

## CHROMATOGRAPHY ON ION EXCHANGE PAPERS

## XIX. ION EXCHANGE OF METAL IONS IN THIOCYANIC ACID\*

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## INTRODUCTION

Ion exchange data are already available for metal ions in systems in which various complexing acids and salts, including thiocyanates, are used (*e.g.* refs. 1-4). However, usually mixtures of a thiocyanate with HCl were studied and to our knowledge no information concerning aqueous HCNS is available.

The differences between the potassium (or ammonium) thiocyanate-HCl system and pure HCNS can be readily envisaged. In the former system, the salting-out effect of the cation as well as the complexing effect of the chloride ion can exert some influence on some of the metal ions, while this is not the case in pure HCNS. The reason for the use of the thiocyanate-HCl system in preference to HCNS alone probably lies in the fact that HCNS is not commercially available. It can, however, be prepared in solutions up to 2 N by simply passing KCNS through a column of the hydrogen form of a cation exchanger.

In this paper we shall present a survey of the ion exchange behaviour of metal ions on several ion exchange papers employing aqueous HCNS as solvent.

## EXPERIMENTAL AND RESULTS

*(a) Preparation of HCNS solutions*

A column (diam. 1.7 cm and length 35 cm) was filled with 70 g of Dowex 50W X 8 (100-200 mesh) and converted to the hydrogen form by washing with HCl and distilled water. 2 N KCNS was then allowed to run through this column. The first column volume was discarded and the following 40 ml collected and a sample titrated with AgNO<sub>3</sub> and NaOH. Usually the difference between the CNS<sup>-</sup> and the H<sup>+</sup> was only 1-2% and the normality of the HCNS approximately 1.8. This solution was then diluted with distilled water to yield 0.5 N, 1.0 N and 1.8 N HCNS.

*(b) Preparation of the ion exchange papers*

Whatman No. 1 paper was washed with HCl and water. The cationic resin paper, Amberlite SA-2, was converted to the hydrogen form by washing with HCl and distilled water. The anionic papers, resin paper Amberlite SB-2, Macherey

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Nagel & Co. quaternary ammonium cellulose paper, Whatman DEAE (DE-20) paper and aminoethylcellulose (AE-30) papers were washed with HCl and water and then converted to the thiocyanate form by immersing twice for 30 min in 1 *N* KCNS and then washing free of excess KCNS with distilled water.

(c) *Preparation of the solutions of the metal ions*

The chlorides or oxides of the metal ions were dissolved in HCNS of the same concentration as was used as eluant and the solutions chromatographed as soon after preparation as possible.

Except for the readily oxidisable or reducible ions such as Sn(II) or Fe(III) solutions in HCNS were stable up to 48 h (see Section (e)).

(d) *The movements of HCNS on the anion exchange papers*

It has already been noted previously<sup>6</sup> that  $CNS^-$  adsorbs very strongly on anion exchange papers and it was thus necessary to measure the distribution of HCNS along the paper after development.

Whatman No. 1 paper, Macherey Nagel anion exchange cellulose paper and Amberlite SB-2 paper (the latter two in the  $CNS^-$  form) were developed for 16 cm with 1.8 *N* HCNS, cut while still wet into 2 cm transverse sections and each section was placed in 50 ml of water and titrated with *N*/10 silver nitrate. Fig. 1 shows the

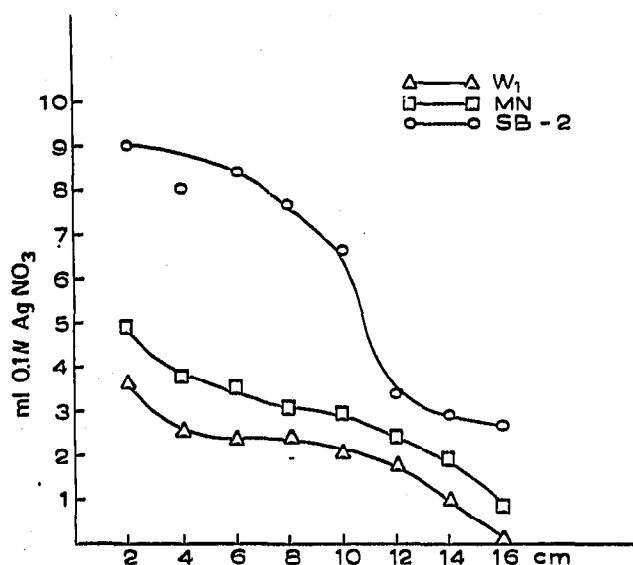


Fig. 1. Movement of 1.8 *N* HCNS on various papers during development. Ordinates: arbitrary units showing HCNS content, abscissae: length of development of the paper. W1 = Whatman No. 1 paper; MN = anionic cellulose exchange paper Macherey Nagel & Co.; SB-2 = anion resin paper SB-2.

number of ml  $AgNO_3$  consumed (*i.e.* the relative  $CNS^-$  content) plotted against the length of the chromatogram. The curves are almost identical with those usually encountered with other acids<sup>6</sup>, with a zone of about 4 cm near the liquid front which is deficient in  $CNS^-$  and an increase in  $CNS^-$  near the eluant level. The latter is due to a higher content of eluant rather than a higher HCNS concentration. It can

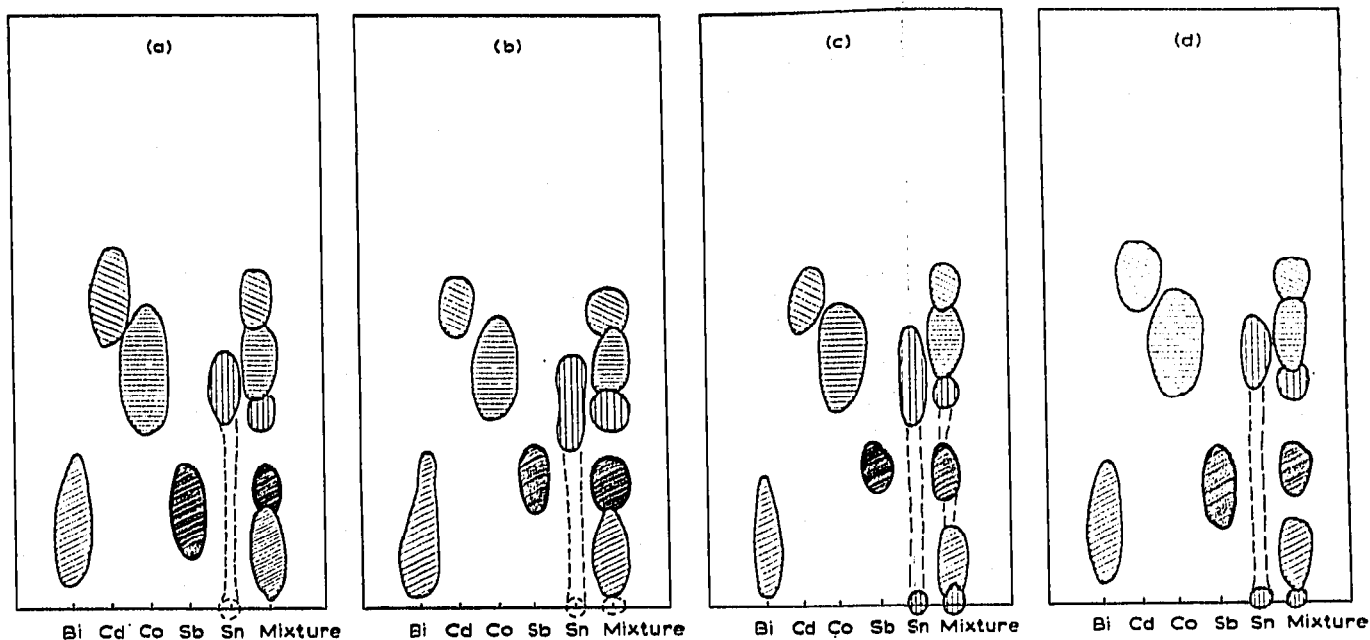


Fig. 2. Movement of several metal ions on Whatman DEAE cellulose paper (DE-20) developed with 1.8 N HCNS. (a) Eluant was aged 2 h and the solutions applied were freshly prepared. (b) Eluant was aged 24 h and the solutions applied were freshly prepared. (c) Eluant was aged 72 h and the solutions were aged 48 h. (d) Eluant and solutions were aged 24 h. The metals chromatographed on each chromatogram (from left to right) are: Bi(III), Cd(II), Co(II), Sb(III), Sn(II), and a mixture of all five.

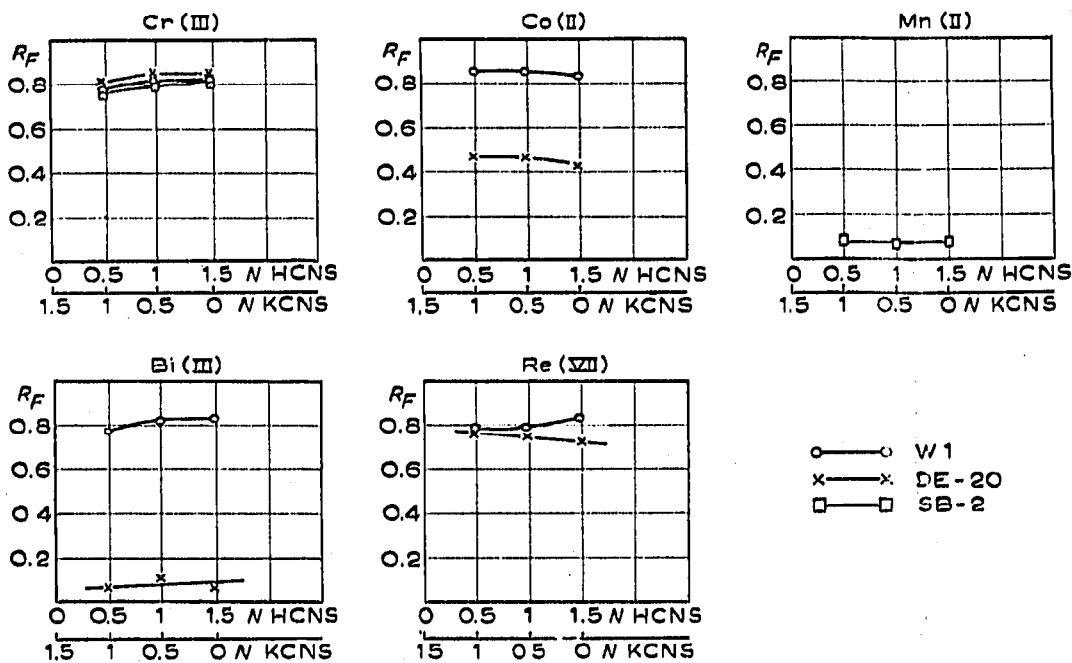


Fig. 3. The variation of the  $R_F$  value when KCNS replaces partially the HCNS in the eluant. The mixtures investigated were: 0.5 N HCNS + 1.0 N KCNS; 1.0 N HCNS + 0.5 N KCNS; and 1.5 N HCNS. W1 = Whatman No. 1 paper; DE-20 = Whatman DEAE paper (DE-20); SB-2 = anion resin paper SB-2.

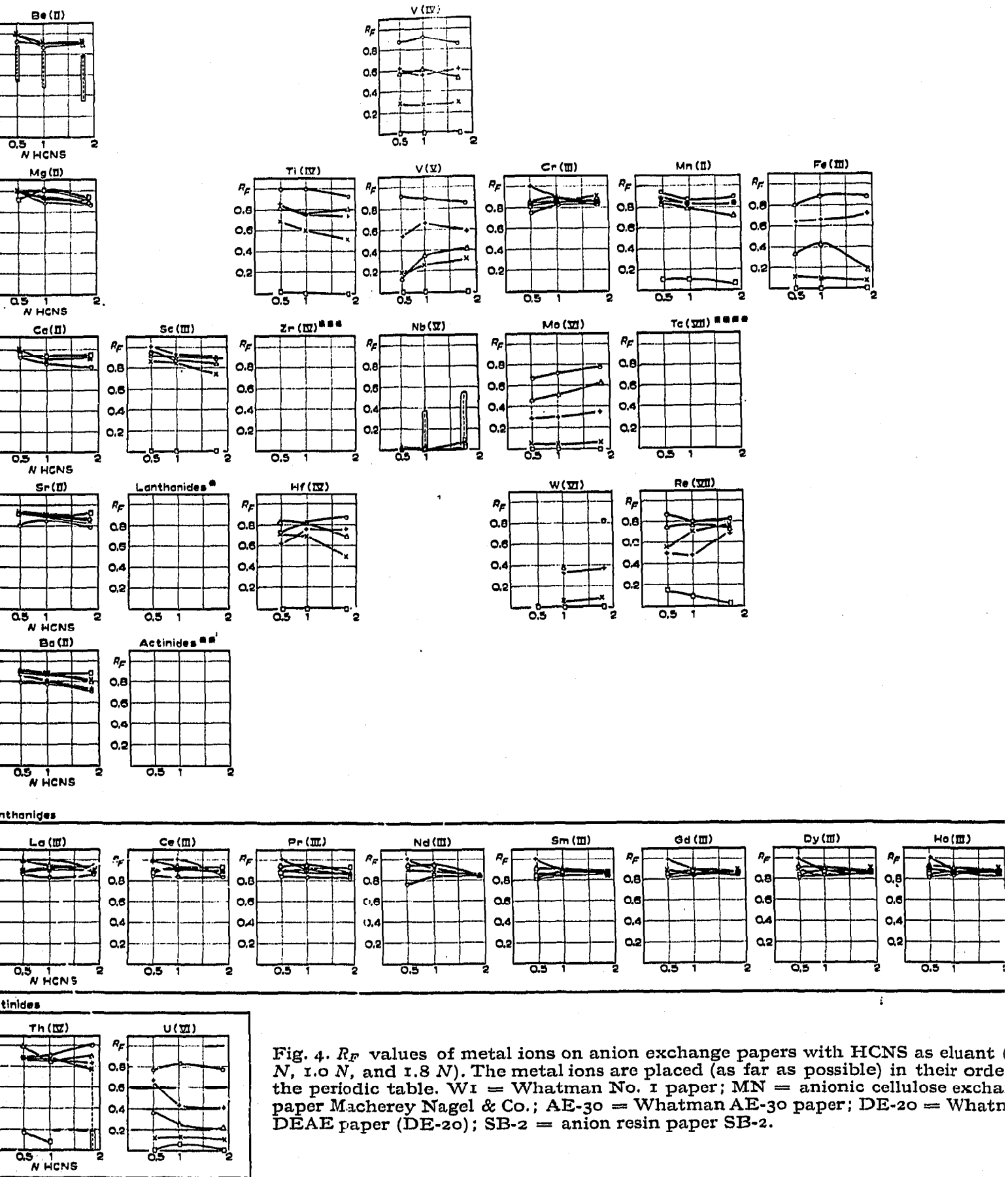
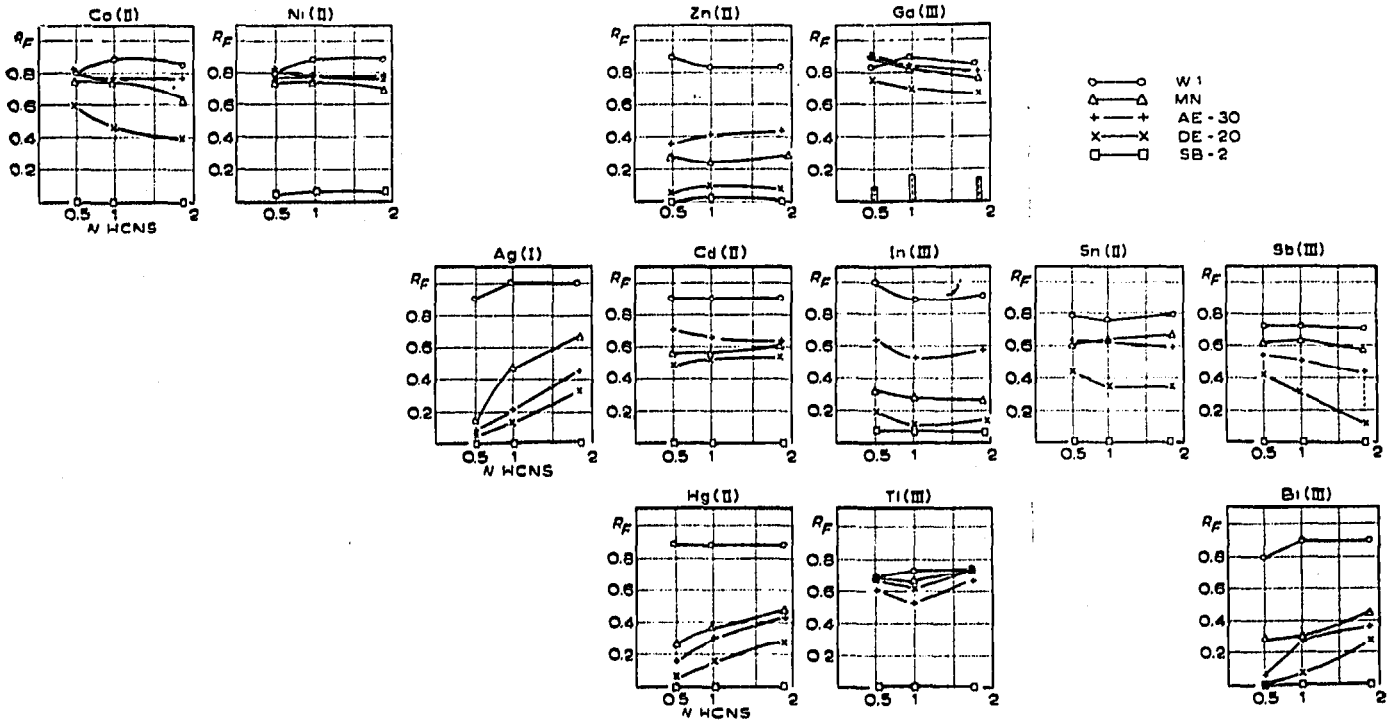
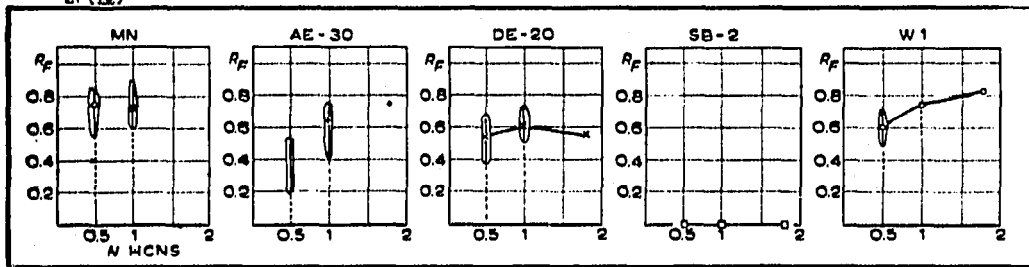


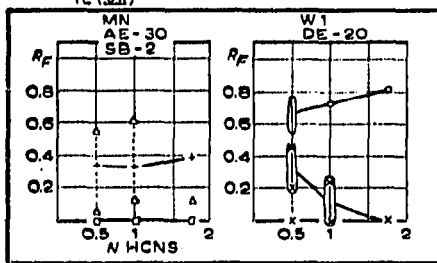
Fig. 4.  $R_F$  values of metal ions on anion exchange papers with HCNS as eluant (0.5 N, 1.0 N, and 1.8 N). The metal ions are placed (as far as possible) in their order in the periodic table. W1 = Whatman No. 1 paper; MN = anionic cellulose exchange paper Macherey Nagel & Co.; AE-30 = Whatman AE-30 paper; DE-20 = Whatman DEAE paper (DE-20); SB-2 = anion resin paper SB-2.



●●● Zr(IV)



●●●● Tc(VII)



thus be assumed that the metal ions, except those with very high  $R_F$  values, move in an eluant having the same concentration as the bulk eluant.

(e) *The stability of HCNS solutions*

It is well known that HCNS is not very stable in aqueous solutions, oxidising in air to  $(\text{CNS})_2$  or yielding polymers. Although these reactions are rather slow in cold dilute aqueous solutions we wanted to establish whether they would have an effect on the results obtained.

A number of metal ions was chromatographed on DE-20 paper with 1.8 N HCNS which had stood at room temperature for 2, 24 and 72 h. The solutions of the metal ions, prepared by dissolving the chlorides in fresh 1.8 N HCNS, were also allowed to stand for 24 h and 48 h, respectively. Fig. 2 shows that there are no differences in the  $R_F$  values for any of the metal ions tested, only Sn(II) yields variable amounts of a second spot (presumably Sn(IV) at  $R_F = 0$ ) and different amounts of a trail to the main spot.

(f) *The effect of the presence of  $K^+$  in the eluant*

The solutions of HCNS prepared by ion exchange did sometimes contain several % of  $K^+$  which had passed through the column. Although this amount was always below 10 % we wanted to investigate the possible effect of the presence of potassium ions on the  $R_F$  values of the metal ions chromatographed.

Fig. 3 shows the  $R_F$  values of several metal ions on Whatman No. 1, DE-20 and SB-2 papers with eluants where the  $\text{CNS}^-$  concentration was maintained at 1.5 N while the  $K^+$  ions were 1, 0.5 and 0 N and the  $H^+$  ions 0.5, 1.0 and 1.5 N, respectively. Even with  $\frac{2}{3} K^+$  and only  $\frac{1}{3} H^+$  the  $R_F$  values were little different from those in pure 1.5 N HCNS.

(g) *The adsorption of metal ions on anion exchange papers*

The  $R_F$  values of metal ions with 0.5, 1.0 and (approx.) 1.8 N HCNS on anion exchange resin paper SB-2, the cellulose anion exchangers, Macherey Nagel (quaternary ammonium) and Whatman AE-30 and DE-20 as well as on the pure cellulose paper Whatman No. 1 are shown in Fig. 4.

The metal ions are placed in the order of the periodic table as far as possible. Zirconium yielded comets on the cellulose exchangers and is shown separately in the figure.

$\text{TcO}_4^-$  was reduced to lower valencies during chromatography and will be discussed in Section (i). Not all the lanthanides were examined as no adsorption could be observed in any of those tested.

(h) *The adsorption on cation exchangers*

A large number of metal ions was chromatographed on the sulphonic resin paper Amberlite SA-2 with 0.5 N; 1.0 N and 1.8 N HCNS.

Numerous metals yielded long comets and the results are best illustrated graphically without giving  $R_F$  values as shown in Fig. 5.

$\text{Cr}(\text{H}_2\text{O})_6^{3+}$  yields a strong fast moving spot and a weaker slow spot.

There are no  $R_F$  differences among the lanthanides. The alkaline earths show some differences, especially in 1.8 N HCNS. The alkaline earths were also studied on

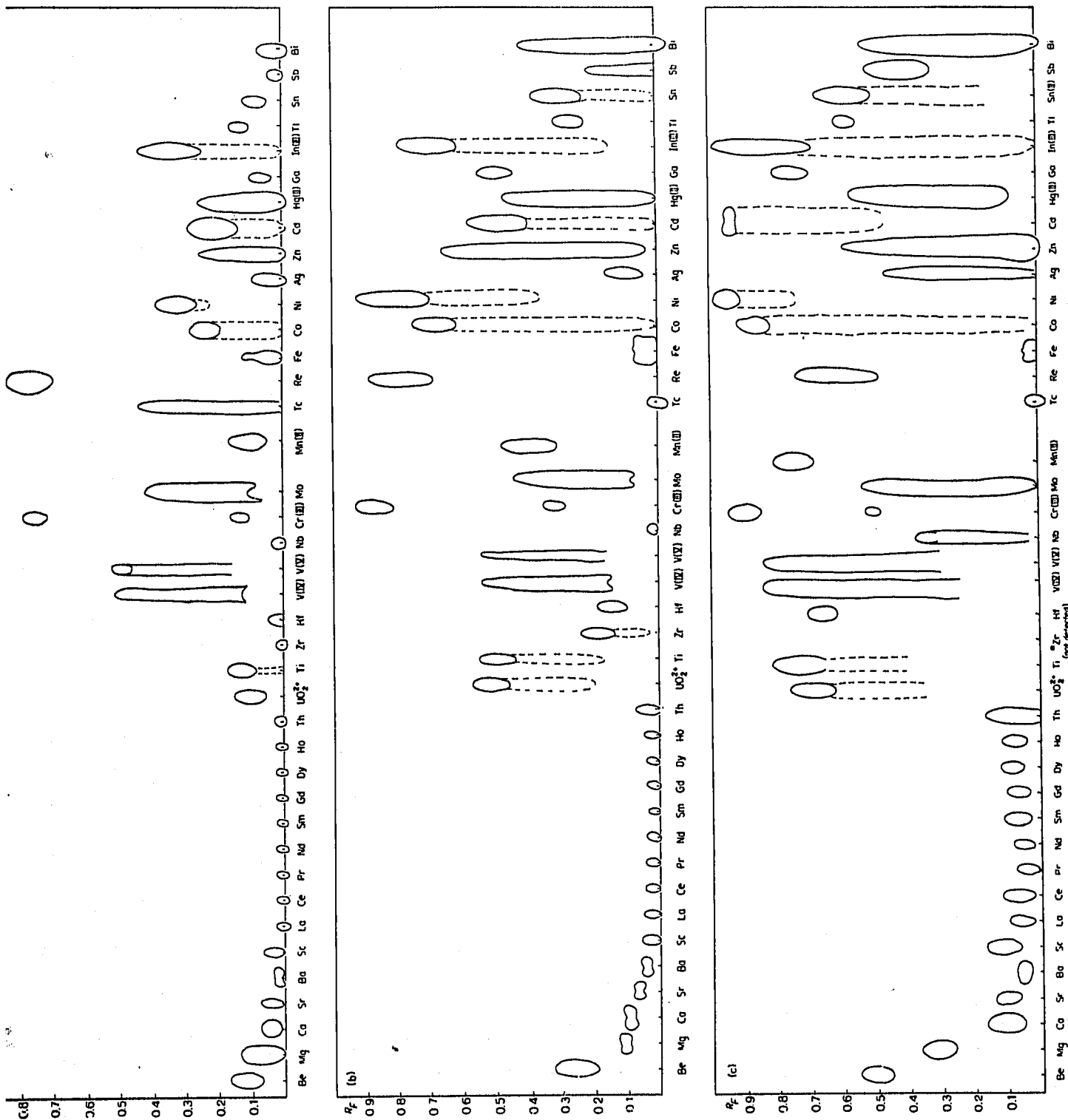


Fig. 5. The movement of metal ions on Amberlite sulphonated resin paper SA-2 with (a) 0.5 N HCNS, (b) 1.0 N HCNS, and (c) approx. 1.8 N HCNS. The shape of the spots is indicated rather than R<sub>F</sub> values as many metals yield long comets.

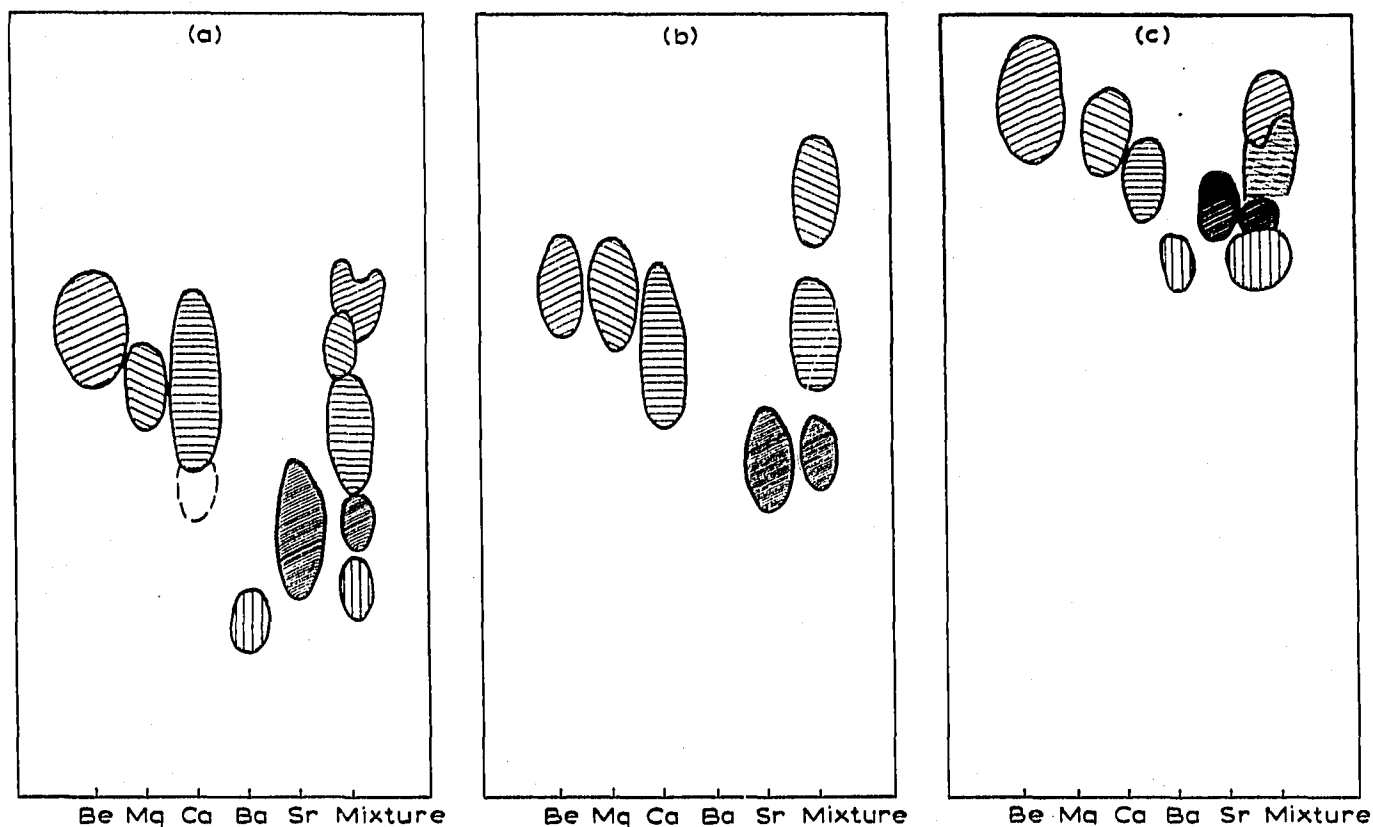


Fig. 6. The movement of the alkaline earth ions on Macherey Nagel sulphonic cellulose paper with (a) 0.5 *N* HCNS, (b) 1.0 *N* HCNS, and (c) 1.8 *N* HCNS. On each chromatogram from left to right Be, Mg, Ca, Ba, Sr and a mixture of all five.

Macherey Nagel sulphonic acid cellulose paper ( $H^+$  form). As shown in Fig. 6 the  $R_F$  values change somewhat with the loading and the presence of other alkaline earths. Separations of Ba–Sr–Ca are readily obtained in 0.5 *N* and 1 *N* HCNS while all the ions move too quickly in 1.8 *N* HCNS.

(i) *The behaviour of  $TcO_4^-$  in HCNS*

The colourless  $TcO_4^-$  ion when added to HCNS yields intensely coloured solutions which change their colour with time.

Fig. 7 shows the number of spots and their colours in chromatograms of aged solutions of  $TcO_4^-$  in HCNS. On Whatman No. 1 paper all species move on or near the liquid front. Good separations are obtained on the cellulose anion exchangers especially on Whatman AE-30 paper while all species are strongly adsorbed on the anionic resin paper SB-2.

DISCUSSION

Aqueous HCNS has been shown to be sufficiently stable for analytical work with ion exchange papers and its preparation seems relatively simple.

With concentrations up to 1.8 *N* of HCNS there is no adsorption of the alkaline earths and lanthanides on anion exchangers. There are some interesting differences between HCNS and HCl or HBr systems such as the adsorption of  $Ni^{2+}$ ,  $Mn^{2+}$ ,



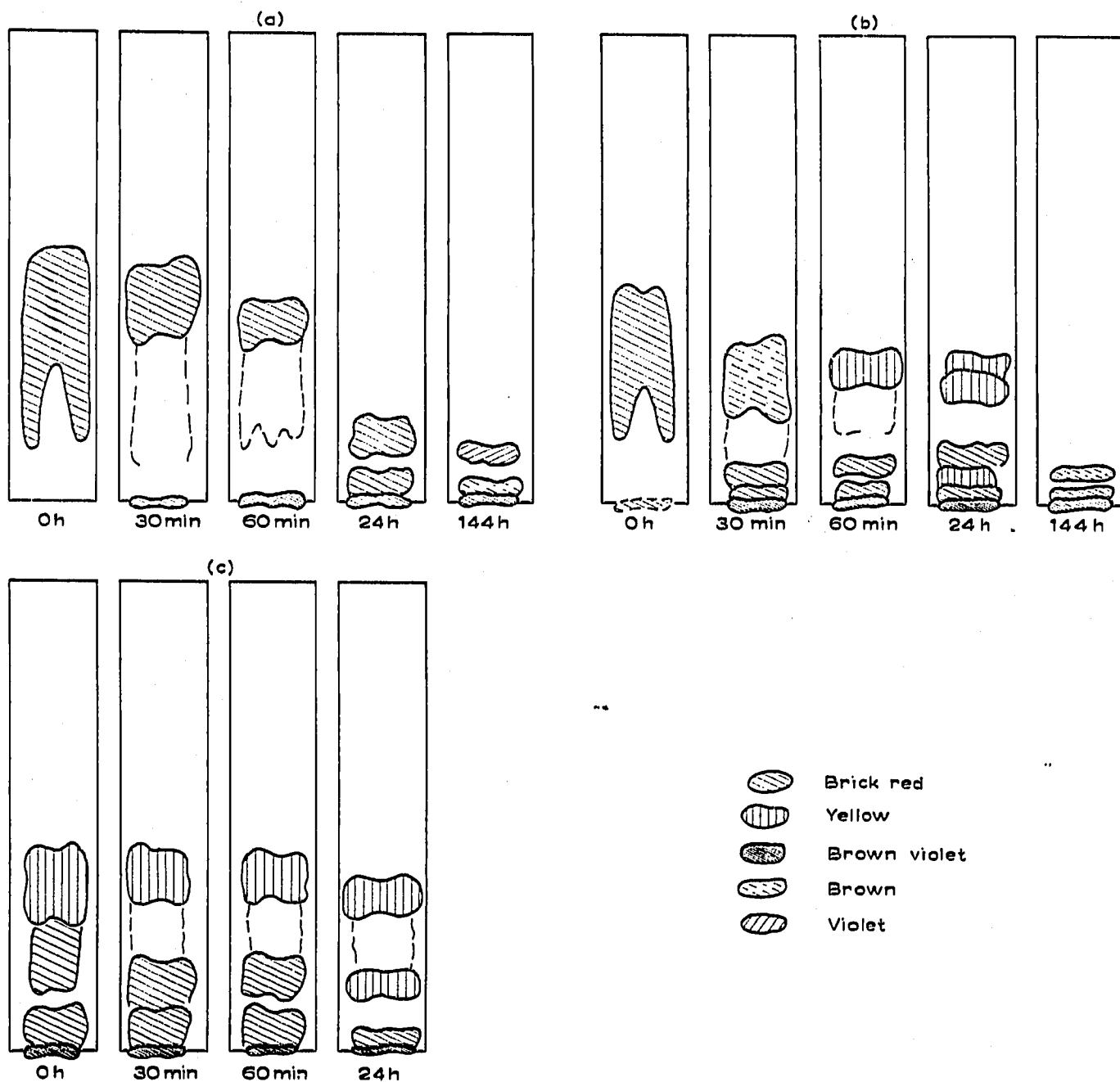


Fig. 7. Typical chromatograms of aged solutions of pertechnetate in HCNS on Whatman AE-30 paper using (a) 0.5 *N*, (b) 1.0 *N*, and (c) 1.8 *N* HCNS as eluant.

Pi(IV) and Th(IV) on the anionic resin papers. Owing to the much higher complexing tendency of HCNS when compared with HCl, many ions are already strongly adsorbed at low concentrations of HCNS while they adsorb only with very high acidities in HCl. This property may be attractive in some radiochemical separations, although the removal of HCNS will then be more difficult than the removal of HCl.

The sequence of adsorption on the various papers is SB-2 (strongest) > DE-20 > MN quaternary > AE-30 > Whatman No. 1 as was earlier found for the HCl and LiCl systems<sup>7</sup>. Exceptions, *e.g.* Ag<sup>+</sup> where this rule is reversed, also exist in the HCNS

system ( $\text{Pb}^{2+}$  could not be chromatographed as it is insoluble in HCNS). There seems to be little application for the cationic resin adsorption. The long comets would indicate preponderance of neutral and weakly charged complexes which adsorb strongly and not quite reversibly on the resin network.

#### SUMMARY

The movement of metal ions on ion exchange papers with aqueous HCNS as eluant was studied. Data with cation and anion exchange papers for about 40 metal ions and three HCNS concentrations (0.5, 1.0 and 1.8 N) are given.

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