

## CHROMATOGRAPHY ON PAPER IMPREGNATED WITH INORGANIC ION EXCHANGERS

### III. CHROMATOGRAPHY OF INORGANIC IONS ON ZIRCONIUM PHOSPHATE PAPER WITH HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub> AND CH<sub>3</sub>COOH AT VARIOUS CONCENTRATIONS

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Paper impregnated with synthetic inorganic exchangers prepared by the authors and described in earlier work<sup>1,2</sup> can be used successfully for the fast separation of a number of inorganic ions; thus it has found applications in the separation of short lived radio-elements<sup>3</sup>, as well as for studying adsorption equilibria<sup>4</sup>.

In this work the behaviour is described of a large number of ions with some inorganic acids as eluents.

#### EXPERIMENTAL

##### *Preparation of paper impregnated with zirconium phosphate*

The preparation of zirconium phosphate (ZP) impregnated paper has been described in an earlier paper<sup>1</sup>. In the present work the process was simplified by eliminating the additional treatment with phosphoric acid and the final drying at 50°. In this way the preparation time is considerably reduced without any noticeable effect on the properties of the strips.

##### *Chromatography with various eluents*

As eluents we used a very weakly complexing acid (HClO<sub>4</sub>) and the inorganic acids commonly employed (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>), at concentrations ranging from 0.1 to 1 *N*. The chromatograms were developed by the method described previously<sup>1</sup>. Table I gives the *R<sub>F</sub>* values of the ions studied. It will be observed that the *R<sub>F</sub>* values obtained with perchloric acid are not appreciably different from those obtained with other inorganic acids. This is due to the fact that the majority of the cations do not form complexes with such acids at the concentrations employed (0.1–1 *N*). Greater differences compared to the values obtained with perchloric acid are observable only for certain ions which are well known to have a marked tendency to form complexes, among them are Cd(II), Zn(II), Cu(II), Co(II), Pb(II) and Bi(III).

The chromatographic behaviour of the ions given in Table I, was also examined using a weak organic acid, namely acetic acid (0.1 and 1 *N*), as eluent. In this case,

TABLE I  
 $R_F$  VALUES OF INORGANIC CATIONS IN VARIOUS ACIDS

Elements*	$R_F$							
	HCl		HNO <sub>3</sub>		H <sub>2</sub> SO <sub>4</sub>		HClO <sub>4</sub>	
	0.1 N	1 N	0.1 N	1 N	0.1 N	1 N	0.1 N	1 N
Li (I)	0.76	0.85	0.77	0.87	0.77	0.84	0.79	0.80
Na** (I)	0.67	0.83	0.75	0.84	0.50	0.77	0.66	0.78
K (I)	0.50	0.60	0.40	0.75	0.30	0.64	0.66	0.78
Rb (I)	0.12	0.48	0.15	0.50	0.07	0.34	0.13	0.47
Cs** (I)	0	0	0	0	0	0	0	0
Ag (I)	—	—	0	0.05	0	0	—	0
Tl (I)	0	0.45	0.05	0.30	0.10	0.25	0.08	0.30
Ca** (II)	0.80	—	0.66	0.81	—	—	0.71	0.82
Sr** (II)	0.77	—	0.62	0.84	—	—	0.68	0.80
Co (II)	0.67	0.77	0.62	0.80	0.53	0.87	0.50	0.73
Zn (II)	0.63	0.76	0.47	0.77	0.64	0.80	0.45	0.78
Ni (II)	0.61	0.85	0.64	0.86	0.63	0.86	0.53	0.80
Cd (II)	0.60	0.81	0.40	0.79	0.46	0.86	0.34	0.80
Cu (II)	0.56	0.78	0.48	0.81	0.41	0.84	0.46	0.83
Pb (II)	—	—	0.08	0.75	—	—	0.08	0.53
Al (III)	0.13	0.77	0	0.75	0.02	0.72	0.05	0.71
Fe (III)	0	0.04	0	0	0	0.02	—	0
Bi (III)	—	0.83	0.06	0.28	0	0	—	0
La (III)	0.28	0.84	0.28	0.80	0.20	0.82	0.20	0.80
Ce (III)	0.25	0.84	0.15	0.76	0.10	0.71	0.05	0.78
Y (III)	0.05	0.65	0.06	0.66	0.01	0.67	0	0.58
Th (IV)	0	0	0	0	0.04	0.04	0	0
UO <sub>2</sub> (II)	0	0.32	0	0.15	0.12	0.29	0.02	0.20

\* The spots were detected by spraying the strips with suitable reagents.

\*\* These elements were also detected by radiochemical methods.

TABLE II  
 $R_F$  VALUES OF SOME CATIONS IN HCl AND HClO<sub>4</sub> AT HIGH CONCENTRATIONS

Elements	$R_F$					
	HCl			HClO <sub>4</sub>		
	1 N	3 N	6 N	1 N	3 N	6 N
Fe (III)	0	0.30	0.51	0	0	0
Bi (III)	0.83	—	—	0	0.16 (tail)	0.35 (tail)
Sn (II)	0	0.42	0.62	0	0	0
UO <sub>2</sub> (II)	0.32	0.47	0.52	0.20	0.26	0.27
Th (IV)	0	0	0	0	0	0
Cs (I)	0	0	0	0	0	0

however, most ions stay at the point of application or yield long comets except a few, such as lithium, which have a weak affinity for the exchanger.

Since the complexing power of an acid is enhanced if its concentration is increased, we also wanted to study the chromatographic behaviour of certain cations when perchloric acid and hydrochloric acid at high concentrations (3 and 6 *N*) are used as eluents. It was not possible to extend the study to ions already showing fairly high  $R_F$  values with dilute acids. Table II gives the  $R_F$  values for some of the ions studied. In the case of Th(IV) and Cs(I), which form relatively weak complexes with HCl, no differences are observed between the values obtained with the two acids. In the case of other ions, however, which tend to form complexes with HCl (*e.g.* uranium, iron and tin), the greater the concentration of the acids the higher the differences obtained. It is thus possible in a very simple and rapid way to obtain useful information on the complexing properties of a given eluent from the chromatographic behaviour of the various ions. Conversely, from the  $R_F$  values with different eluents it is possible to select the best conditions for a given separation.

### $R_M$ values

The authors proposed to verify whether the equation  $XpH = R_M^* + \text{const.}$ , proposed by LEDERER AND KERTES<sup>5</sup> for papers impregnated with Dowex 50, was valid also for ZP-impregnated paper. Considerable difficulties were met with, however, when determining experimentally the  $R_M$  values as a function of the pH. In the first place, since ZP acts as a weak cation exchanger, it is only partially ionized in strong acid solutions. Thus, at pH = 0 most of the ions, except for a certain number that reveal a marked affinity for the ZP, travel with an  $R_F$  value close to 1. It is also not possible to elute with solutions of pH = 1, because also with ZP-impregnated paper (as shown by PICKERING for non-impregnated paper<sup>6</sup>) the acid front does not correspond to the liquid front (Fig. 1). Since many cations travel with the acid front even

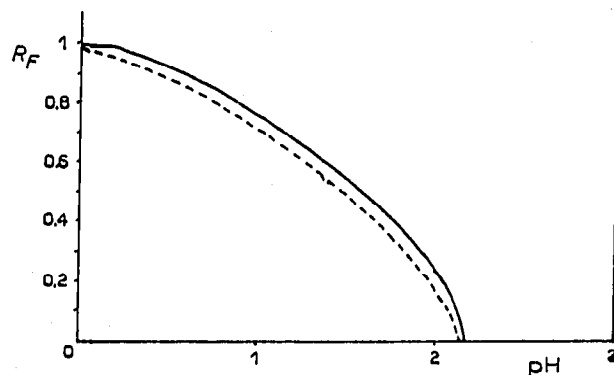


Fig. 1.  $R_F$  values of the acid front plotted against pH. Continuous line: Amberlite WA-2 ion exchanger paper. Dotted line: ZP-impregnated paper.

when eluted with dilute acid solutions, the  $R_M$  values calculated from the liquid front do not correspond to the degree of adsorption of the ion. The same observations apply in the case of papers impregnated with a weak carboxylic resin, *e.g.* Amberlite WA-2.

$$R_M = \log \left( \frac{1}{R_F} - 1 \right)$$

Experiments with these papers have shown that most of the cations travel with the acid front at a pH value of 1–2. This is explained by the fact that Amberlite WA-2 is an even weaker ion exchanger than ZP. It is therefore not possible to determine  $R_M$  values as a function of the pH for papers impregnated with very weak ion exchangers. The authors nevertheless attempted to determine the  $R_M$  values for certain ions showing a great affinity for ZP and which therefore do not travel with the acid front at pH values between 0 and 1.5.

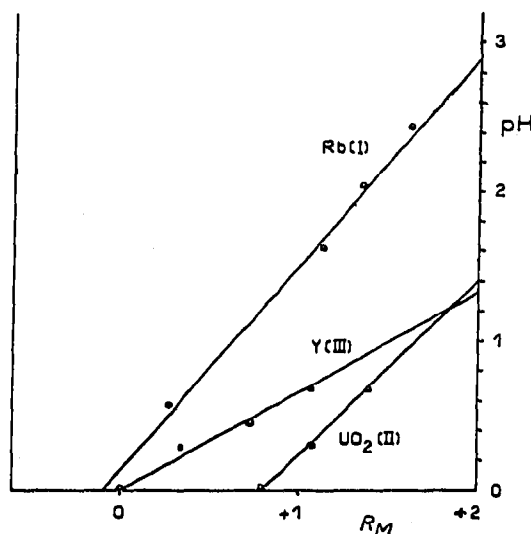


Fig. 2.  $R_M$  values of Rb(I),  $UO_2$ (II) and Y(III) plotted against pH on ZP paper in the hydrogen form. Eluent:  $HClO_4$ .

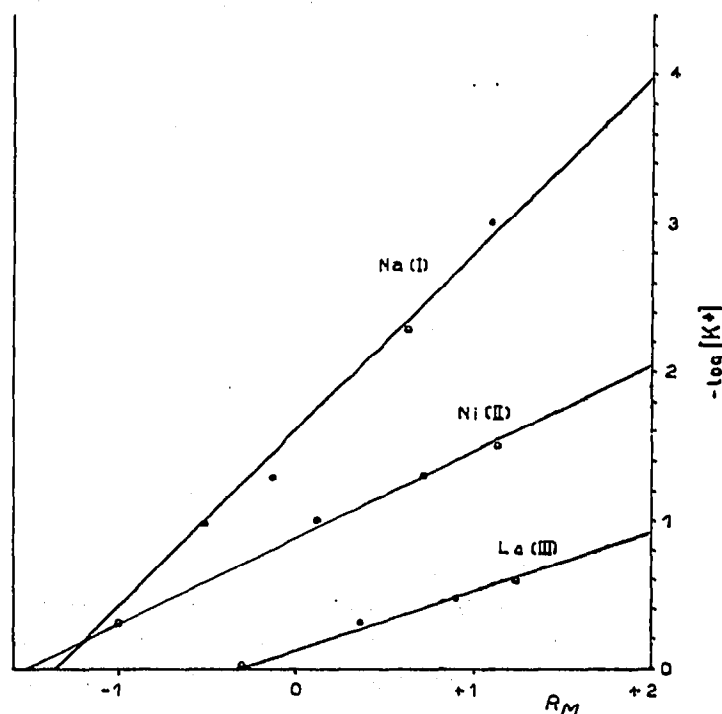


Fig. 3.  $R_M$  values of Na(I), Ni(II) and La(III) plotted against  $-\log [K^+]$  on ZP paper in the potassium form. Eluent: KCl.

Fig. 2 gives results obtained for Rb(I),  $\text{UO}_2$ (II) and Y(III). The  $R_M/\text{pH}$  ratio increases as the valency of the ion, but the equation  $X\text{pH} = R_M + \text{const.}$  no longer applies.

In order to avoid the difficulties met with in determining  $R_M$  values as a function of the pH, an attempt was made to transform the exchanger into the sodium or potassium form and then to elute with solutions at increasing concentrations of  $\text{Na}^+$  or  $\text{K}^+$ . In this way the exchanger is completely dissociated. Further, since the elution can be carried out with solutions at fairly high concentrations of  $\text{K}^+$  and  $\text{Na}^+$  (in view of their lower eluting power compared with the  $\text{H}^+$  ion) a single chromatographic front is obtained.

Fig. 3 shows  $R_M$  values as a function of  $-\log[\text{K}^+]$ . The straight lines obtained correspond to the equation:

$$-X \log [\text{K}^+] = R_M + \text{const.}$$

where  $X$  = valence of the ion under consideration.

This equation differs from that proposed by LEDERER AND KERTES<sup>5</sup> only in the substitution of other eluent ions for the  $\text{H}^+$  ion.

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#### SUMMARY

The chromatographic behaviour of a large number of inorganic ions on zirconium phosphate paper is described. Inorganic acids commonly employed such as  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  at concentrations ranging from 0.1 to 6 *N* are used as eluents. The application of equation  $X\text{pH} = R_M + \text{const.}$  for papers impregnated with weak ion exchangers or ZP-impregnated papers is discussed.

#### REFERENCES

- <sup>1</sup> G. ALBERTI AND G. GRASSINI, *J. Chromatog.*, 4 (1960) 83.
- <sup>2</sup> G. ALBERTI AND G. GRASSINI, *J. Chromatog.*, 4 (1960) 423.
- <sup>3</sup> J. P. ADLOFF, *J. Chromatog.*, 5 (1961) 366.
- <sup>4</sup> M. J. NUNES CA COSTA AND M. A. S. JERÓNIMO, *J. Chromatog.*, 5 (1961) 456.
- <sup>5</sup> M. LEDERER AND S. KERTES, *Anal. Chim. Acta*, 15 (1956) 226.
- <sup>6</sup> W. F. PICKERING, *J. Chromatog.*, 1 (1958) 274.