

THE CHROMATOGRAPHIC PROPERTIES OF PAPER IMPREGNATED WITH TITANIUM HYDROXIDE

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INTRODUCTION

Since work on the ion exchange properties of hydrous oxides was started in connection with nuclear energy problems, papers impregnated with zirconium phosphate, phosphomolybdic acid etc.¹ have found application both for exploratory work on the exchangers and for separations of metal ions and radionuclides². The field has been reviewed by ALBERTI³ but so far relatively little data are available on the oxides themselves (much more being available on the phosphates, tungstates, etc.) or on their behaviour in the neutral region or in higher concentrations of electrolytes.

DAVIES *et al.*⁴ have recently recommended titanium oxide precipitated on muslin or glass wool for the removal of uranium from sea water. These authors also mention that according to their findings, uranium is found in sea water as an anionic carbonato complex of hexavalent uranium. The electrophoretic movement of U(VI) in sea water as electrolyte⁵ had been studied previously by one of us and it was observed that the uranium behaved as a neutral species. However there is a difference between the micro amounts of naturally occurring uranium in sea water and the amount which must be used in electrophoretic experiments in order to detect the "spot" with ferrocyanide; we therefore thought it would be of interest to obtain further data on the adsorption of titanium oxide in order to explain the strong adsorption without having to assume the anionic nature of U(VI) in sea water.

Paper impregnated with titanium oxide was the material of choice for these studies, as it is practically identical to the material used for recovering uranium from sea water (*i.e.* titanium oxide on muslin), and yet permitted us to use all the advantages of paper chromatographic techniques for this study. We also thought it of interest to compare the adsorption properties of titanium oxide with those of zirconium oxide and of ferric hydroxide. In addition to U(VI), we also studied the behaviour of some other cations and anions which are readily detected on the hydrous oxides.

EXPERIMENTAL AND RESULTS

(i) *Preparation of papers impregnated with hydrous oxides*

Whatman No. 1 paper was dipped in molar solutions of the respective metal ion in 4 N HCl, blotted with filter paper to remove excess liquid and dipped into 10 % ammonia, agitating carefully to avoid uneven precipitation. The papers were then

washed several times with distilled water and air dried overnight. The titanium solution was prepared by breaking an ampoule of TiCl_4 under the required amount of 4 N HCl, the zirconium solution from ZrOCl_2 (Merck) and the ferric solution from ferric nitrate (Carlo Erba).

(ii) *General remarks on chromatograms with neutral solutions*

All the substances chromatographed here yielded, at best, elongated spots and usually comets from the origin. In the graphs the centre of gravity of the main portion of the spot was taken as the " R_F " value although it is in many cases not possible to speak of R_F values proper.

As it was thought that hydrolysis is one of the contributory reactions, the pH value on Whatman No. 1 and on the impregnated papers after development with 0.1, 0.5 and 1.0 N NaCl was determined by spraying the papers immediately with universal indicator.

The impregnated papers have a slight pH gradient from the solvent to the liquid front which starts at pH 6-7 and reaches about 5, while the pure cellulose Whatman No. 1 paper (washed or untreated) has a gradient from pH 8 to about 3-4. The impregnated papers thus have pH consistently below 7.

To obtain some idea of the ion exchange capacity of the papers impregnated with hydrous oxides we carried out some frontal analysis experiments with neutral UO_2SO_4 as shown in Fig. 1.

It is interesting to note that up to about 0.1 M the R_F value of the uranium front increases linearly with the concentration, *i.e.*, that whatever the mechanism there is a direct proportionality between the uptake and the uranium concentration.

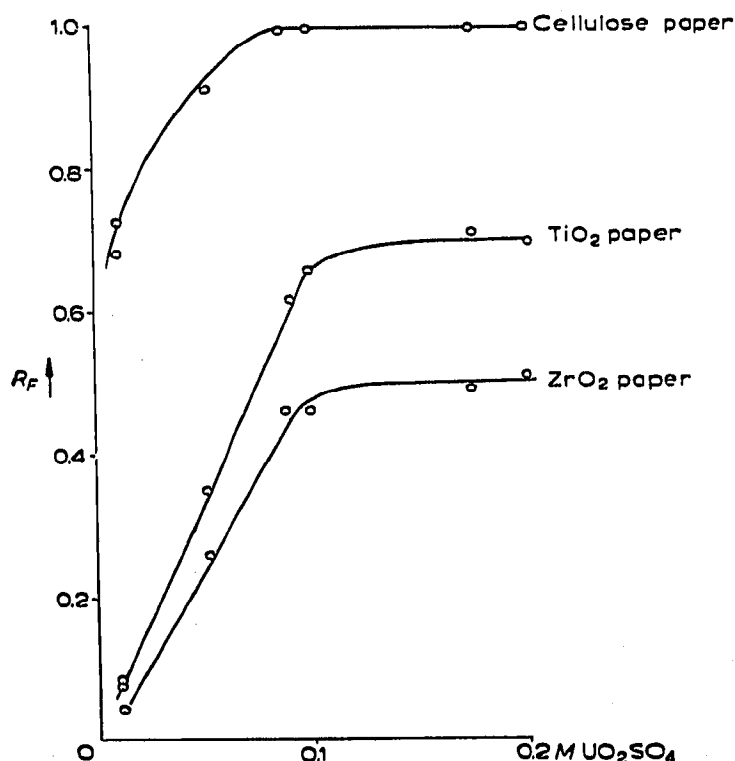


Fig. 1. " R_F value" of the U(VI) front plotted against the molarity of UO_2SO_4 in frontal analysis experiments with uranium sulphate solutions on various papers.

Above 0.1 M, the activity of uranium sulphate solutions is such that it can easily account for the flattening of the curve. The ion exchange capacity calculated from Fig. 1 is rather high, of the order of 0.7–1.0 g U per g of titanium oxide. Such high capacities were also noted by KRAUS *et al.*⁶ for a number of ions.

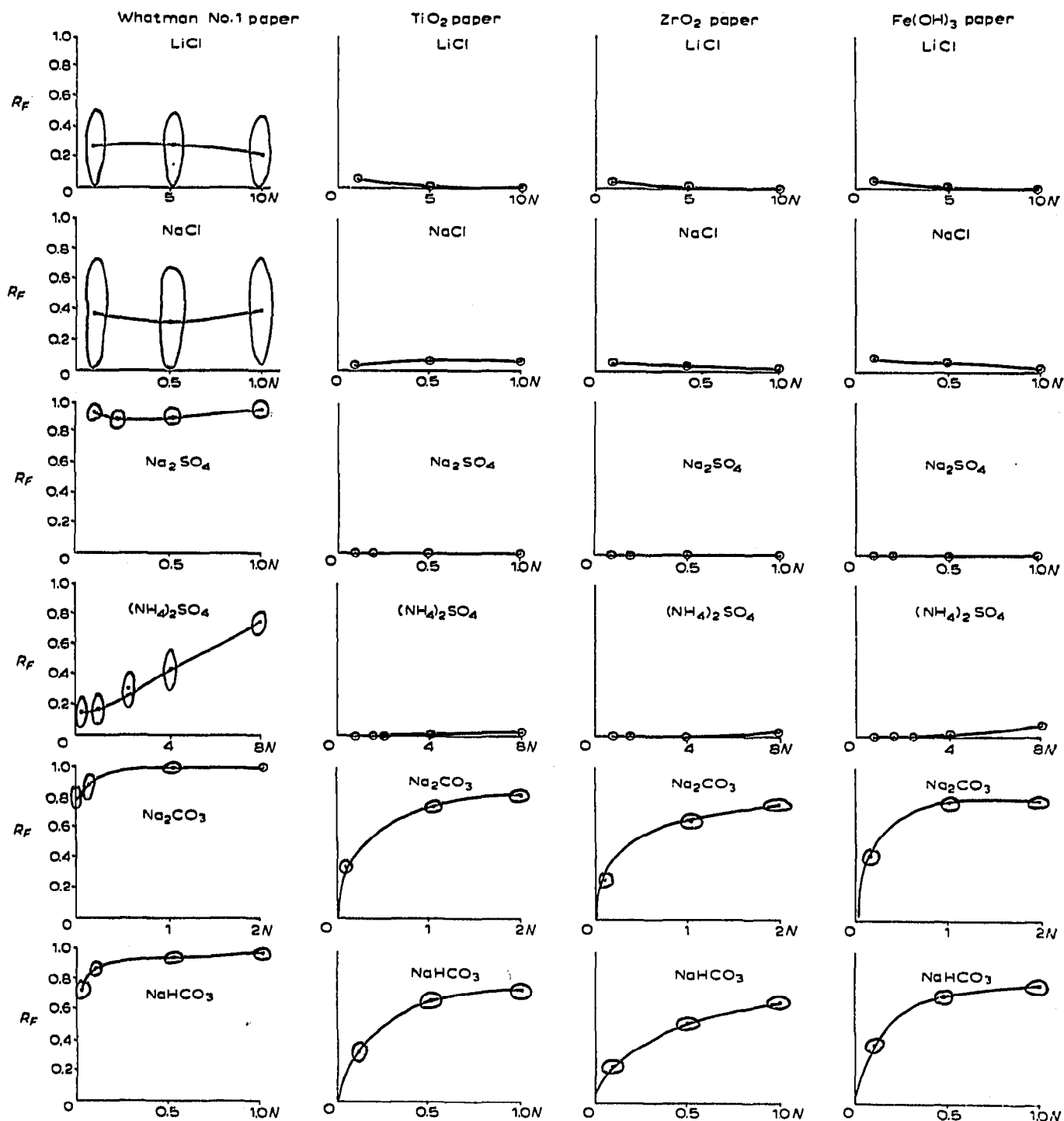


Fig. 2. R_F values of U(VI) on cellulose paper and papers impregnated with titanium, zirconium oxide and ferric hydroxide. Eluants from top to bottom: LiCl, NaCl, Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, Na_2CO_3 and NaHCO_3 .

(iii) *The movement of U(VI) in various electrolytes*

Fig. 2 shows the R_F values of U(VI) on Whatman No. 1 paper, titanium hydroxide paper, zirconium hydroxide paper and ferric hydroxide paper. Whenever there is movement of the U(VI) the length of the spots is shown schematically. U(VI) was placed on the paper with the same anion as the eluting solution, *e.g.*, as chloride when eluted with NaCl, etc.

It is evident that there is retention at the point of application with all electrolytes on the hydrous oxides except with carbonate and bicarbonate and that even 10 *N* LiCl does not desorb U(VI).

We feel that the hypothesis of DAVIES *et al.*⁴ that a carbonato complex is adsorbed from sea water is quite unnecessary and titanium hydroxide will probably be just as useful for concentrating uranium(VI) from solutions which do not contain carbonate.

Two further points are of interest. The spots tend to move less with an increase of the electrolyte concentration on the hydrous oxides (except perhaps on ferric hydroxide) and this would make it difficult to consider this adsorption in terms of "ion exchange". The second point is that in carbonate and bicarbonate U(VI) is readily eluted and the results agree with those obtained by DAVIES *et al.*⁴ on muslin impregnated with titanium oxide. This desorption seems to be due to the high affinity of the hydrous oxides to OH groups as well as to a desorption due to complexation. U(VI) is also anionic in ammonium sulphate solutions yet strongly adsorbed, while other anions which adsorb strongly from neutral solution desorb from sodium carbonate (Fig. 7).

(iv) *The movement of some metal ions in various electrolytes*

The movement of Ni(II), Co(II), Cu(II) and Fe(III) with various electrolytes is shown in Figs. 3 and 4. Ferric hydroxide paper was not studied here because the detection of the spots with usual reagents proved rather difficult.

A gradual desorption with an increase in electrolyte concentration can be seen here for all systems, suggesting that an ion exchange mechanism is at least a contributing factor.

We were rather impressed by the poor adsorbability of Co(II) and Ni(II) from ammonium sulphate and ammonium chloride solutions. The colour of the spots does not suggest complex formation with the anions and the ammonium ion cannot be held responsible either, as they are strongly adsorbed from ammonium acetate. From the results obtained we think that poor adsorbability is due to small pH changes, ammonium chloride and ammonium sulphate being slightly more acid than the other salts and, as shown by KRAUS *et al.*⁶, the apparent cation exchange capacity drops quickly at lower pH's owing to the preferential adsorption of H⁺ ions. The study of several complex Co(III) cations seems to confirm this assumption (Fig. 5). For example $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ adsorb quite strongly from ammonium acetate but much less from ammonium chloride. In both cases the R_M values plotted against the log (anion) yield straight lines, thus adsorption can be expressed as a law of mass action (see Fig. 6).

If one now compares the adsorption of Fe(III) and Cu(II) with that of $[\text{Co}(\text{en})_3]^{3+}$ it is strongly suggested that both Fe(III) and Cu(II) are precipitated as hydroxides or adsorbed as hydrolysed species; a phenomenon which is already well-known on

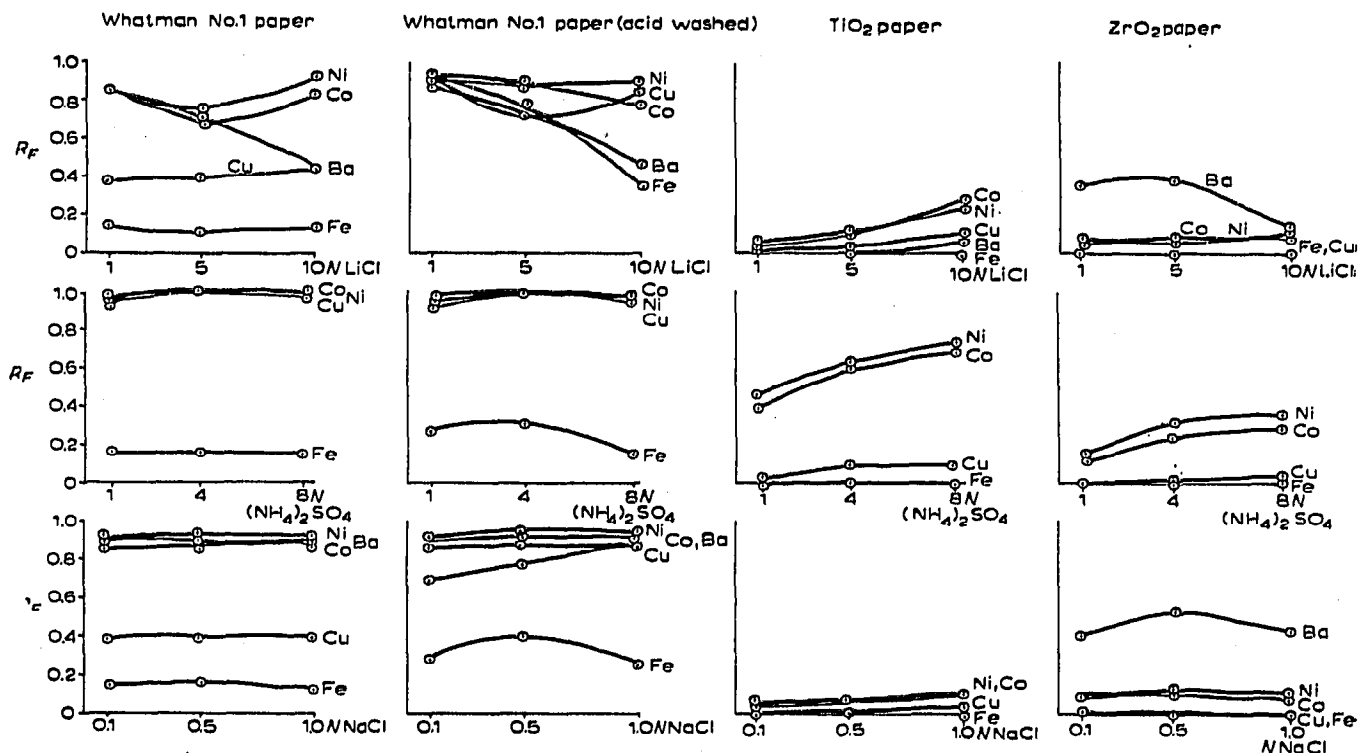


Fig. 3. R_F values of some metal ions on cellulose paper and papers impregnated with titanium oxide and zirconium oxide developed with aqueous LiCl, $(NH_4)_2SO_4$ and NaCl.

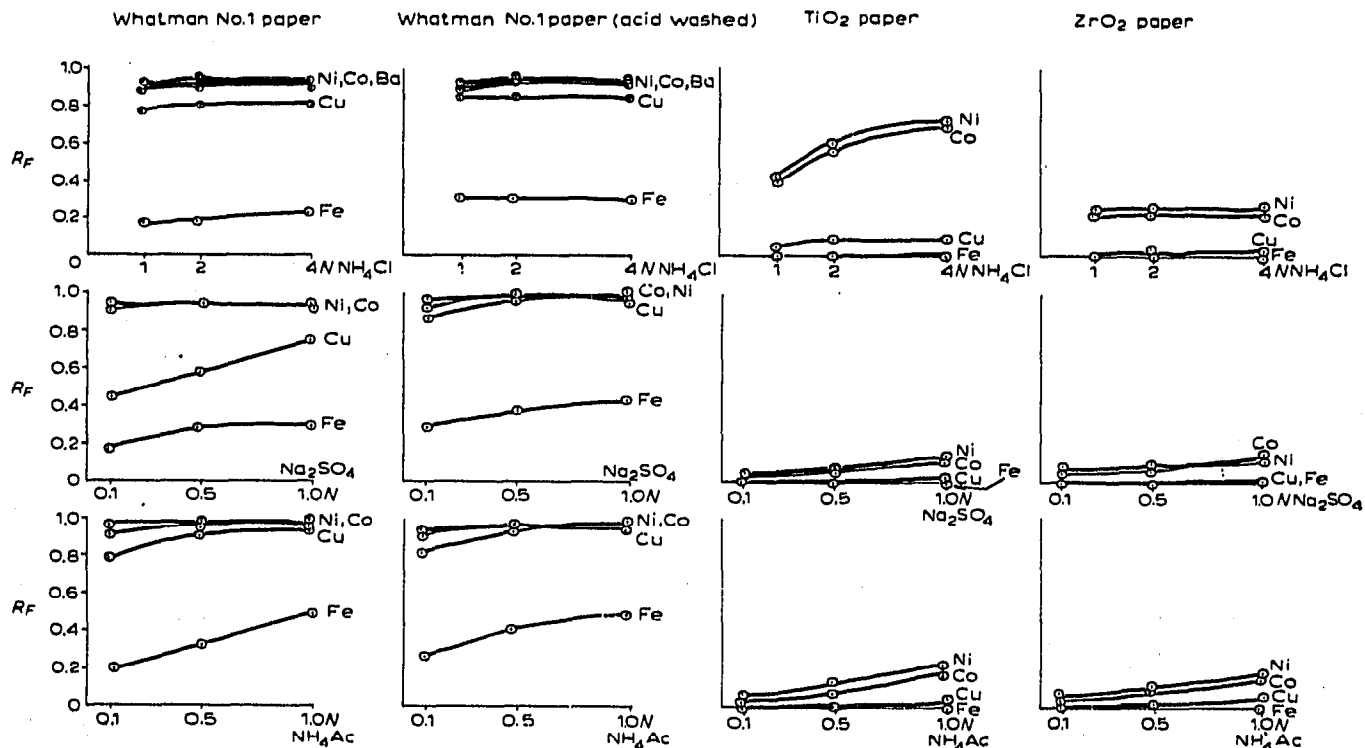


Fig. 4. R_F values of some metal ions on cellulose paper and on papers impregnated with titanium oxide and zirconium oxide developed with aqueous NH_4Cl , Na_2SO_4 and ammonium acetate.

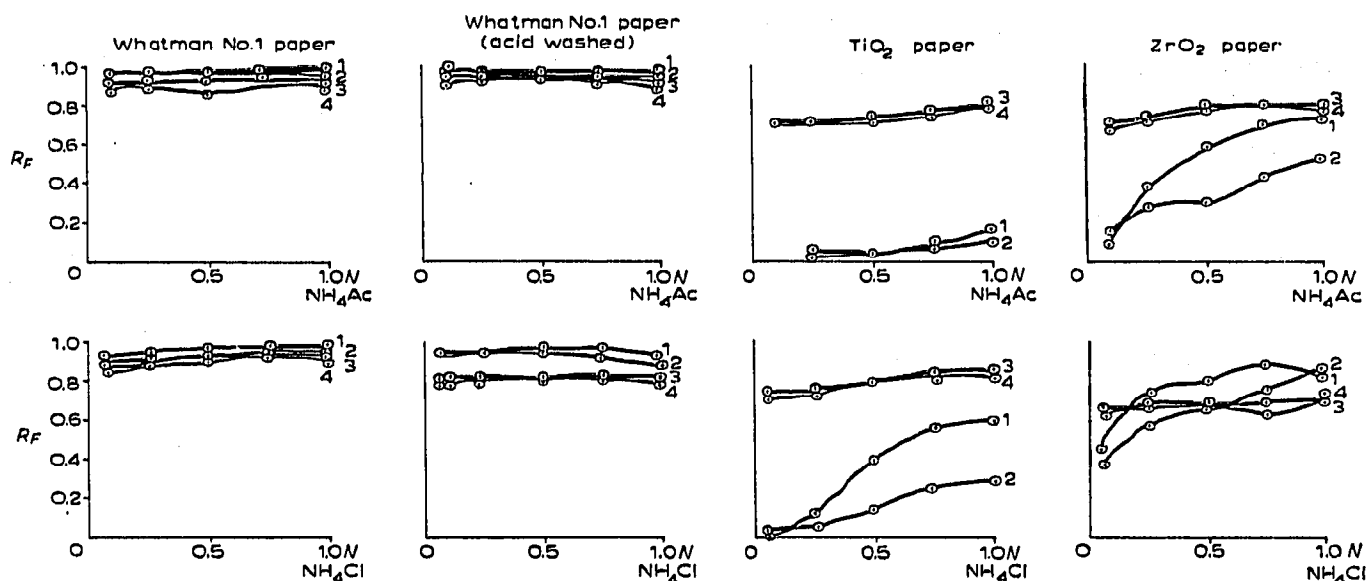


Fig. 5. R_F values of some Co(III) complexes on cellulose and impregnated papers with ammonium acetate and ammonium chloride as developers. 1 = $[\text{Co}(\text{en})_3]\text{Cl}_3$; 2 = $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$; 3 = *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$; 4 = *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.

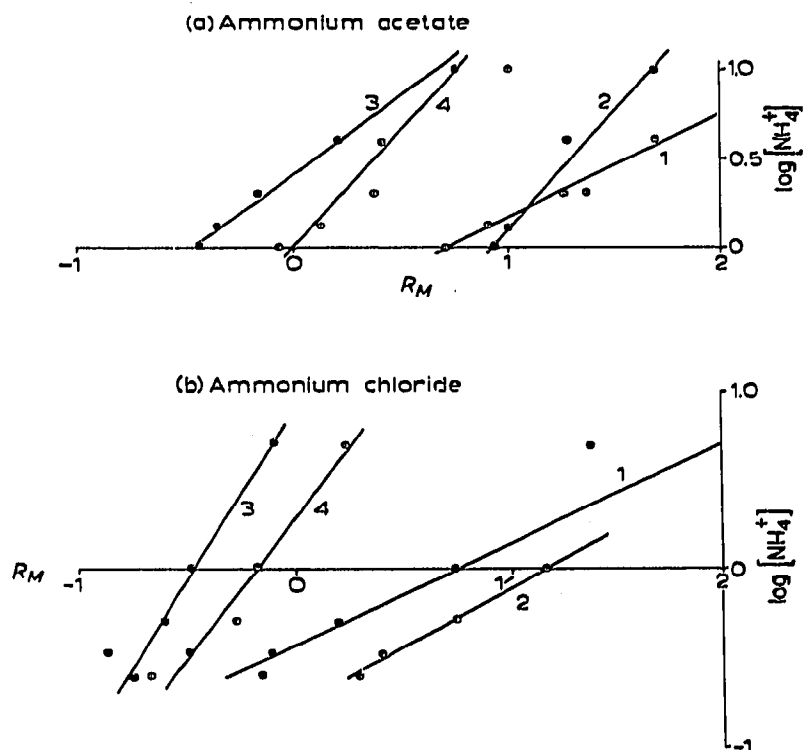


Fig. 6. R_M - $\log(\text{anion})$ plots for the movement of Co(III) complexes on TiO_2 and ZrO_2 papers. (a) Developed with ammonium acetate. 1 = $[\text{Co}(\text{en})_3]^{3+}$ on TiO_2 paper; 2 = $[\text{Co}(\text{NH}_3)_6]^{3+}$ on TiO_2 paper; 3 = $[\text{Co}(\text{en})_3]^{3+}$ on ZrO_2 paper; 4 = $[\text{Co}(\text{NH}_3)_6]^{3+}$ on ZrO_2 paper. (b) Developed with ammonium chloride. 1 = $[\text{Co}(\text{en})_3]^{3+}$ on TiO_2 paper; 2 = $[\text{Co}(\text{NH}_3)_6]^{3+}$ on TiO_2 paper; 3 = $[\text{Co}(\text{en})_3]^{3+}$ on ZrO_2 paper; 4 = $[\text{Co}(\text{NH}_3)_6]^{3+}$ on ZrO_2 paper.

alumina⁷, and also on ThO_2 and ZrO_2 ⁸. To sum up, in neutral solutions both hydrolytic adsorption and actual cation exchange occurs. It thus seems that the strong retention of U(VI) discussed in section (iii) is most likely to be due to hydrolytic adsorption and perhaps other factors.

(v) *The movement of some anions in various electrolytes*

Again the choice of anions was governed by detectability rather than by other criteria, and thus ferrocyanide, ferricyanide, chromate and thiocyanate were first examined as shown in Fig. 7. In both KCl and Na_2SO_4 , chromate adsorbs more strongly with the increase in electrolyte concentration, while the other anions are relatively unaffected. The colour of the ferrocyanide spot during the development is worthy of discussion. On the ferric hydroxide paper it moves as a blue spot and on

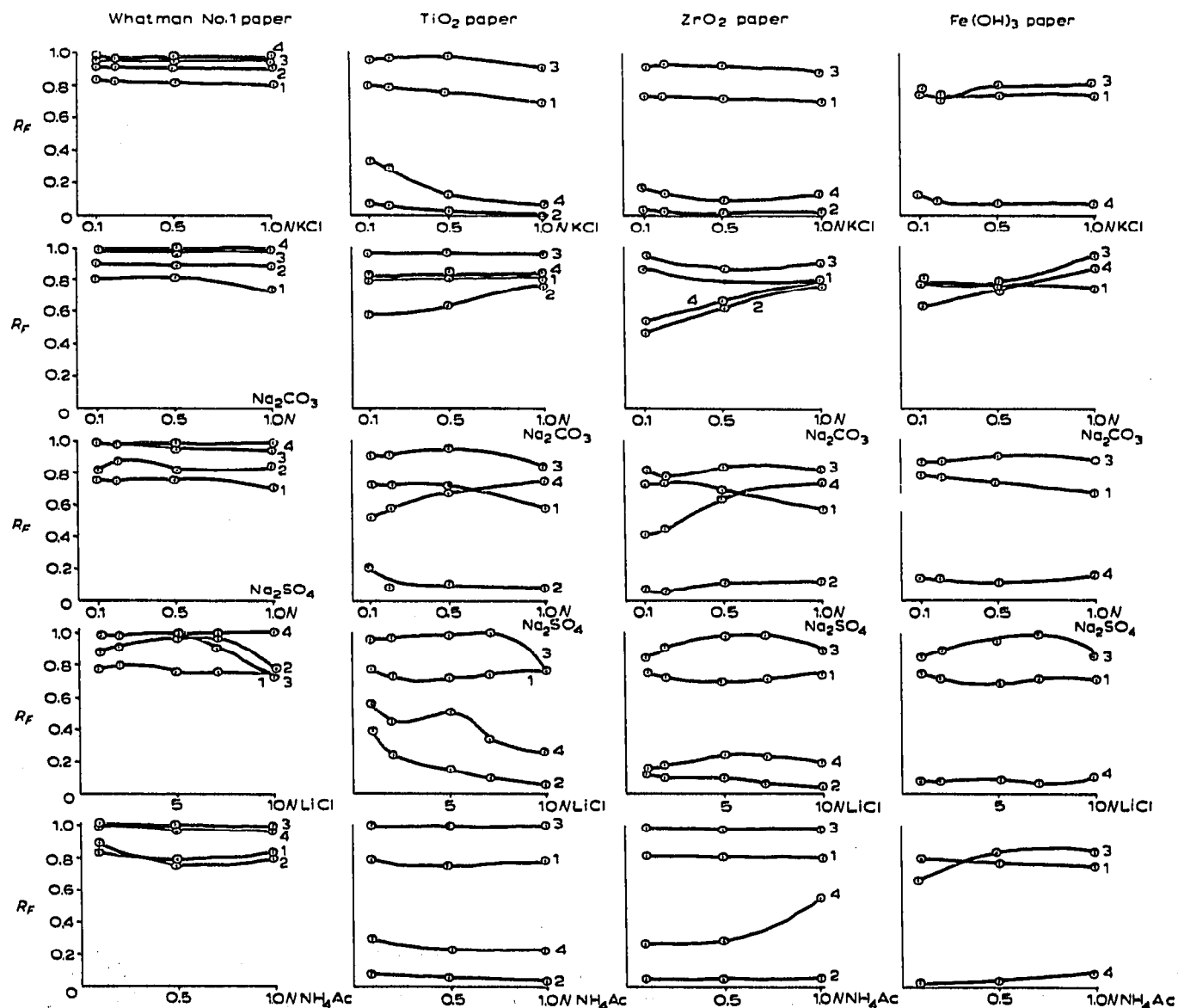


Fig. 7. The movement of ferrocyanide, ferricyanide, chromate and thiocyanate on various hydrous oxide papers developed with KCl, Na_2CO_3 , Na_2SO_4 , LiCl and ammonium acetate. 1 = CNS^- ; 2 = CrO_4^{2-} ; 3 = Fe(CN)_6^{3-} ; 4 = Fe(CN)_6^{4-} .

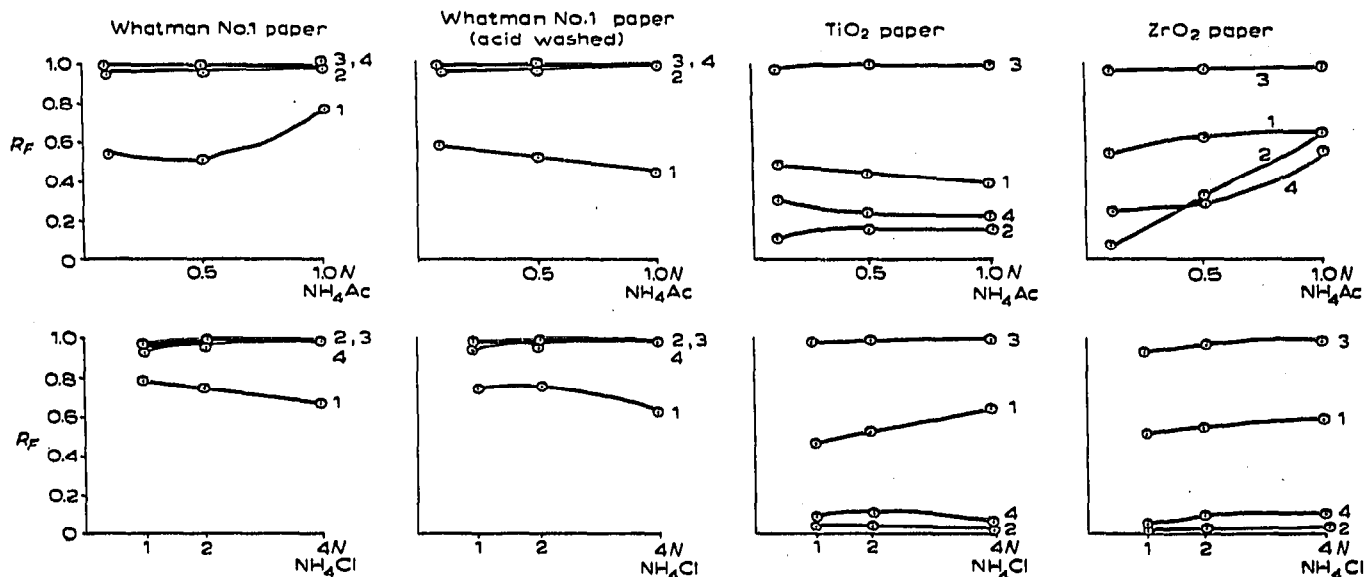


Fig. 8. The movement of potassium ferrocyanide, potassium ferricyanide, $\text{Na}_2\text{Fe}[\text{NH}_3(\text{CN})_5]$ and Reinecke's salt, $\text{NH}_4[\text{Cr}^{\text{III}}(\text{NH}_3)_2(\text{CNS})_4]$ on various hydrous oxide papers with ammonium acetate and ammonium chloride as developers. 1 = $[\text{Cr}^{\text{III}}(\text{NH}_3)_2(\text{CNS})_4]^-$; 2 = $\text{Fe}[\text{NH}_3(\text{CN})_5]^{2-}$; 3 = $\text{Fe}(\text{CN})_6^{3-}$; 4 = $\text{Fe}(\text{CN})_6^{4-}$.

the titanium hydroxide as a yellow-brown spot. The combination of movement and colour would suggest that reversible precipitation occurs on the surface of the precipitate.

In sodium carbonate there is desorption with increase of the concentration for all ions and this is no doubt due to the decrease of the apparent capacity.

The study of some other anionic complexes and also ferro- and ferricyanide with ammonium acetate and ammonium chloride (Fig. 8) again gives no conclusive evidence for a desorption which follows the law of mass action irrespective of the valency of the anion.

In the literature so far anion exchange on hydrous oxide has only been investigated in detail for the equilibrium nitrate-bromide and -chloride and not for polyvalent anions, although the extremely high affinity of CrO_4^{2-} for hydrous oxides had been pointed out⁶.

From our results it appears that "anion exchange" seems to be rather the exception on hydrous oxides and the adsorption would be best considered for some anions as a reversible precipitation.

SUMMARY

A study with neutral electrolytes and papers impregnated with hydrous oxides has shown that U(VI) is very strongly adsorbed irrespective of the anions present and is not desorbed even in 10 N LiCl. Some cations examined show that there is usually a desorption with increasing electrolyte concentration unless hydrolysis interferes and thus an ion exchange mechanism may be considered as most likely. With anions, the adsorption increases with the electrolyte concentration in some instances and the colour of the moving ferrocyanide spot on $\text{Fe}(\text{OH})_3$ or titanium oxide

paper would suggest that for polyvalent ions some type of reversible compound formation can occur. If anion exchange takes place it is certainly accompanied by other reactions in most of the anions studied.

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