On the Separation of Phosphorus and Iron by Means of Cation Exchange Resin

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The rapid and accurate method of determination of phosphorus by means of ion-exchange column was for the first time proposed by Helrich and Rieman[1] for the analysis of phosphate rocks. The author once attempted to apply this method to the determination of phosphorus in the iron-bearing samples for the purpose of geochemical studies on the distribution of phosphorus in the limonite ores of Japan.[2] But, owing to the incompleteness of the separation of phosphoric acid from tervalent iron by cation exchange resin, the attempt did not succeed. Later, the problem of interference of ferric iron was pointed out by several workers.[3,4,5] In connection with it, the author had observed the same phenomena in the studies of ion-exchange separation of arsenic acid from ferric ion and the problem could be solved by previous reduction of the test solution by sulfur dioxide.[6]

It is now proved that the same techniques are also applicable to the quantitative separation of phosphate ion from tervalent iron by cation exchange resin. This paper also describes some investigations on the behavior of phosphorus on the column using P^{32} tracer as well as high frequency oscillators.

Experimental

The Cation Exchange Resins and Reagents.—Amberlite IR-120 and Amberlite IR-112 (A. G.) (both 50 to 100 mesh) were used.

Both acetate and borate comparison buffers were prepared according to Helrich and Rieman's original paper,[1] except that, in place of methyl red, bromocresol green indicator was added to acetate buffer. Carbonate free 0.1 N sodium hydroxide solution was standardized against 0.1 M potassium dihydrogen phosphate solution from pH 4.63 to pH 8.98 using comparison buffers.[4]

Ion Exchange Separation of phosphate Ion from Tervalent Iron by Reduction with Sulfur Dioxide.—To a mixture of 10cc. of 0.1M ferric chloride solution and a definite volume of 0.1 M potassium dihydrogen phosphate solution, add 1N hydrochloric acid of one tenth of the total volume in order to prevent formation of precipitate. Heat the solution on a water bath and pass a rapid current of sulfur dioxide for about half an hour in order to convert ferric ion into ferrous state. Then, pass the solution through a column of sodium form cation exchanger at a rate of 1—2cc. per minute. Wash with 30cc. of distilled water in several portions at the same rate. The effluent and washings are collected in a 100cc. Erlenmeyer flask, into which a small piece of porcelain is added as a boiling chip. Then, attach a glass joint spray trap and outlet tube bending downward. Heat flask gently and expel a greater part of excess sulfur dioxide. Add bromine water until coloration takes place and again distil off the excess of bromine. Rinse the attachments with a small volume of water and cool the solution. Then, add 0.25cc. of bromocresol green indicator and neutralize with 1N sodium hydroxide until indicator turns slightly blue. Adjust the pH at 4.63 with 0.1N hydrochloric acid and 0.1N sodium hydroxide using acetate buffer. Then, add 0.3 cc. of phenolphthalein and titrate with standard sodium hydroxide solution to the pH 8.98 using borate buffer. Table 1 shows the results obtained in such determinations.

Determination of Phosphate in Ferric Oxide Deposit and Vivianite.—Weigh out about 1 gram of fine powdered sample and treat with 20 cc. of aqua regia. Evaporate the so-

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1) Helrich, K. and Rieman, W., *Anal. Chem.*, **19**, 651 (1947).

2) Yoshino, Y., *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 503 (1951).

3) Kubo. S. and Tsutsumi, C., *Bull. Chem. Soc. Japan*, **23**, 187 (1950).

4) Goudie, A. J. and Rieman, W., *Anal. Chem.*, **24**. 1067 (1952).

5) Salmon, J.E., *J. Chem. Soc.* 2316 (1952).

6) Yoshino, Y., This Bulletin, **24**, 39 (1951).

Table 1

Separation of Phosphate from Ferric Iron

Phosphate ion			
taken (m. mol.)	found (m. mol.)	Error (%)	Resin (g.)
1.000	0.998	−0.2	5 (Amberlite IR-120)
1.000	1.006	+0.6	5 (〃)
1.000	0.999	−0.1	5 (〃)
0.500	0.498	−0.4	7 (〃)
2.000	2.005	+0.25	10 (Amberlite IR-112)

lution to syrupy state and add 5 cc. of concentrated hydrochloric acid and dry up. Repeat this operation once more. Then, add 10 ml. of 1*N* hydrochloric acid. The solution is heated and filtered. Collect the filtrate and washings in a 100 cc. measuring flask and fill up to the mark with water. Taking aliquot portion of the sample solution, phosphate content was determined according to the same procedure as was described in a previous paragraph. The comparison of results obtained by both ion-exchange[※] and gravimetric method weighing as $Mg_2P_2O_7$ is given in Table 2.

Tracing of Phosphate Ion on Elution by Means of Radioactive P^{32}—The acidified solution containing 1 millimol of ferric chloride and potassium phosphate labeled with 0.3 microcurie of P^{32}[※] was passed in a bed of 10 grams of sodium form Amberlite IR-120. The column was washed with 0.01 *N* hydrochloric acid up to 450 cc. The percentage of phosphate in each step of filtrate was estimated by the radioactivity measurement. The results obtained are shown in Table 3.

Table 2

Determination of Phosphorus in Iron-bearing Samples

Sample	P_2O_5(%)		No. of detn.	Difference
	Gravimetric	Ion Exchange		
Ferric oxide deposit of Meiji-yu Hot Spring, Nagano Pref.	8.94	8.96	3	+0.02%
Vivianite from Himeshima mine, Ôita Pref.	24.44	24.14	1	−0.30%

Table 3

Phosphate added (m.mol.)	% of Phosphate found in the Effluent and Washings					
	Effluent+50 cc.,	50∼150,	−250,	−350,	−450cc.,	Total
2.000	85.0	6.6	3.5	(2.4)		97.5
1.000	71.9	7.8	3.2	2.3	1.2	86.4
0.100	45	13	7.7	7.0	6.0	78.7
0	6.1	3.6	2.5	2.4	1.9	16.5

It is observed that under these conditions, the percentage of separation of phosphate from tervalent iron becomes remarkably less, the less the ratio of P/Fe in test solution. The gradual flowing out of phosphate ion in the washings may be due to the relatively weak linkage between phosphorus and ferric iron. This situation is quite similar to that observed in the system of arsenic acid and tervalent iron.6)

Examination of the Distribution of Phosphate held on the Column using P^{32} and High Frequency Oscillators.—The solution containing 1 millimol of ferric chloride and 1 millimol of phosphoric acid labeled with about 10 microcurie of P^{32} was passed through a column of hydrogen form Amberlite IR-120 ($0.9\ cm.^2 \times 11\ cm.$) and the column was washed with 30 cc. of water in three portions. Then, 3 cc. of hydrogen form resin was packed to

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[※] 10 grams of Amberlite IR-112 (A.G.) were employed.

[※] Obtained through the Isotopes Division of the Atomic Energy Commission. Decay and radiation properties were scanned and identified.

the head. The glass tubing was enveloped with a lead sheet having a window (10×10 mm.) and sliding the tube, vertical distribution of the radioactivity was measured by a Lauritsen electroscope. At the same time, a radioautograph was taken using X-ray film.

Fig. 1 represents the results obtained. The radioactivity is observed to be concentrated at the head of the original bed.

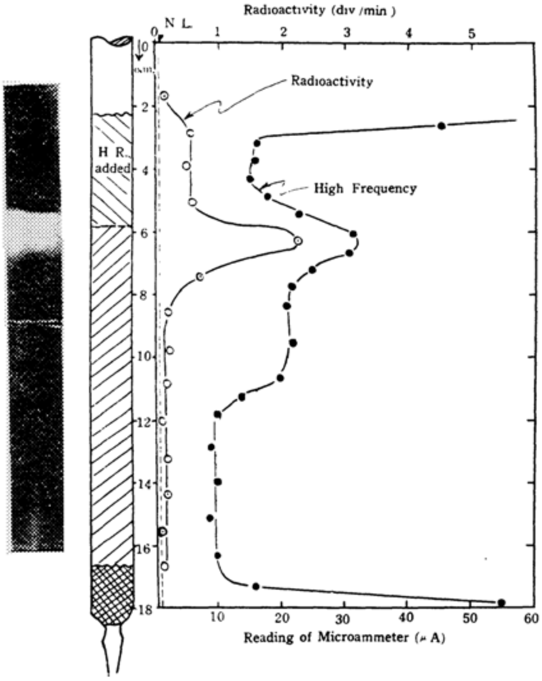

Fig 1

Then, the column was subjected to high frequency measurements[7] and the results are shown also in Fig. 1. The peak of the reading of a microammeter, which may be due to the band of ferric ion adsorbed, coincides with that of radioactivity. The position of the iron band could be also detected by the color change when Amberlite IR-112 was used.

From these experiments, it may be concluded that the holding of phosphate ion on the column is caused by direct interaction between phosphate and ferric iron. Whether this is due to the formation of complex or physical absorption is not known as yet.

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[7] M. Honda,, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 529 (1952).