enough to permit unequivocal determination of the amino-acid composition of small peptides.

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Chromatography on ion exchange papers

XVI. The adsorption of metal ions on cation exchangers from solutions of sodium perchlorate

The adsorption of metal ions from $HClO_4$ on sulphonic cation exchangers was discussed by NELSON *et al.*[1] and by LEDERER AND SARACINO[2]. No adequate explanation for the increase in adsorption of metal ions in higher concentrations of $HClO_4$ has so far been advanced. NELSON *et al.*[1] pointed out that accurate information for a number of the variables, *e.g.*, electrolyte invasion of the resin, activity coefficients of the metal ions in the supporting electrolyte, was lacking. We have shown[2] that this phenomenon was not confined to sulphonic polystyrene resins but occurred also with cellulose sulphonic exchangers. As no data were available for the behaviour of metal ions in various perchlorates as electrolytes we decided to investigate perchlorates in the hope that the data might shed some light on the problem.

Chromatography was carried out on Amberlite SA-2 resin paper as described previously[2]. The perchlorate solutions used as developing solvent had to contain 1 *N* $HClO_4$ so as to avoid hydrolysis of the metal ions and to avoid the formation of several fronts by demixion during development. Amongst the salts of perchloric acid only the sodium and the barium salt are sufficiently soluble in water to permit comparisons with $HClO_4$ over a wider range of concentrations. Preliminary results with barium perchlorate showed that it changed the equilibria owing to the divalent cation and hence only sodium perchlorate (containing 1 *N* $HClO_4$) could be compared

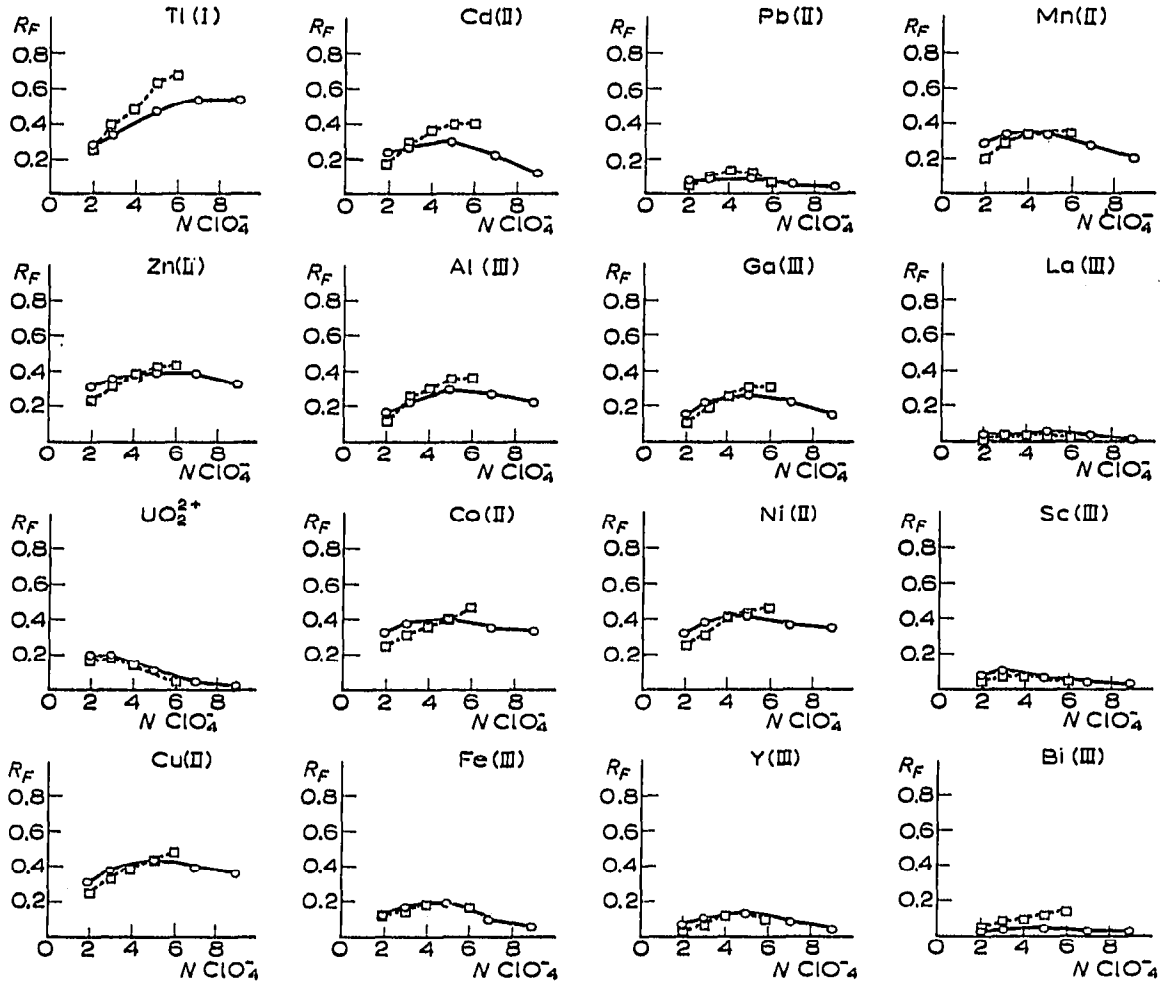

Fig. 1. R_F values of metal ions on sulphonic resin paper Amberlite SA-2 plotted against the concentration of ClO_4^-. ○—○—⊙ = the sodium form of the paper developed with mixtures of $NaClO_4$ with 1 *N* $HClO_4$. □—□—□ = the hydrogen form of the paper developed with $HClO_4$.

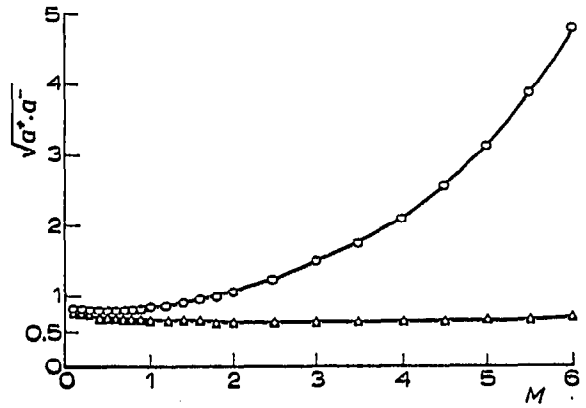

Fig. 2. The activity of perchloric acid and sodium perchlorate plotted against the concentration (values taken from ref. 3). ⊙——○ = $HClO_4$; △—△ = $NaClO_4$.

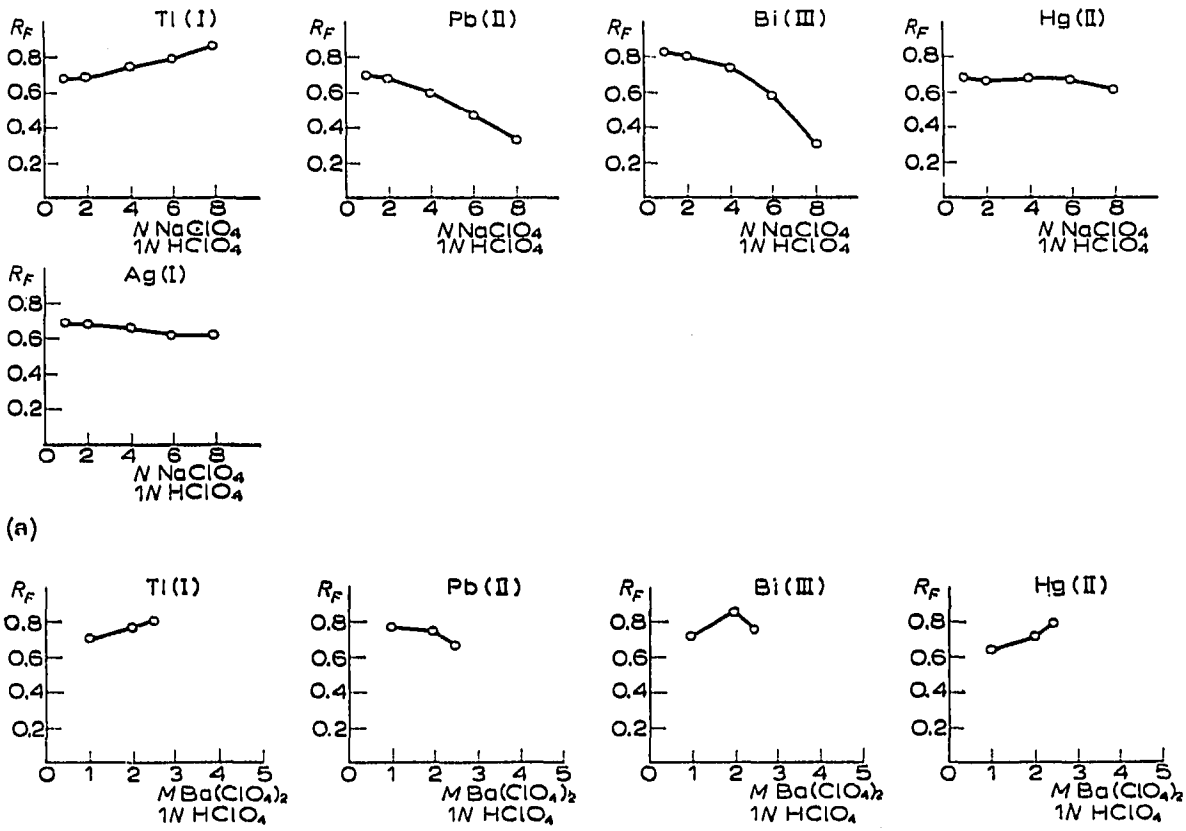

Fig. 3. R_F values of some metal ions on Whatman No. 3MM (cellulose) paper developed (a) with mixtures of $NaClO_4$ and 1 N $HClO_4$ plotted against the concentration of $NaClO_4$, and (b) with mixtures of $Ba(ClO_4)_2$ and 1 N $HClO_4$ plotted against the concentration of $Ba(ClO_4)_2$.

with $HClO_4$. Fig. 1 shows the R_F values of 16 metal ions both in sodium perchlorate and perchloric acid and we were surprised to find that for all intents and purposes the two electrolytes give the same R_F values for all ions. This is the more surprising as the activity coefficients of $HClO_4$ and $NaClO_4$ differ considerably at higher concentrations as shown in Fig. 2.

Fig. 3 shows the R_F values of a number of ions on cellulose paper with $NaClO_4$ and $Ba(ClO_4)_2$ as solvents. The ions examined here had shown adsorption in $HClO_4$[2].

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