

TABLE III  
A FEW  $R_F$  VALUES IN SOME HCl AND HClO<sub>4</sub> SYSTEMS

Metal ions	$R_F$ values*					
	HCl			HClO <sub>4</sub>		
	1 N	3 N	5 N	1 N	3 N	5 N
Sb(III)	0.09	0.82	0.87	0.04	0.17	0.20
Fe(III)	0.06	0.46E	0.71	0.04	0.13	0.15
Zr(IV)	0.00	0.00	0.00	—	—	—
Th(IV)	0.00	0.09	0.15	0.03	0.03	0.13
Ti(IV)	0.00	0.00	0.00	—	—	—
UO <sub>2</sub> (II)	0.35 E	0.54 E	0.74 E	0.37 E	0.32 E	0.32 E

\* E = elongated.

The  $R_F$  values of some metal ions, *e.g.* Pb(II), Cu(II), Cd(II), Bi(III), Ni(II), Co(II), Pd(II), U(VI), Ce(III), La(III) and Y(III) increase with increase in hydrochloric acid concentration (Table II). However, an increase in the perchloric acid concentration has no effect upon them (Table III). This shows that the change in  $R_F$  values is probably due to complex formation.

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- 1 G. ALBERTI AND G. GRASSINI, *J. Chromatog.*, 4 (1960) 83.
- 2 J. M. P. CARBAL, *J. Chromatog.*, 4 (1960) 86.
- 3 M. J. NUNES DA COSTA AND M. A. S. JERÓNIMO, *J. Chromatog.*, 5 (1961) 546.
- 4 K. HUSAIN, *M. Sc. Thesis*, A.M.U., Aligarh, 1964.
- 5 Y. INOUE, *Bull. Chem. Soc. (Japan)*, 36 (1963) 1316.

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### The adsorption of metal ions on exchangers with phosphoric groups from perchloric acid solutions

The curious increase of adsorption of metal ions on Dowex-50 with an increase in the concentration of HClO<sub>4</sub> was first described by NELSON *et al.*<sup>1</sup>, and we have since shown<sup>2,3</sup> that it occurs also on cellulose sulphonic exchangers and from solutions of

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sodium perchlorate. In the present communication we have extended the study of the adsorption of metal ions from  $\text{HClO}_4$  to two further exchangers, zirconium phosphate and cellulose phosphate. The two differ in their behaviour with  $\text{HClO}_4$ ; zirconium phosphate seems to break down at higher  $\text{HClO}_4$  concentrations resulting in a desorption of the metal ions, while on cellulose phosphate there is the same increase of adsorption as on sulphonic exchangers. We have investigated a large number of metal ions on cellulose phosphate as there are several analytical possibilities. However, it should be kept in mind that cellulose phosphate also decomposes in higher acidities and is only stable if the development time is rather short (less than one hour or so).

### Experimental

(a) *Zirconium phosphate.* Macherey, Nagel & Co. paper holding 15% zirconium phosphate was used in this work, 11.7 N  $\text{HClO}_4$  (Carlo Erba) was employed and all other concentrations were prepared by diluting it with water. All chromatograms were developed by the ascending method and the spots detected with the usual spray reagents. The results with a number of metal ions are shown in Fig. 1.

The only ions which do not adsorb on cellulose (Pb and Bi do adsorb) and which are relatively strongly adsorbed on zirconium phosphate are  $\text{Fe(III)}$  and  $\text{UO}_2^{2+}$ . After an initial increase to 1.7 N, the  $R_F$  values remain almost constant up to 5.8 N and then both ions desorb rapidly. Most other metal ions do not adsorb above about 1 N  $\text{HClO}_4$  and hence little further data can be obtained about them. However, comparing the results for  $\text{Fe(III)}$  and  $\text{UO}_2^{2+}$  with those on cellulose phosphate (below), it seems likely that the desorption is due to the properties of the adsorbant (*i.e.* its destruction) and not to the alteration of the ionic state of the metal ions.

(b) *Cellulose phosphate.* Whatman cellulose phosphate paper P 20 was converted to the hydrogen form by washing with 1 N  $\text{HCl}$  and water and then drying. Fig. 2 shows the  $R_F$  values of numerous metal ions in up to 7 N  $\text{HClO}_4$ .

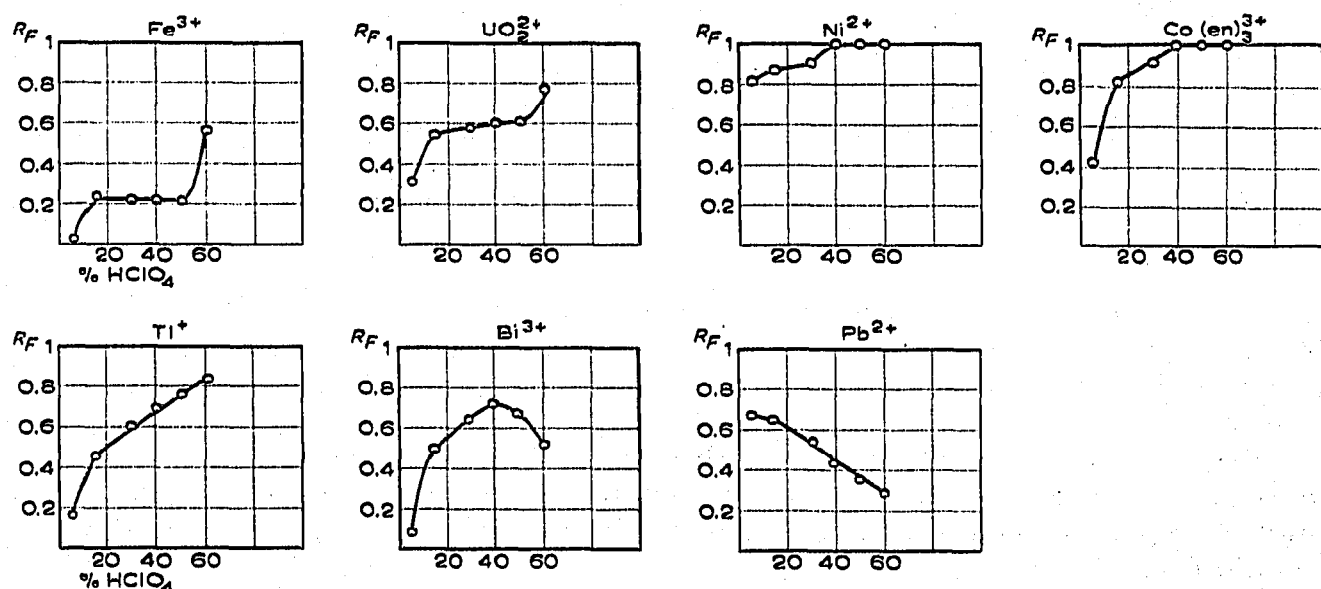


Fig. 1.  $R_F$  values of some metal ions plotted against the  $\text{HClO}_4$  concentration on Macherey, Nagel & Co. zirconium phosphate paper (15% ZP). The  $\text{HClO}_4$  concentration is expressed in % (100% = 11.7 N).

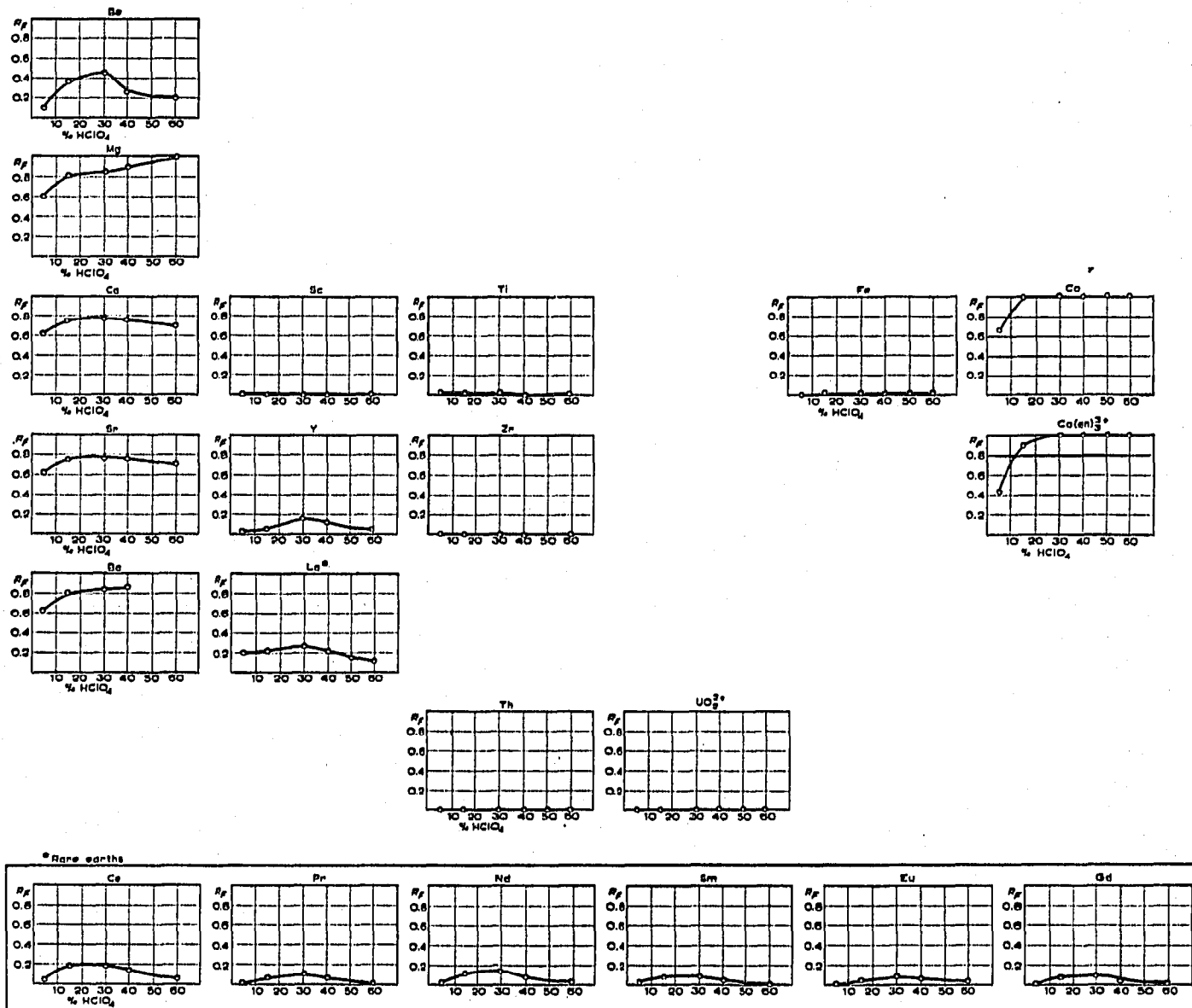
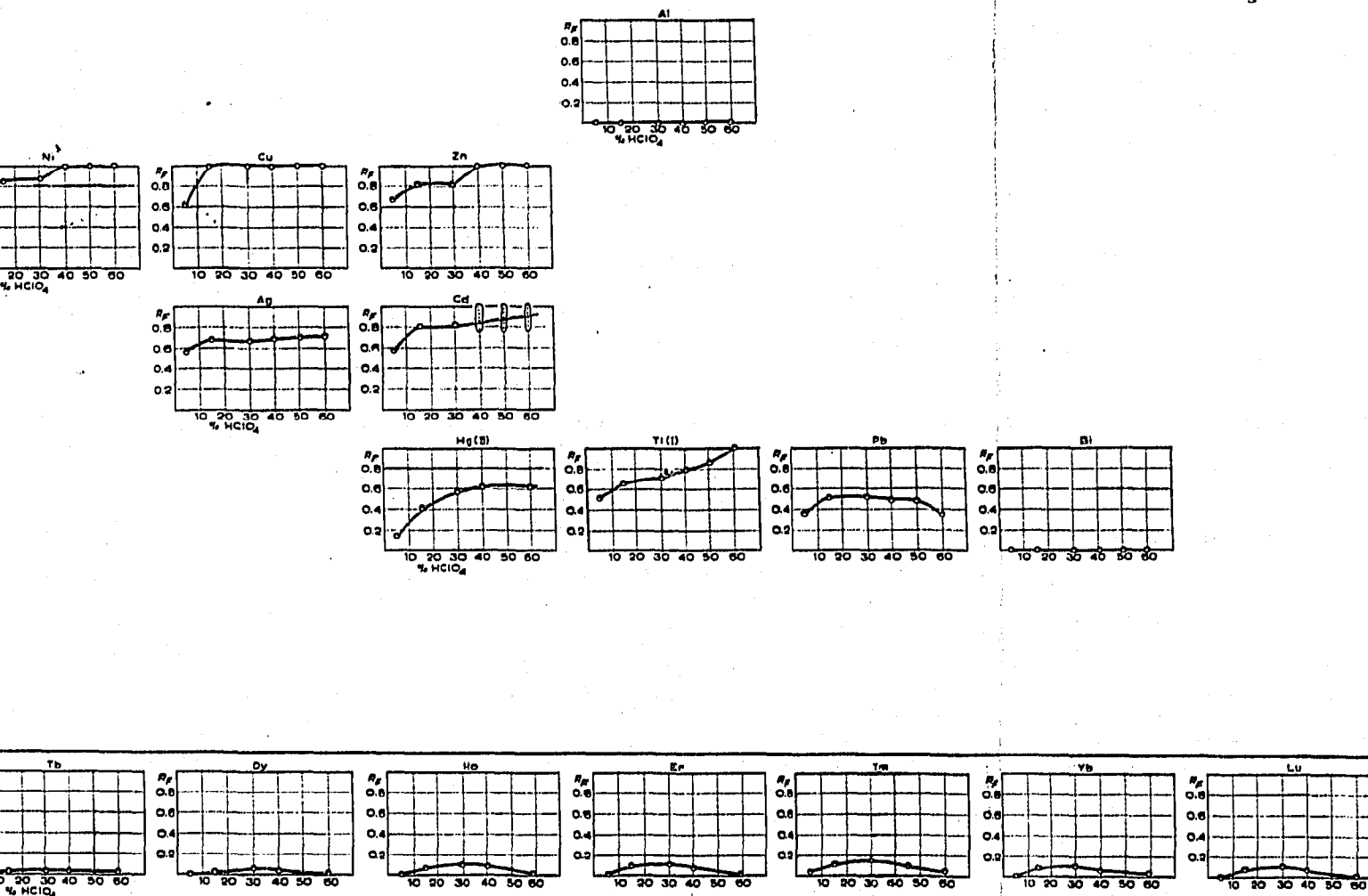


Fig. 2.  $R_F$  values of some metal ions on Whatman cellulose phosphate paper P 20. The  $\text{HClO}_4$  concentration is expressed in % (100% = 11.7 N).

Most transition metals are only little adsorbed while the tetravalent ions such as Zr, Th and Ti remain near  $R_F$  0. The rare earths, yttrium and beryllium show the bell shaped  $R_F$  curve which is typical for adsorptions from  $\text{HClO}_4$  on sulphonic exchangers with a maximum around 3.5 N.

There seem to be well defined  $R_F$  differences between the rare earths, the light ones being less adsorbed than the intermediate ones, however, as stated above this cannot be exploited readily with a lengthy development owing to the unstable nature of cellulose phosphate.

The very strong adsorption of Fe(III) and Al(III) and the weak adsorption of  $\text{Co(en)}_3^{3+}$  emphasises again that the adsorption does not bear much relation to the charge of the metal ion as to complexation with the phosphoric groups.



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- 1 F. NELSON, T. MURASE AND K. A. KRAUS, *J. Chromatog.*, 13 (1964) 503.
- 2 M. LEDERER AND F. SARACINO, *J. Chromatog.*, 15 (1964) 80.
- 3 F. SARACINO, *J. Chromatog.*, 17 (1965) 425.
- 4 G. ALBERTI, F. DOBICI AND G. GRASSINI, *J. Chromatog.*, 8 (1962) 103.

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