

**42.** *Ion-exchange Studies of Phosphates. Part II.<sup>1</sup> Phosphoric Acid as an Eluant in the Column Separation of Tervalent Iron from Bivalent Copper and Manganese.*

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The results of batch experiments with the metal ( $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Mn}^{2+}$ ) form of a cation-exchange resin and phosphoric acid solutions are used as a guide in establishing the conditions (pH, temperature, time of contact, resin particle size, and degree of cross-linking of the resin) necessary for the column separation of macro-quantities of iron(III), which is eluted first, from the bivalent metals.

Batch experiments are also used to estimate qualitatively the relative degrees of complex-formation between the three metal ions studied and phosphate, chloride, and nitrate ions, respectively, in acid solutions containing the various anions at corresponding concentrations.

IN Part I <sup>1</sup> it was shown that complex formation between phosphate and several trivalent metals, including iron, was much more marked than it was between phosphate and various bivalent metals including copper and manganese. This observation suggested to us the possibility of using phosphoric acid as a complex-forming eluant in column separations of trivalent iron from bivalent copper and manganese.

In the present work the use of batch experiments, in which the effects of various factors are examined to establish the conditions for such separations, is described. An empirical relation has been found to give a better guide to the optimum conditions than that based on the distribution ratio ( $K_d$ ),<sup>2</sup> presumably because the metal ion concentrations are greatly above "tracer" level. The batch experiments are used to assess the relative

<sup>1</sup> Part I, Holroyd and Salmon, *J.*, 1956, 269.

<sup>2</sup> Mayer and Tompkins, *J. Amer. Chem. Soc.*, 1947, **69**, 2866.

degrees of complex-formation between the metal ions and various anions, including phosphate.

#### EXPERIMENTAL

*Resins.*—For the batch experiments, the hydrogen form of the cation exchanger Zeo Karb 225 (normal degree of cross-linking unless otherwise stated) was completely converted into the metal form ( $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Mn}^{2+}$ ) by passage of an excess of a solution of the chloride or sulphate (Analytical Grade) through a column of the resin. The capacity of the completely washed and air-dried resin was determined by elution of the metal from 0.500 g. samples in small columns with 300 ml. of 2*N*-acid, followed by determination of the metal content of the eluate. The results were checked by a separate determination of the capacity of the hydrogen form, obtained after elution with acid, by a method previously described.<sup>3</sup> For the column experiments the hydrogen form of the resin Zeo Karb 225 (40–80 mesh) was used. This was treated with excess of 2*N*-acid and washed thoroughly before use.

*Procedure.*—In the batch experiments, 0.500 g. samples of resin were swirled gently with solutions of phosphoric and other acids (50 ml.) for known times at room temperature ( $20^\circ \pm 3^\circ$ ) or at  $40^\circ (\pm 1^\circ)$ , after which the resin was filtered off and an aliquot part of the filtrate was analysed to determine what percentage of metal originally present in the resin phase had passed into the aqueous phase.

In the column-experiments, the resin bed was 8 in.  $\times$   $\frac{1}{2}$  in. in the fully washed hydrogen form. Satisfactory packing of the column was achieved by allowing the resin to settle under gravity after back-washing with a stream of water of sufficient velocity to lift the resin bodily to the top of the column (10 in. long). The column was loaded by passage of a known volume of a 0.1*N*-solution of the metal chloride or sulphate (Analytical Grade) through the column (5–10 mequiv. of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Mn}^{2+}$ , as required). The metals were sorbed in a sharp band at the top of the column. The resin was then washed until free from acid and the metals were eluted with a phosphoric acid solution of known pH at a rate of flow of 100 ml. per hour. The temperature was controlled, where necessary, by means of an electrical heating element wrapped round the tube.

*Analysis.*—pH was measured with a commercial pH-meter with a glass electrode-saturated calomel electrode system. In the case of the perchloric acid solutions a sodium nitrate salt bridge was used to separate the calomel half-cell from the test solution; the meter was standardized against the buffer solutions under the same conditions.

Iron and copper were determined volumetrically with standard potassium dichromate and standard sodium thiosulphate solutions respectively. Manganese was determined by Lingane and Karplus's method.<sup>4</sup>

#### RESULTS AND DISCUSSION

The amounts of metal removed from the iron(III), manganese(II), and copper(II) forms of Zeo Karb 225 (22–30 mesh) by phosphoric and other acid solutions of various pH values, either after 7 days at  $20^\circ (\pm 3^\circ)$  or after 2 days at  $40^\circ (\pm 1^\circ)$ , are shown in Fig. 1. Preliminary experiments had shown that these would be equilibrium values. It is apparent from Fig. 1 that whilst, over the pH range 0.2–1.2, the amounts of iron(III) removed at room temperature by the various acids are in the order  $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3 \geq \text{HCl} \sim \text{HClO}_4$ , the amounts of the bivalent metals removed are in the order  $\text{H}_2\text{SO}_4 > \text{HCl} \geq \text{HNO}_3 > \text{H}_3\text{PO}_4$ . Although an increase in temperature to  $40^\circ$  produces a slightly higher rate of exchange, it has little effect on the amounts of the three metals removed at equilibrium. With hydrochloric acid, on the other hand, the final amount of each metal removed is greater at the higher temperature, but the ratio of the amounts of metals removed is little affected.

Now for each metal the lowest curve for a given temperature must represent the closest approach to the simple equilibrium



(where barred formulæ represent ions in the resin phase), with a minimum disturbance

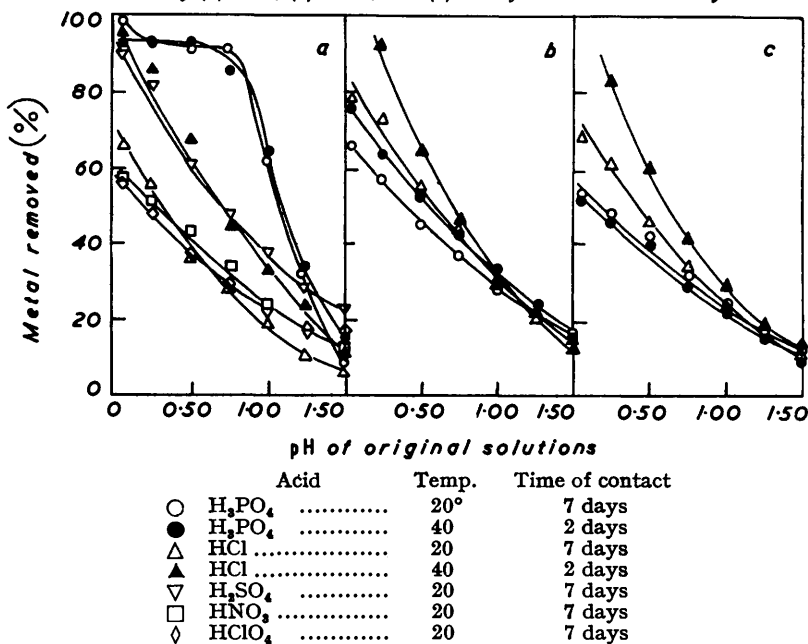
<sup>3</sup> Salmon, *J.*, 1953, 2644.

<sup>4</sup> Lingane and Karplus, *Ind. Eng. Chem. Anal.*, 1946, 18, 191.

from complex formation in solution. The higher curves must indicate, however, an increasing degree of complex formation, with a resultant displacement of equilibrium (1) to the right as the effective concentration of  $M^{2+}$  ions in solutions falls.

Now at the acid concentrations considered here we assume as a reasonable approximation that (a) phosphoric acid ionizes to yield principally  $H_3O^+$  and  $H_2PO_4^-$  ions; and (b) a given pH corresponds to the same hydrogen ion concentration for the various acids considered (*i.e.*, that the activity coefficients are not too widely separated). Hence it appears that results quoted for a given pH may be taken, in the cases of the monobasic

FIG. 1. The removal of (a)  $Fe^{3+}$ , (b)  $Mn^{2+}$ , and (c)  $Cu^{2+}$  from Zeo Karb 225 by various acids.



and phosphoric acids, as applying to approximately the same anion concentrations. Thus, although the total phosphate concentrations are high in the phosphoric acid solutions, the  $H_2PO_4^-$  ion concentration is of the same order as the chloride, nitrate, and perchlorate ion concentrations in the solutions with which they are compared. Thus the relative positions of the curves plotted in Fig. 1 can be taken as indicating, at least qualitatively, the order of complex-formation between the metal ions and the various acid anions.

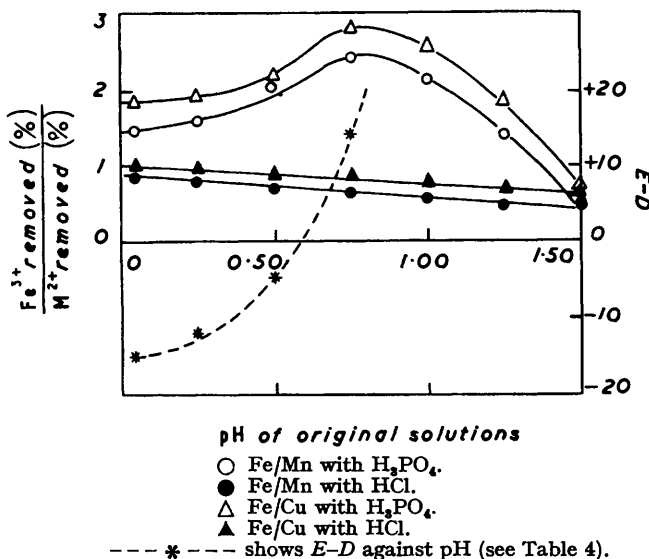
The results recorded in Fig. 1 therefore provide additional confirmation of Holroyd and Salmon's results<sup>1</sup> indicating that complex formation between ferric ions and phosphate is marked, whilst that between the bivalent metal ions and phosphate is negligible. It is further apparent that, whilst the proportion of iron(III) removed at any pH by nitric or hydrochloric acid is less than the proportion of copper or manganese removed, which is in accord with the higher affinity of the trivalent ion for the resin, the reverse is true of phosphoric acid. Use of hydrochloric acid as an eluting agent should therefore lead to the elution of copper or manganese before iron(III), but the use of phosphoric acid should result in the elution of the iron first. A plot of the ratio of the percentages of iron(III) removed at equilibrium to that of  $M^{2+}$  against the pH of the solutions for phosphoric and hydrochloric acid solutions makes this more apparent, since the values of the ratio are always greater than unity in the first case and always less than unity in the second (Fig. 2). The maximum in the curves for phosphoric acid at about pH 0.75 suggests that an optimum separation should be obtained with a phosphoric acid eluant of that pH.

Generally the possibility of such separations is deduced from the value of the ratio of  $K_d$  for metal(II) to that of iron(III), where  $K_d$  is given by<sup>2</sup>

$$K_d = \frac{\text{Metal in resin at equilibrium (\%)}}{\text{Metal in solution at equilibrium (\%)}} \times \frac{\text{Volume of solution (ml.)}}{\text{Mass of resin (g.)}}$$

The use of such relationships, however, requires the conditions to be such that the concentration of metal ions is low in both the resin and the aqueous phase (see refs. 2 and 5). Now in the chromatographic separation of macro-concentrations of multivalent metal ions on a column (as in our batch experiments) the first condition is not fulfilled, for the concentration of metal ions in the chromatogram bands is high. Likewise the second condition will only be satisfied for iron, which will be present in solution mainly as complex

FIG. 2. Ratio of  $\text{Fe}^{2+}$  to  $\text{Cu}^{2+}$  (or  $\text{Mn}^{2+}$ ) removed at various pH values.



ions and not as free ferric ions, but not for copper or manganese which do not form complexes in phosphoric acid solutions in the pH range considered here.<sup>1</sup> In fact the values of the  $K_d$  ratios calculated from our data (Table 1) are all greater than the value of 1.2 generally assumed to be necessary for good separation over the pH range 0.05—1.25 and

TABLE 1. Values of  $K_d$  in phosphoric acid solutions.

pH	0.05	0.25	0.50	0.75	1.00	1.25	1.50
$K_d^{\text{Fe}}$	1.01	7.53	8.70	9.89	61.3	213	1150
$K_d^{\text{Mn}}$	51.5	75.4	122	170	245	355	525
$K_d^{\text{Cu}}$	88.7	108	138	213	317	488	733
$K_d^{\text{Mn}}/K_d^{\text{Fe}}$	51.0	10.0	14.0	17.2	4.0	1.7	0.5
$K_d^{\text{Cu}}/K_d^{\text{Fe}}$	87.8	14.4	15.9	21.6	5.2	2.1	0.6

indicate that a particularly good separation should be obtained at pH 0.05. Nevertheless, experience showed that good separations could not be attained at pH values of 0.50 or less. For these reasons we believe that Mayer and Tompkins's relation will not be reliable under conditions such as we describe, as in fact they themselves indicated.<sup>2</sup>

Table 2 shows that a marked increase in the overall rate of exchange of ferric ions for hydrogen ions occurs with the finer particle size (40—80 mesh), whilst a smaller increase

<sup>5</sup> Glueckauf, Society of Chemical Industry Symposium on Ion Exchange and its Applications, 1954, 27.

is to be noted with the bivalent metal ions. Thus the use of a smaller particle-size resin, which is desirable in column operation, should enhance any separation of iron(III) from copper(II) or manganese(II). Variations in the degree of cross-linking of the resins,

TABLE 2. *Effect of particle size of Zeo Karb 225 on rate of removal of iron(III), copper(II), or manganese(II) by phosphoric acid solutions.*

Metal	pH	Mesh size *	Metal removed (%) after contact for (hr.)				
			$\frac{1}{4}$	$\frac{1}{2}$	1	2	4
Fe .....	0.05	22—30	38	46	69	89	97
		40—80	72	84	96	98	100
	0.50	22—30	45	66	76	90	94
		40—80	65	78	89	94	98
	1.00	22—30	21	26	36	40	41
		40—80	34	38	41	46	52
Cu .....	0.05	22—30	47	49	51	52	53
		40—80	47	49	51	53	54
	0.50	22—30	37	38	40	41	42
		40—80	38	39	39	41	42
	1.00	22—30	22	23	25	26	27
		40—80	23	24	26	28	28
Mn .....	0.05	22—30	28	32	56	59	62
		40—80	30	34	51	60	64
	0.50	22—30	22	25	31	35	36
		40—80	25	29	34	37	39
	1.00	22—30	14	17	20	26	24
		40—80	17	20	23	25	26

\* Dry sieved; normal degree of cross-linking (*ca.* 10%).

TABLE 3. *Amount of iron removed from Zeo Karb 225-Fe(III) (40—80 mesh \*) by phosphoric acid solutions (pH 0.5).*

Degree of cross-linking of resin (%) †...	2	4	8	12	15	20
Fe removed from resin (%)						
(a) after $\frac{1}{4}$ hr. ....	95	93	91	76	27	21
(b) after 4 hrs. ....	100	99	97	94	85	68
Ratio a/b .....	0.95	0.94	0.94	0.81	0.32	0.31

\* These resins, which were kindly provided by Dr. Kressman of The Permutit Company Ltd., were wet sieved.

† Nominal cross-linking in each case.

however, do not cause any significant changes in the rate of exchange, except for the most highly cross-linked resins (Table 3; similar results were obtained with solutions of pH 0.05 and 1.00). With resins of average (*ca.* 10%) or less than average cross-linking, diffusion phenomena within the resin beads do not therefore seem to be rate-determining processes. Indeed, with the more viscous phosphoric acid solutions (*i.e.*, those of low pH), diffusion of ions in the boundary layer surrounding the beads and in the bulk electrolyte may play a more important rôle.

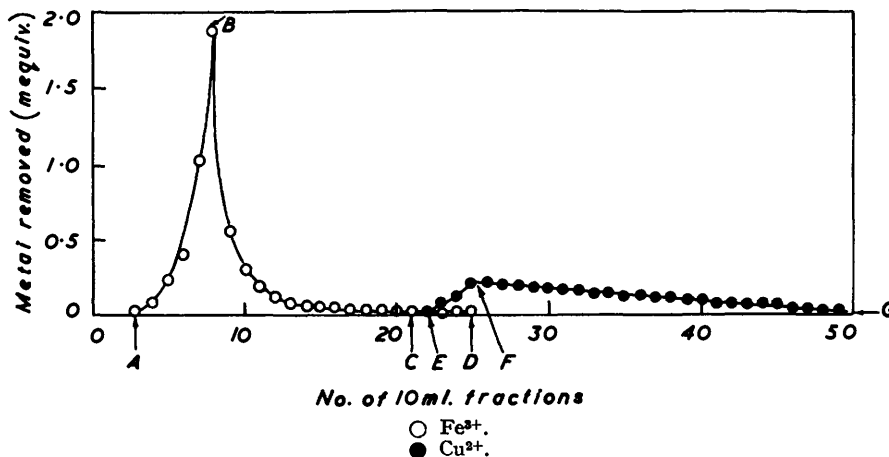
Experiments in which iron and copper were eluted separately from a column bed 8 in. long by  $\frac{1}{2}$  in. in diameter (40—80 mesh resin) supported the conclusions based on the batch experiments. The results for two typical cases, in which iron and copper respectively (5 mequiv. of each) were eluted from a column of 4% cross-linked resin by phosphoric acid solution of pH 0.50 at a flow rate of 100 ml. per hour, are shown in Fig. 3. Since the shapes of the curves obtained in other experiments were very similar, the numbers of the fractions (each 10 ml.) corresponding to points A to G in Fig. 3 have been listed in Table 4 for the individual cases (A is the first fraction containing iron; B, the fraction with maximum iron content; C, that with iron content less than 0.02 equiv.; D, that with no further trace of iron; E, first fraction containing copper; F, that with maximum copper content; G, that with no further trace of copper).

The shape of the iron peak is slightly asymmetric, but a more important feature is the long tail (points C to D, Fig. 3). Whilst this might be caused by a too high rate of flow,

this does not seem to be the case for otherwise the length of the tail should be decreased by any factors tending to increase the rate of exchange, but is, in fact, unaffected by (a) decrease in degree of cross-linking of resin from 10% to 4% (Table 4); (b) increase in temperature from 20° to 50° (Table 4); (c) increase in pH of aqueous layer from 0.75 to 0.05 (Table 4); or (d) decrease in rate of flow of eluant from 100 ml. to 50 ml. per hour (Table 4).

Now, whilst the column which we used would probably correspond to only a few theoretical plates, the large difference in the extent of complex formation between ferric ions and phosphate on the one hand and the bivalent ions and phosphate on the other, will certainly effectively increase this by a large factor. It is probable therefore that the number of "effective" theoretical plates in the column will be sufficiently high to justify the high

FIG. 3. Elution curves for Fe<sup>3+</sup> and Cu<sup>2+</sup> with H<sub>3</sub>PO<sub>4</sub> at pH = 0.50.



flow rate used.<sup>6</sup> Since useful separations could be achieved in practice by using this flow rate, there seemed little point in decreasing it.

It is apparent from Table 4 that the main effect of change in pH of the phosphoric acid

TABLE 4. Elution data for copper(II) and iron(III) with phosphoric acid solutions.

pH of H <sub>3</sub> PO <sub>4</sub> soln.	Cross-linking (%)	Temp	Eluate fraction corresponding to *						
			A	B	C	D	E	F	G
0.05	10	20°	1	4	22	27	—	—	—
	4	20	1	3	19	25	10	15	38
	4	50	2	5	17	25	10	16	38
0.25	10	20	3	7	23	27	—	—	—
	4	20	2	6	22	26	14	16	50
	4	50	3	6	18	25	14	17	52
0.50	10	20	3	7	21	26	—	—	—
	4	20	2	8	20	26	21	26	>50
	4 †	20	3	7	22	25	—	—	—
0.75	4	50	2	7	20	28	22	27	>50
	4	20	6	16	27	29	43	49	>60
1.00	4	20	15	44	80	94	185	197	>250

\* See Fig. 3 and text (p. 260) for explanation (10 ml. fractions.)

† Flow rate reduced to 50 ml. per hour.

solutions is to alter initial points at which iron (A) or copper (E) first appears in the eluate. As the tailing in the iron band (E) is not affected by changes in pH (in the range up to pH 0.75), the pH of the eluate has to be such that the first appearance of the bivalent

<sup>6</sup> Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.

metal comes after the end of the iron tail<sup>7</sup> ( $[E - D]$  positive in Fig. 2) if a separation is to be achieved. From Fig. 2 it can be seen that any pH above 0.6 should be suitable from this point of view. The separation appears to be enhanced when the two metals (Fe + Cu or Fe + Mn) are present together on the column and separations achieved with an eluant of pH 0.5 have already been reported elsewhere.<sup>7</sup> However, the separations are sharper and the chance of cross-contamination of the fractions is reduced if an eluant of pH 0.6 is used (preferably with 4% cross-linked resin, 40–80 mesh). With eluants of pH 1 or higher, the marked tailing of the iron requires the use of much larger volumes of eluant, with consequent increase in time taken. Thus separations are possible in the range where the ratio (Fe<sup>2+</sup> removed)/(M<sup>2+</sup> removed) is greater than 2 : 1 (Fig. 2).

An unusual feature of these separations is that the metal which has the highest affinity for the resin (Fe<sup>3+</sup>) is eluted before the metals having a lower affinity (Cu<sup>2+</sup> or Mn<sup>2+</sup>). Thus hydrochloric acid (of *ca.* pH 0.6) will elute copper before iron, without, however, giving a complete separation on an 8'' column. This reversal of elution order is not found in the separation of the rare-earth (or alkaline-earth) elements when using complex-forming eluants such as citrates, where the separation is enhanced, but the order of elution undisturbed. Reversals of elution order have been observed with certain of the actinides<sup>8</sup> with the alkaline-earth elements<sup>8,9</sup> and with the alkali metals,<sup>9</sup> but always at high acid concentrations (at least 6M-HCl, and higher for the multivalent ions). Now a phosphoric acid solution of pH 0.5 is approximately 2M in total H<sub>3</sub>PO<sub>4</sub> so that the reversal in order is not likely to be due to the phenomena responsible for the reversal in concentrated solutions, but rather to the selective complex-forming action of the eluting agent used.

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<sup>7</sup> Genge, Holroyd, Salmon, and Wall, *Chem. and Ind.*, 1955, 357.

<sup>8</sup> Diamond, Street, and Seaborg, *J. Amer. Chem. Soc.*, 1954, **76**, 1461.

<sup>9</sup> Diamond, *J. Amer. Chem. Soc.*, 1955, **77**, 2978.

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