CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION-EXCHANGE RESINS

III. THE SEPARATION OF SOME CATION MIXTURES

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In the second part of this series[1] we have established the relation $x\mathrm{pH} = R_M + \text{constant}$ for the elution of cations from filter paper impregnated with colloidal Dowex-50 resin. However, after proving it experimentally with La^{+++} and Ni^{++} ions, we have only applied it to the separation of selenite and tellurite with numerous developing acids.

In this paper we shall describe some applications of the above equation in choosing a suitable concentration of developing acid and thus in predicting the conditions under which ion-exchange separations may be effected when using only the cation–H^+ equilibrium without any complexing agents. In the above equation x represents the valency of the cation, and, as is well known already, the lower the charge on an ion the easier its displacement from the resin by hydrogen ions. The significance of this is best illustrated by plotting R_F against pH when, as shown in Fig. 1, telluryl, Ni^{++} and La^{++} (experimental data from[1]) change their R_F values logarithmically with the pH.

In this work the paper was impregnated with Dowex-50, as described in the two previous communications[1,2], and HCl at various concentrations was used throughout this work as developing acid. Usually, the chromatogram was 24 cm long with the sample applied as a thin line 4 cm from one end, and the paper was developed by the ascending method.

The separation Cu–Cd

From electrophoretic and paper chromatographic data it is known that Cd exists in dilute HCl as an equilibrium of $CdCl^+$, $CdCl_2^0$, and $CdCl_3^-$, while Cu^{++} remains uncomplexed in concentrations of HCl up to 1 N (at least). It may be presumed that Cu^{++} will thus have R_F values essentially similar to those of Ni^{++} in Fig. 1 since its radius and hydration are alike. Thus, all that is required to predict a good separation is to look for a concentration of HCl where Cu^{++} stays well behind a monovalent cation such as $CdCl^+$. A concentration between 0.2 N and N would fulfill these conditions. Thus 0.1 N, 0.3 N, 0.5 N and 0.7 N were tried; they gave the chromatograms shown in Fig. 2. The best separation was in 0.3 N HCl or 0.5 N HCl.

Separations of some trivalent and tetravalent ions

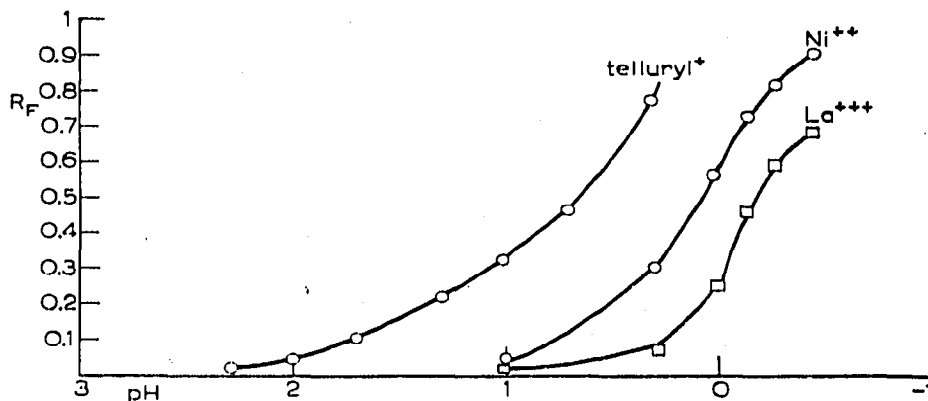(a) *Behaviour of Fe(III)*. Ferric iron behaves like an intermediate between a

Fig. 1. The R_F–pH relationship of typical mono-, di- and tri-valent cations when eluted with H_2SO_4 (data from ref.[1]).
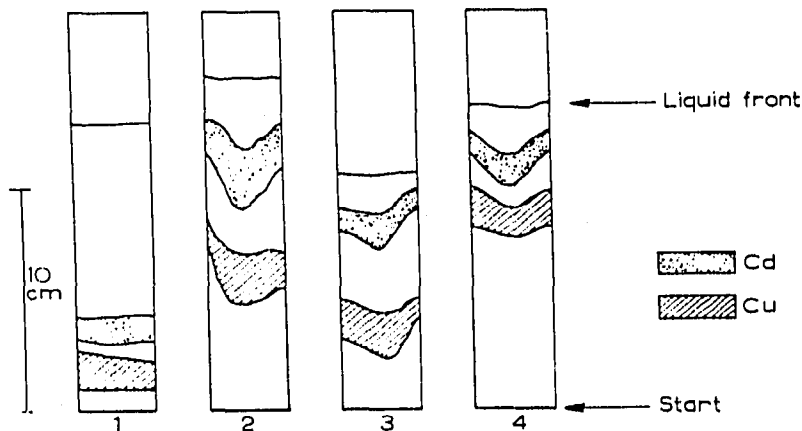
Fig. 2. Separation Cu–Cd on Dowex-50 paper with (1) 0.1 N HCl, (2) 0.3 N HCl, (3) 0.5 N HCl, (4) 0.7 N HCl. All paper strips were dried and dipped in $(NH_4)_2S$ solution to reveal dark CuS and yellow CdS.
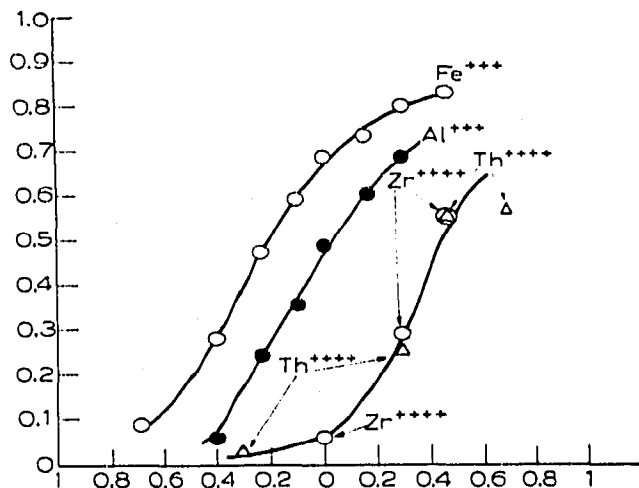
Fig. 3. The R_F–pH relationship of tri- and tetra-valent cations when eluted with HCl. Fe^{+++} has a curve rather like a divalent cation, presumably owing to the preponderance of $FeCl^{++}$ ions. Ti(IV), not shown here, precedes Fe(III) and is also not present as Ti^{+++}.

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divalent and trivalent cation in dilute HCl, presumably because an equilibrium between $FeCl^{++}$ and Fe^{+++} exists in the concentrations examined. The R_F–pH curve is thus well removed from that of Al^{+++}, as shown in Fig. 3.

(b) Th^{++++} and Zr^{++++} seem to be true tetravalent cations, with respect to an ion exchanger at least, and move considerably slower than trivalent ions such as Ce^{+++} and Al^{+++}; their R_F–pH curves coincide completely, as shown in Fig. 3.

(c) Ti^{++++}, on the other hand, moves well ahead of Fe(III), indicating considerable complexing with HCl.

To confirm our findings we have carried out some separations of analytical or radiochemical interest, which are shown in Fig. 4.
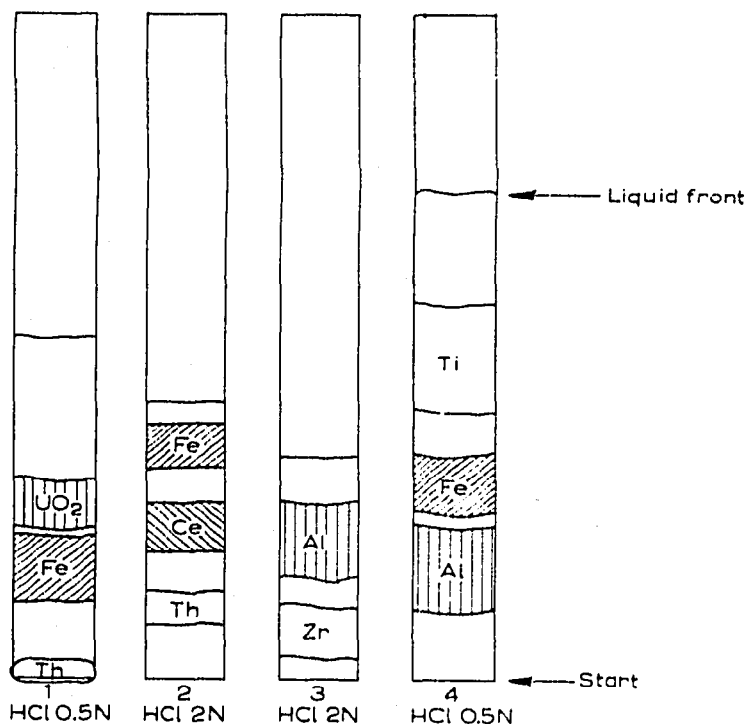

Fig. 4. Some successful separations of tetravalent cations from di- and tri-valent cations.

(d) Th–$Fe(III)$–UO_2^{++} are readily separated with 0.5 N HCl with a short development. After drying, the paper is dipped into an alcoholic ammoniacal solution of oxine, which yields a brown band for Th, a black one for Fe, and an orange one for UO_2^{++}.

(e) Th–$Fe(III)$–$Ce(III)$ separate in this order in 2 N HCl with oxine as in (d). Ce yields a pale brown band. Other rare earths can similarly be separated from Th.

(f) Al–Zr separate also in 2 N HCl. Oxine yields a colourless band with green fluorescence in ultraviolet light for Al and an orange band (green in ultraviolet light) for Zr.

(g) Ti–Fe–Al separate in 0.5 N HCl. This separation required a longer development than the three preceding ones since their R_F differences are smaller even in the optimum region. Oxine yields an orange band for Ti invisible in the ultraviolet light.

SUMMARY

Ion-exchange papers (Dowex-50) are used, with HCl as developing solvent, for the separations Cu–Cd, Th–Fe–UO_2^{++}, Th–Ce–Fe, Al–Zr and Ti–Fe–Al. The concentration of HCl to yield a separation may be predicted by using the equation xpH $= R_M +$ constant.

REFERENCES

[1] M. LEDERER AND S. KERTES, Anal. Chim. Acta, 15 (1956) 226.
[2] M. LEDERER, Anal. Chim. Acta, 12 (1955) 142.