4 and decreased at pH 6.8.

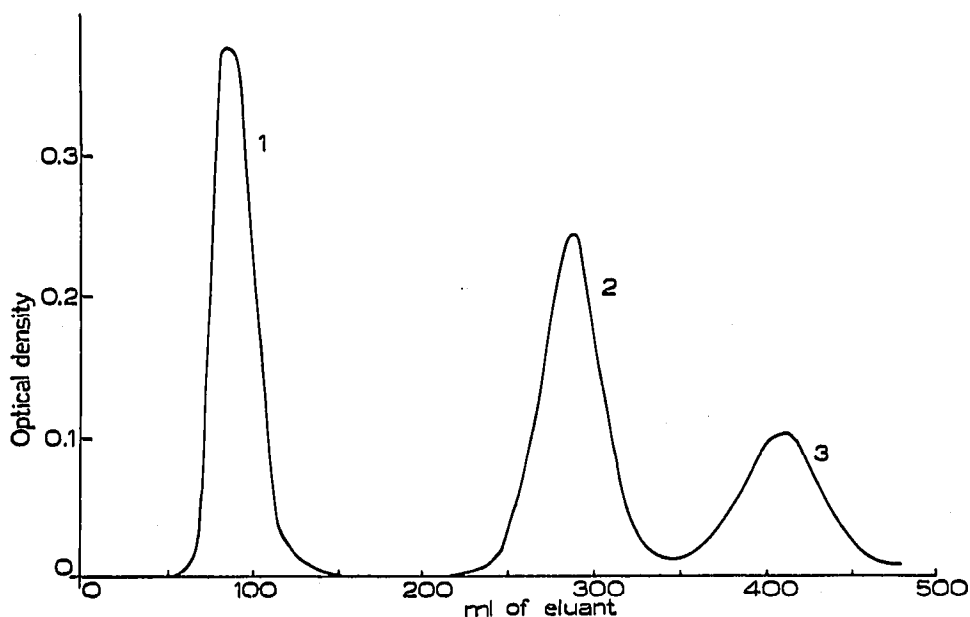


Fig. 2. Separation at a pH of 11.4 at 18°. (1) Hypophosphite; (2) phosphite; (3) phosphate.

Further work in these laboratories has shown that at pH 6.8 the condensed lower oxyanions of phosphorus¹¹, and at pH 11.4 the thioxyanions both of low and high phosphorus oxidation number¹² have greater retention volumes than the three anions separated by this scheme. As a result, these anions do not interfere with the method of analysis outlined in this paper.

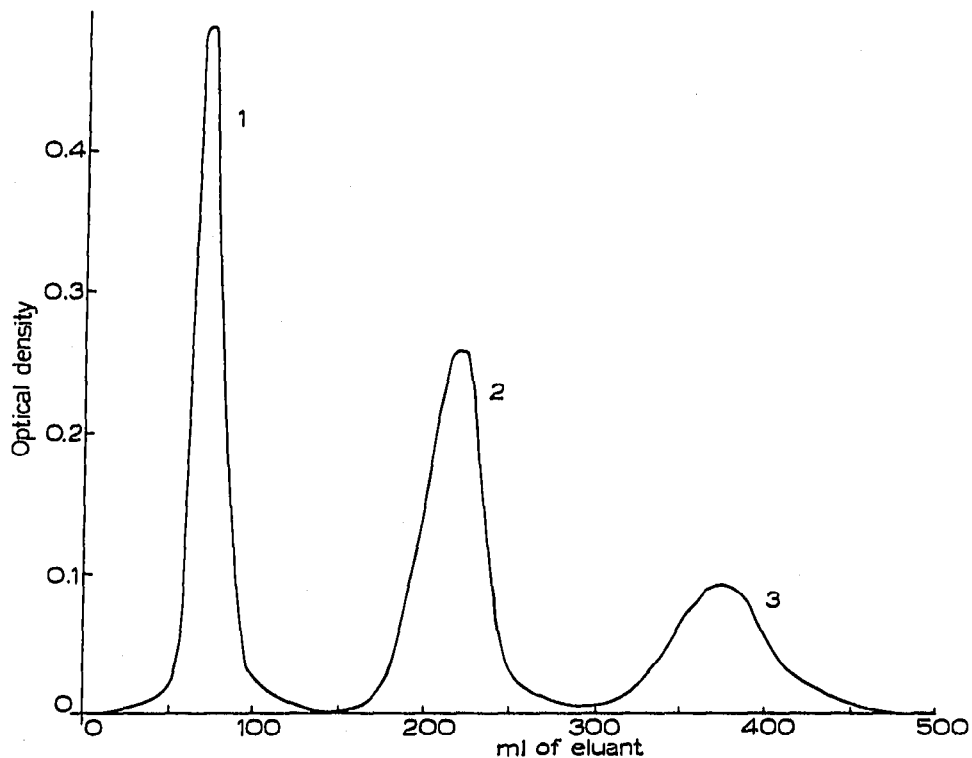


Fig. 3. Separation at a pH of 11.4 at 2°. (1) Hypophosphite; (2) phosphite; (3) phosphate.

SUMMARY

Separations of hypophosphite, phosphite and phosphate have been developed using gradient elution anion-exchange chromatography at pH 6.8 and 11.4. The separation at pH 11.4 is improved by reducing the column temperature to ~2°.

REFERENCES

- ¹ L. WOLF AND W. JUNG, *Z. anorg. Chem.*, 201 (1931) 353.
- ² R. T. JONES AND E. H. SWIFT, *Anal. Chem.*, 25 (1953) 1272.
- ³ J. E. GRANDE AND J. BEUKENKAMP, *Anal. Chem.*, 28 (1956) 1497.
- ⁴ T. V. PETERS AND W. RIEMAN III, *Anal. Chim. Acta*, 14 (1956) 131.
- ⁵ C. J. BARTON, *Anal. Chem.*, 20 (1948) 1068.
- ⁶ C. E. HIGGINS AND W. H. BALDWIN, *Anal. Chem.*, 27 (1955) 1780.
- ⁷ R. F. JAMESON, *J. Chem. Soc.*, (1959) 752.
- ⁸ J. BEUKENKAMP, W. RIEMAN III AND S. LINDENBAUM, *Anal. Chem.*, 26 (1954) 505.
- ⁹ D. P. LUNDGREN AND N. P. LOEB, *Anal. Chem.*, 33 (1961) 366.
- ¹⁰ R. E. KITSON AND M. G. MELLON, *Ind. & Eng. Chem., Anal. Ed.*, 16 (1944) 379.
- ¹¹ F. H. POLLARD, G. NICKLESS AND M. T. ROTHWELL, unpublished results.
- ¹² F. H. POLLARD, G. NICKLESS AND D. E. ROGERS, unpublished results.