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ION-EXCHANGE PAPER CHROMATOGRAPHY OF INORGANIC IONS

XIX. FURTHER RESULTS ON THE "PERCHLORATE EFFECT"

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SUMMARY

R_F values of numerous metal ions are given for HCl + 1 N HClO₄ mixtures on SB-2 resin paper and for HNO₃ + 1 N HClO₄ on SB-2 and SA-2 papers. Some partition systems formed by impregnating the paper with salt solution and developing with organic solvents have been examined for the presence of a "perchlorate effect", but none was observed.

INTRODUCTION

In our previous paper¹ on the "perchlorate effect", we were able to show that this effect is not limited to anion exchange, that other anions can also exhibit the effect and that no "perchlorate effect" could be noted in partition systems although it was found to be very strong in both adsorption and ion-exchange systems. We also emphasized the analytical possibilities of the use of the "perchlorate effect". With this in mind, we wanted to extend the study to a survey of many metal ions in some systems that are of analytical interest.

THE SYSTEM HCl + 1 N HClO₄ ON SB-2 ANION-EXCHANGE RESIN PAPER

The behaviour of numerous metal ions on SB-2 paper developed with HCl solutions (1-10 N) had been reported some years ago². The present study was carried out to determine how the R_F values would change when the metal ions were developed on the chloride form of the resin paper with various concentrations of HCl containing 1 N HClO₄.

Fig. 1 shows the R_F values both with HCl alone and with HCl + 1 N HClO₄ as developing solvent.

In order to interpret these results, one has to consider first the "HClO₄ front" that is formed when solutions of HCl + HClO₄ move over the chloride form of the SB-2 paper. This is shown in the upper left-hand corner of Fig. 1. It then becomes clear that a number of ions move on the "perchlorate front", *e.g.*, ReO₄⁻, In(III), Cu(II) at higher HCl concentrations, and Pd(II). Others are desorbed by the presence of perchlorate but move below the perchlorate front, *e.g.*, Hg(II), Bi(III) and Sb(III).

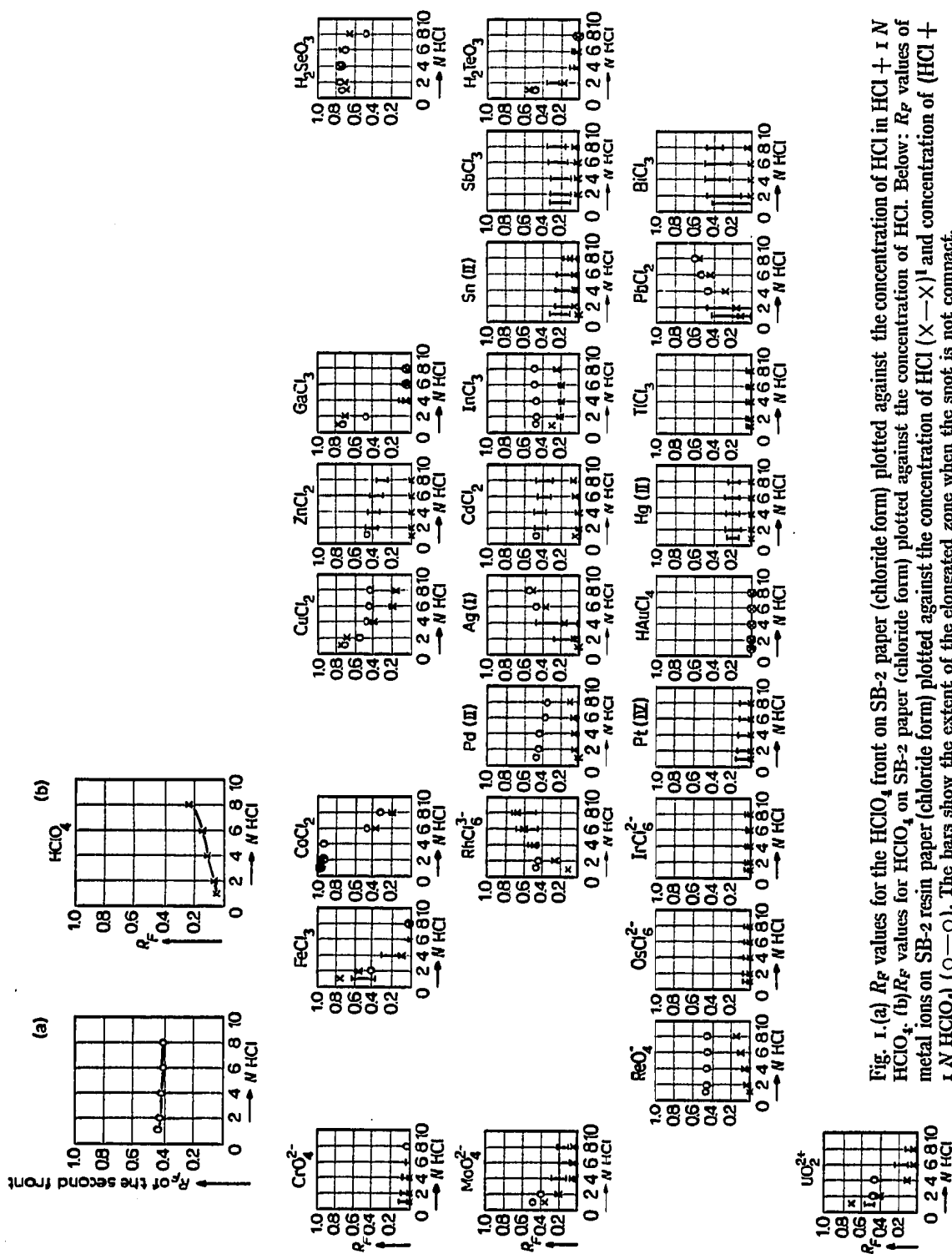


Fig. 1. (a) R_F values for the $HClO_4$ front on SB-2 paper (chloride form) plotted against the concentration of HCl in HCl + 1 N $HClO_4$. (b) R_F values for $HClO_4$ on SB-2 paper (chloride form) plotted against the concentration of HCl. Below: R_F values of metal ions on SB-2 resin paper (chloride form) plotted against the concentration of HCl (×—×)¹ and concentration of (HCl + 1 N $HClO_4$) (○—○). The bars show the extent of the elongated zone when the spot is not compact.

One feature of these metal ions is that they form elongated trails rather than compact spots. Finally, a large number of metal ions are not desorbed at all, such as Au(III), Ga(III) at higher HCl concentrations, and Fe(III) at HCl concentrations of 6 and 8 *N*. Very little desorption is noted with Os(IV), Ir(IV), Pt(IV) and Tl(III).

Some hints as to the reason for this behaviour are obtained if one compares the results with the K_d values published by KRAUS AND NELSON³. As a general rule, the very strongly adsorbed metal ions (K_d values above 10^4) are not desorbed by perchlorate while those with lower K_d values show varying degrees of desorption. This rule has, however, numerous exceptions. For example, Os(IV), Ir(IV) and Pt(IV) have much lower K_d values than Hg(II), but Hg(II) is much more desorbed by perchlorate.

Perchlorate does not seem to influence the complexing equilibria between chloride and the metal ions in such instances as Fe(III), Co(II) and Ga(III), for which reversible equilibria exist, and the curves of the R_F values are not noticeably different in the presence and absence of perchlorate.

The analytical advantages of such HCl-HClO₄ systems seem to reside mainly in the better separation of the metals that are unaffected by HClO₄, *i.e.*, those very strongly adsorbed from those which are desorbed. However, the formation of comets may cause trouble in some instances.

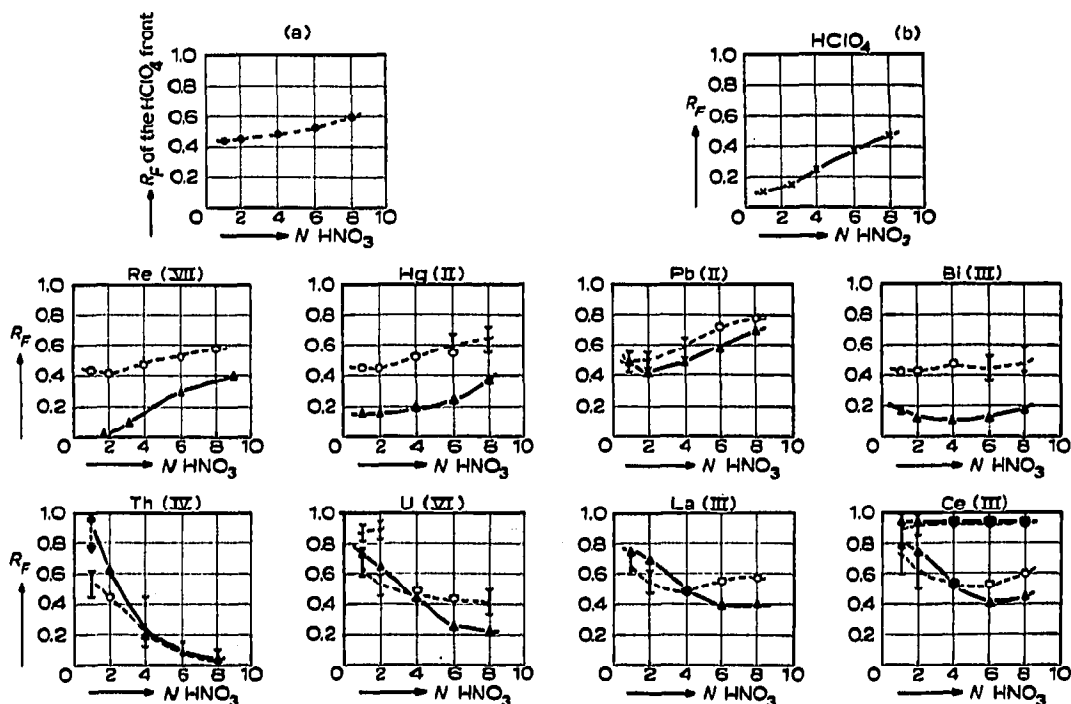


Fig. 2. (a) R_F values of the HClO₄ front in the system SB-2 resin paper (nitrate form) - aqueous solution of the HNO₃ + 1 N HClO₄. (b) R_F values of HClO₄ in the system SB-2 resin paper (nitrate form) - aqueous solution of HNO₃. Below: R_F values of metal ions in the system SB-2 resin paper (nitrate form) - aqueous solution of HNO₃ (▲—▲) and of HNO₃ + 1 N HClO₄ (○----○).

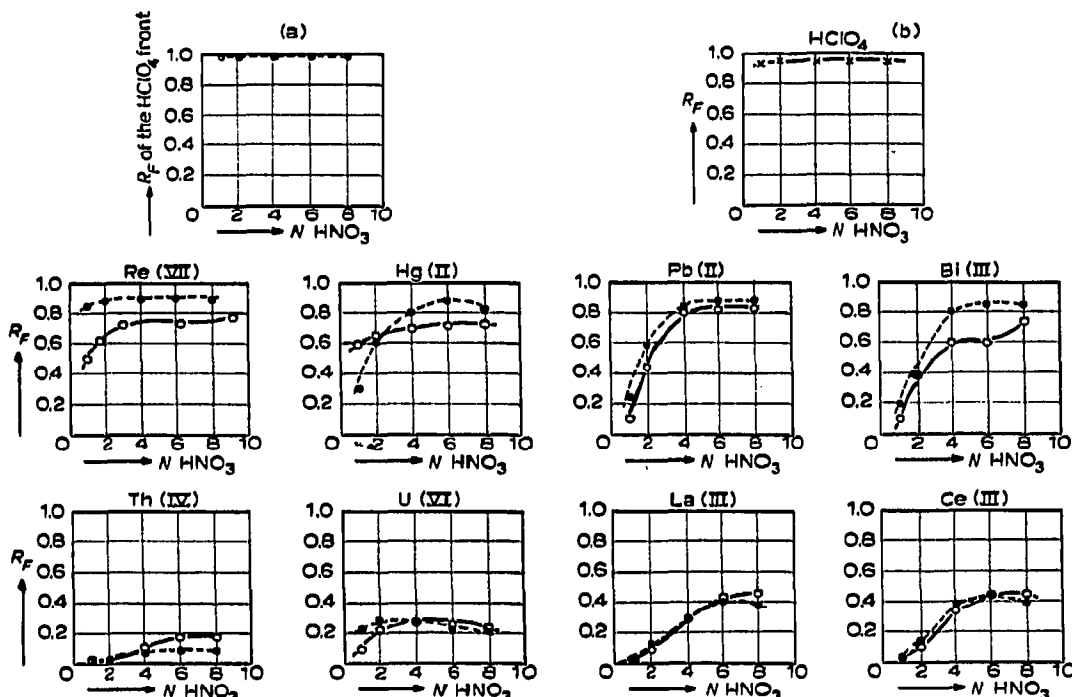


Fig. 3. (a) R_F values of the HClO_4 front on SA-2 paper (nitrate form) plotted against the concentration of HNO_3 in $\text{HNO}_3 + 1 N \text{HClO}_4$. (b) R_F values of HClO_4 on SA-2 paper (nitrate form) plotted against the concentration of HNO_3 . Below: R_F values of metal ions on SA-2 paper (nitrate form) plotted against the concentration of HNO_3 (O—O) and concentration of $\text{HNO}_3 + 1 N \text{HClO}_4$ (●-----●).

THE SYSTEM $\text{HNO}_3 + 1 N \text{HClO}_4$ ON SB-2 ANION-EXCHANGE RESIN PAPER

Fig. 2 shows the R_F values of some ions on the nitrate form of SB-2 paper developed with HNO_3 and with $\text{HNO}_3 + 1 N \text{HClO}_4$.

In the upper left-hand corner, the R_F value of the perchlorate front is shown and it is evident that ReO_4^- , Hg(II) , Pb(II) and Bi(III) move more or less on this front in HNO_3 - HClO_4 mixtures.

Metal ions that form reversible complexes with nitrate, such as Th(IV) , UO_2^{2+} , La(III) and Ce(III) , show only a small or no "perchlorate effect" at higher concentrations of HNO_3 .

The system therefore shows many characteristics of the HCl - HClO_4 system. Our interest in it was due to the fact that the nitrate ion also shows a "perchlorate effect". The results obtained here seem to indicate that perchlorate, having a much stronger effect, can also desorb ions from HNO_3 solutions.

THE SYSTEM $\text{HNO}_3 + 1 N \text{HClO}_4$ ON SA-2 CATION-EXCHANGE PAPER

As shown in Fig. 3, the perchlorate front is very close to the liquid front on the sulphonic resin paper. There is a small perchlorate effect with ReO_4^- , Hg(II) , Pb(II) and Bi(III) , but none with Th(IV) , U(VI) , La(III) and Ce(III) .

SOME PARTITION SYSTEMS

One of us (R.M.) had studied partition systems with paper impregnated with complexing salts, such as NH_4CNS . We had examined previously only the system butanol-HCl-HClO₄-water and we therefore wanted to try also some systems with impregnated papers. As shown in Fig. 4, there is no measurable "perchlorate effect" in the systems chosen and we conclude again that so far no "perchlorate effect" could be observed in partition systems.

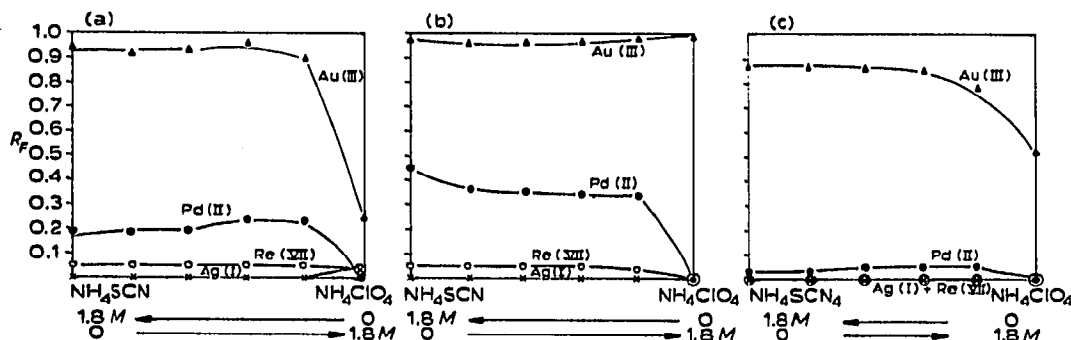


Fig. 4. (a) R_F values of Au(III), Pd(II), ReO_4^- and Ag(I) on Whatman No. 1 paper impregnated with mixtures of NH_4CNS and NH_4ClO_4 and developed with octanol. (b) R_F values of the same ions as in (a) on paper impregnated as in (a) and developed with methyl isobutyl ketone. (c) R_F values of the same ions as in (a) on paper impregnated as in (a) and developed with butyl acetate.

DISCUSSION

All of the results obtained in this work seem to indicate that the "perchlorate effect" is due to competition between anions and perchlorate for adsorption or ion-exchange sites. When the adsorption of the anion is much stronger than that of perchlorate, no desorption will occur. When the adsorption is weak or of the same order as that of perchlorate, the anion will be desorbed. This kind of competition is obviously not limited to perchlorate and can be exhibited by all strongly adsorbed anions. Perchlorate seems to give the strongest effect so far noted. The formation of elongated zones in many instances is not clear. It may be due to a perchlorate gradient being formed along the chromatogram or to adsorption-desorption equilibria that are slower than the speed of the development. We think that the former is more probable than the latter.

REFERENCES

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- 4 L. OSSICINI, *J. Chromatogr.*, **17** (1965) 625.