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## DETERMINATION OF PHOSPHORUS IN SIMPLE STEELS USING ION-EXCHANGE CHROMATOGRAPHY

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### SUMMARY

An analytical method has been developed in which phosphorus, as the  $\text{H}_2\text{PO}_4^-$  ion, is deposited on an alumina column and any interfering ions present in the solution are removed by washing or subsequent selective solvent extraction. The phosphate ion is eluted from the column with a sodium hydroxide solution and the phosphorus estimated colorimetrically as the phospho-molybdenum blue over a concentration range of 2–50 ppm.

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### INTRODUCTION

The current production of “cleaner” steels, low in phosphorus content and with consistently high mechanical properties, makes necessary the determination of phosphorus at concentrations down to 2 ppm.

A review of existing methods for the determination of phosphorus shows that all are subject to various forms of interference which lead to time consuming manipulation or gross lack of sensitivity. As the degree of interference is dependent upon the concentrations of the particular elements, an intimate knowledge of the composition of the steel is necessary before satisfactory conditions can be established for the accurate determination of phosphorus. In an endeavour to eliminate as many interfering ions as possible, a separative technique involving ion exchange chromatography on activated  $\alpha$ -alumina has been developed. Alumina was chosen as the exchanger since it has improved stability over synthetic resin ion exchangers and is highly specific for phosphate ions ( $\text{H}_2\text{PO}_4^-$ ).

### EXPERIMENTAL

#### *Reagents and apparatus*

Analytical-grade reagents were used throughout this work except where otherwise specified.

The water used was distilled, then passed through a mixed bed ion-exchange column consisting of a sulphonic acid cation exchanger in the hydrogen form and a quaternary ammonium anion exchanger in the hydroxyl form and stored in polypropylene containers.

All glassware was washed in an aqueous solution of "Decon 90" (phosphate free) and then rinsed three times in fresh volumes of water.

Considerable attention was paid to the composition of storage containers. Some types made of low density polythene were found to be highly permeable to phosphate ions. Containers made of high density polypropylene were selected for use and these were pre-rinsed several times with the solution to be stored in them.

*Standard phosphate solution.* Potassium dihydrogen phosphate (0.0088 g) was dissolved in water and the solution diluted to 1 l and then stored in a polypropylene container (1 ml contained  $2 \cdot 10^{-6}$  g of P/ml).

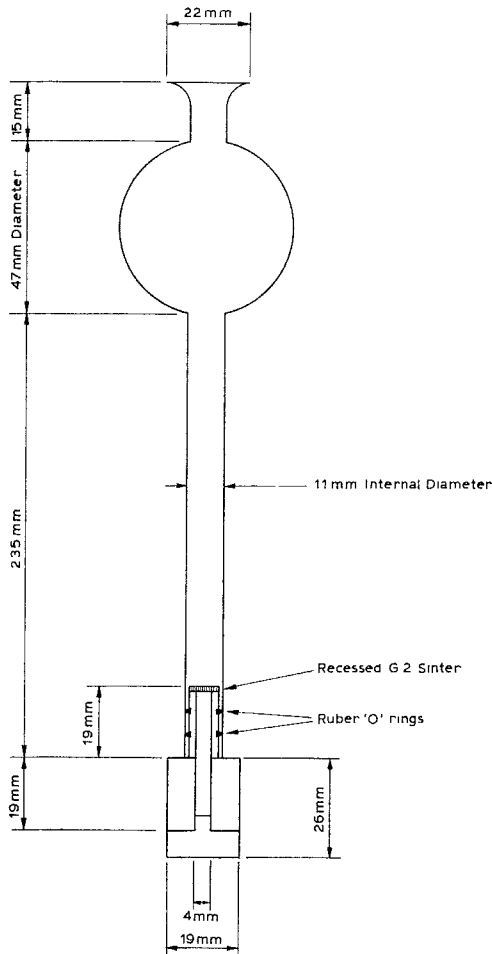


Fig. 1. Ion-exchange column (not to scale).

*Sodium molybdate solution.* Sodium molybdate (50 g) was dissolved in water and the solution diluted to 1 l.

*Tin(II) chloride solution.* Tin(II) chloride (4.0 g) was dissolved in 10 ml of concentrated hydrochloric acid with warming. This solution was freshly prepared as required.

*Reducing agent.* Ascorbic acid (1.3 g) was dissolved in water (20-ml) and to this was added freshly prepared tin(II) chloride solution (1.3 ml), followed by sulphuric acid (15 ml, 4.5 M) and water to a total volume of 100 ml. This solution was renewed weekly.

*Extraction solvents.* Ethyl acetate boiling range 76.5–78.5°C. Amyl acetate of which not less than 95% distils between 138 and 142°C.

A Pye Unicam Model SP 500 spectrophotometer was used.

#### *Preparation of chromatographic column*

A 100-g amount of aluminium oxide active Brockman grade I "acidic" (BDH, Poole, Great Britain) was soaked in water for *ca.* 1 h freed from fines by washing and decantation until the supernatant liquor was clear after standing for 1 min and dried at  $105 \pm 2^\circ\text{C}$ . The dried material was sieved and that portion which passed a 200 British Standard sieve rejected.

Details of the column used are shown in Fig. 1. The column was filled with an aqueous slurry of the prepared alumina to a height of 120 mm. It was back-washed with water to ensure even particle size distribution and then the alumina was allowed to settle freely.

#### *Qualitative check of the retention of phosphorus on the column*

Steel panels measuring  $150 \times 100 \times 6$  mm, supplied to British Standard 1449, were used as a source of phosphorus. This is the same type of steel used previously in the sulphate determinations<sup>1</sup>. Three panels, which had been grit blasted, were examined by emission spectroscopy before being milled into small pieces for carbon, sulphur and phosphorus determination, with the following results:

<i>Panel</i>	<i>1(%)</i>	<i>2(%)</i>	<i>3(%)</i>
Manganese	0.25	0.34	0.36
Nickel	0.05	0.05	0.05
Chromium	0.05	0.05	0.05
Molybdenum	0.01	0.01	0.01
Vanadium	0.005	0.005	0.005
Copper	0.01	0.01	0.01
Aluminium	0.06	0.06	0.06
Cobalt	0.02	0.02	0.02
Silicon	0.01	0.01	0.01
Carbon	} Bulk sample after milling	0.068	
Sulphur		0.013	
Phosphorus*		0.004	

\* Precipitated as ammonium phospho-molybdate and estimated by a titrimetric method. The carbon and sulphur were determined by means of an auto-analyser (Leybold Hareaus 2001).

A quantity of steel (2.0 g) was dissolved in nitric acid (45 ml; 40%, v/v) and oxidised with a saturated solution of potassium permanganate. After destruction of the excess oxidant with sodium nitrite, the solution was boiled to remove oxides of nitrogen, allowed to cool and passed through the prepared alumina column which had been conditioned with sodium hydroxide (50 ml, 1.5 *M*) and water (50 ml). After passage of the iron solution, the column was washed with water (50 ml). A test on the water washings for the presence of phosphate proved negative. The column was then treated with sodium hydroxide (100 ml, 1.5 *M*) and the effluent gave a very positive result when tested for phosphate. Further washings of the column with sodium hydroxide (50 ml, 1.5 *M*) gave a negative result for phosphate.

*Preparation of calibration curves without alumina column*

Quantities of 2.0, 5.0, 10.0, 15.0 and 20.0 ml of standard phosphate solution (1 ml contains  $2 \cdot 10^{-6}$  g of P) were pipetted into five 250-ml separating funnels, each containing sodium hydroxide (100 ml, 1.5 *M*). The solutions were acidified with hydrochloric acid (20 ml, 10 *M*) and shaken for 30 sec. After the addition of ammonium molybdate solution (10 ml) each solution was shaken for 1 min and allowed to stand for 5 min before the complex formed was extracted into  $2 \times 20$  ml aliquots of amyl acetate. The combined extracts were shaken with  $2 \times 5$  ml portions of the reducing solution and the resulting aqueous layers were transferred to a standard flask and made up to the mark.

*Preparation of calibration curves using ion-exchange column*

Phosphate solutions (2.0, 5.0, 10.0, 15.0 and 20.0 ml each made up to 50.0 ml with water) (1 ml contains  $2 \cdot 10^{-6}$  of P) were passed through the column in the hydroxyl form. For each solution sodium hydroxide solution (100 ml, 1.5 *M*) was used as the eluting agent and the column washed with water (50 ml) after each elution.

The alkaline column effluents (100 ml) were worked up to obtain the phosphomolybdenum blue complex as described previously and the results are shown in Fig. 2.

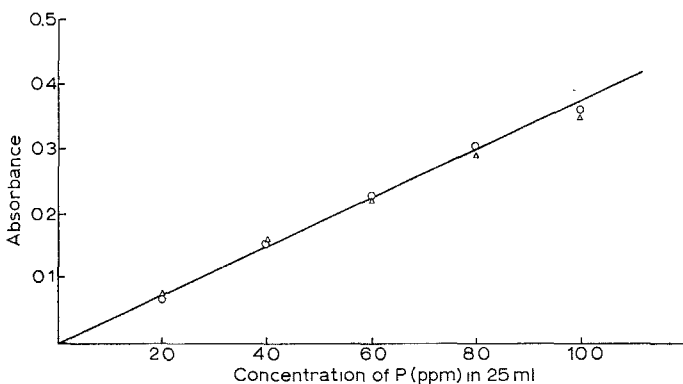


Fig. 2. Calibration curves. Molybdenum blue method with (O) and without ( $\Delta$ ) alumina column, at 720 nm; 2-cm cells; low concentration of phosphorus (1–10 ppm).

The above procedure was repeated for volumes of phosphate solution (1.0, 2.0, 3.0, 4.0 and 5.0 ml) which gave a range of concentrations of phosphorus 0–10 ppm. The results are shown in Fig. 3.

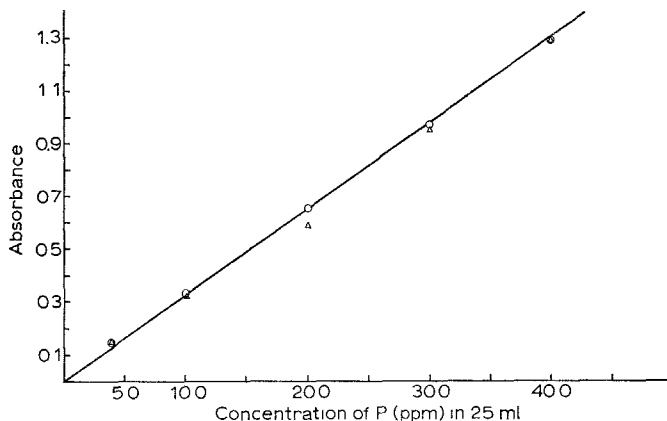


Fig. 3. Calibration curves. Molybdenum blue method, with ( $\Delta$ ) and without ( $\circ$ ) alumina column, at 720 nm; 2-cm cells.

#### *The determination of phosphorus in a simple steel using ion-exchange chromatography*

The steel sample used was a British Chemical Standard 149/3 supplied by the Bureau of Analysed Samples Limited.

A 1.00-g sample was dissolved in nitric acid (45 ml; 40%, v/v) and the exact procedure followed as previously described for the qualitative investigation of retention of phosphorus in the alumina column. Determinations were carried out for a total of 7 samples. The results are recorded in Table I.

TABLE I

Weight of sample taken, 1.000 g. Final volume of solution, 50.0 ml. Cell path length, 2 cm; wavelength, 720 nm.

Absorbance	Phosphorus (ppm)
0.65	41
0.68	42
0.64	41
0.68	42
0.62	38
0.68	42
0.66	42

## RESULTS AND DISCUSSION

### *Displacement of phosphate from the column*

Nydahl<sup>2</sup> postulated a relative order of displacement of the common ions on an alumina column which can be represented as follows:  $\text{OH}^- > \text{F}^- \approx \text{H}_2\text{PO}_4^- \approx$

$\text{HSO}_4^- > \text{Cr}_2\text{O}_7^{2-} > \text{Cl}^- \approx \text{NO}_3^- \approx \text{ClO}_4^-$ . The exact experimental conditions under which the series was established has not been stated and how critical the order in terms of pH and salt concentration does not appear to be documented.

The relative positions of  $\text{OH}^-$  and  $\text{HSO}_4^-$  in the series have been confirmed by both Nydahl<sup>2</sup> and Davies<sup>1</sup>. In the determination of sulphate associated with steel plate the author prepared two calibrations, one using the column and the other on similar quantities of solution without the column. Recoveries using the column were  $94 \pm 1\%$ . It seemed therefore desirable to carry out a similar experiment using phosphate solution where previously a sulphate solution had been used, particularly since  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$  are supposed to be adjacent to each other in the displacement series.

However, in spite of the use of similar conditions in terms of alumina, column preparation and flow-rates a desorption pattern for phosphate similar to that previously established for sulphate, could not be found. The fact that concentrations of between 0.1 and 14 M ammonium hydroxide were tried<sup>3</sup> and found to be unsuccessful in achieving quantitative desorption would suggest that the situation is more complex than the one previously encountered in the determination of sulphate.

A series of experimental determinations has shown that phosphate can be removed with sodium hydroxide solution and that for the column and conditions employed a volume of 100 ml of 1.5 M is required. In contrast with the results for sulphates, the recovery of the phosphate ions from the column is quantitative.

#### *Solvent extraction and colorimetric determination*

The method used to determine phosphate was based on the colorimetric procedure evolved by Jintakanon *et al.*<sup>4</sup> which has been confirmed to give a straight line calibration<sup>3</sup>.

A difficulty encountered using this method to detect phosphate in the column effluent of nitric acid was that ethyl acetate, used to extract the reduced phosphomolybdate, was appreciably miscible with the acid solution. The solution was therefore first evaporated to low bulk (1 ml) and then made up to a volume of 50 ml with water.

A step by step approach to establish the most favourable conditions for the colorimetric finish using the molybdenum blue method led to the following:

(i) The volume of sodium molybdate (6 ml, 60 g/l) used in the suggested method is sufficient for quantities up to 100 ppm of phosphate.

(ii) The volume of 3 ml of reducing solution employed is sufficient for determining up to 100 ppm of phosphate.

(iii) Wadelin and Mellon<sup>5</sup> in a detailed study of the extraction of heteropoly acids, found that 0.96 M hydrochloric acid was the optimum for extraction of the heteropoly molybdophosphate into butanol, whereas 0.15 M hydrochloric acid was the optimum acid concentration for the extraction of the corresponding silicon complex into the same reagent. Hence the use of acid concentrations in excess of 0.76 M in the extraction solution should assist in the suppression or removal of silicon interference, both at the complex formation and at the extraction stages. This optimum acid concentration is confirmed in the plot of acid concentration against colour intensity (Fig. 4).

(iv) The use of amyl acetate rather than ethyl acetate confirms the findings of

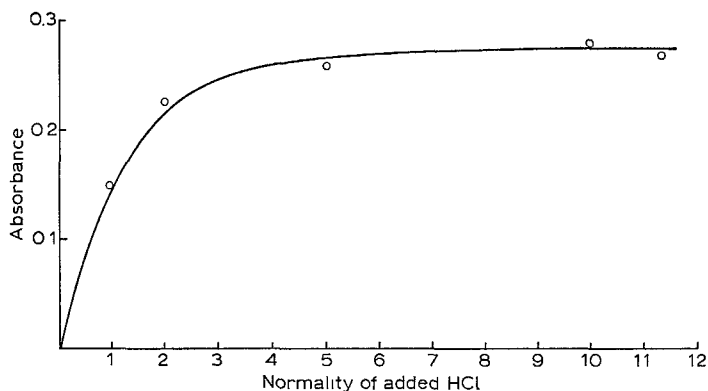


Fig. 4. Intensity of molybdenum blue colour with increasing concentration of HCl.

De Sesa and Rogers<sup>6</sup> namely that the interference of silica and arsenic in the solution containing phosphate is minimised. The reason that ethyl acetate could not be used as extracting agent in this work was mainly due to its high solubility in the very high concentration of sodium hydroxide in the eluant, necessary to displace successfully all the phosphate ion ( $\text{H}_2\text{PO}_4^-$ ) from the column.

Results also confirm (Table II) that up to 100-fold excesses of arsenic, silicon and chromium can be tolerated either singularly or collectively with no significant influence on the phosphorus determination.

TABLE II

1 ml  $\text{K}_2\text{Cr}_2\text{O}_7$  solution =  $1 \cdot 10^{-4}\text{g}$  Cr, 1 ml  $\text{As}_2\text{O}_5$  solution =  $1 \cdot 10^{-4}\text{g}$  As, 1 ml  $\text{Na}_2\text{SiO}_3$  solution =  $1 \cdot 10^{-3}\text{g}$  Si.

Weight of steel taken (g)	Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ (ml)	Volume of $\text{As}_2\text{O}_3$ (ml)	Volume of $\text{Na}_2\text{SiO}_3$ (ml)	Final volume (ml)	Absorbance	Phosphate (ppm)	
						Found	Expected
1.00	10.0	10.0	1.0	50.0	0.70	43	41
1.00	20.0	20.0	2.0	50.0	0.70	43	41
1.00	30.0	30.0	3.0	50.0	0.70	43	41
1.00	40.0	40.0	4.0	50.0	0.70	43	41
1.00	50.0	50.0	5.0	50.0	0.68	42	41
1.00	Nil	Nil	Nil	50.0	0.68	42	41

## CONCLUSIONS

Thus from the experimental results obtained it is concluded:

(a) That an alumina column in the hydroxyl form retains phosphate from a strongly acid solution containing a large preponderance of  $\text{Fe}^{3+}$  ions.

(b) The cations associated with the column could be removed by washing with water, whilst all the phosphate present was retained on the column.

(c) The phosphate can be completely removed from the column using 100 ml, of 1.5 M sodium hydroxide solution.

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## REFERENCES

- 1 J. E. Davies, *J. Oil. Col. Chem. Assoc.*, 54 (1971) 425-435.
- 2 J. Nydahl, *Anal. Chem.*, 26 (1954) 580-584.
- 3 J. E. Davies, *M.Sc. Thesis*, Thames Polytechnic, London, 1978.
- 4 S. Jintakanon, G. L. Kerven, D. G. Edwards and C. J. Asher, *Analyst (London)*, 100 (1975) 408.
- 5 C. Wadelin and H. G. Mellon, *Anal. Chem.*, 25 (1953) 1668-1673.
- 6 M. A. De Sesa and L. B. Rogers, *Anal. Chem.*, 26 (1954) 1381-1383.