

permanganate-periodate³ at room temperature for 2 h, whereby the ethylenic linkage of oleate is attacked, and the resulting free carboxyl group was esterified with diazomethane. Chromatography of this mixture under the same conditions gave an additional peak at 240° for cholesteryl azelate, while that at 290° diminished in area. Since azelate arises on oxidation of all the common unsaturated esters, oleate, linoleate and linolenate, these will be estimated together as cholesteryl azelate. A method for distinguishing these esters by preliminary separation on a silicic acid-silver nitrate column as described by DE VRIES⁴ is being worked out.

Separation by GLC of serum lipids, extracted by BLOOR's method and esterified with diazomethane, was examined. Temperature programming was carried out from 100-330°. The free fatty acid esters, mono- and di-glycerides, cholesterol, cholesteryl palmitate, cholesteryl stearate/oleate and triglycerides separated into distinct peaks. Quantitative aspects will be published elsewhere.

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Notes

Chromatography on ion-exchange papers

XV. The adsorption of metal ions on cation exchangers from perchloric acid solutions

In a recent paper NELSON *et al.*¹ report the adsorption of metal ions on Dowex-50 from HCl and HClO₄ solutions and noted a deviation from "ideal" exchange consisting of a general trend towards increased adsorption at higher concentrations of HClO₄. In previous papers² we have compared cellulose anion exchangers with anion resin papers and thus could show the extent to which the network influences adsorption. We hence thought that it would be interesting to apply the same comparative technique to cation exchangers and the perchloric acid system as this non-ideal behaviour in concentrated HClO₄ has not been adequately explained so far. The

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comparison in this case was made between a cellulose sulphonic acid exchanger and a resin sulphonic acid exchanger. The first is marketed now (by Macherey, Nagel & Co.) in the form of paper sheets (capacity 0.4–0.7 mequiv.).

Furthermore no data for inorganic ions have so far been published for the cellulose sulphonate paper. Such data are, of course, of more interest if reported in comparison with the sulphonic resin papers under identical conditions.

Experimental

The following papers were employed:

Amberlite SA-2 paper (containing 45 % of Amberlite IR-120, a nuclear sulphonic resin on a styrene base), washed twice with 2 *N* HCl and distilled water for 30 min and air dried.

MN-Ionenaustauscherpapier (stark sauer), a cellulose sulphonic acid exchanger (capacity 0.4–0.7 mequiv./g) washed twice with 2 *N* HCl and distilled water for 30 min and air dried.

Whatman No. 3MM cellulose paper.

Ascending development of strips about 20 cm long in small volume jars was employed throughout, always chromatographing all three papers simultaneously.

The perchloric acid used was reagent quality (Carlo Erba, Milan) and all dilutions were prepared from 70 % HClO₄.

The metal ions were placed on the paper as solutions of the nitrates in 2 *N* HClO₄.

Fig. 1 shows the R_F values of 20 metal ions obtained at a room temperature of $20^\circ \pm 2^\circ$.

Discussion

The lowering of R_F values of some metal ions on the resin paper is identical to that observed by NELSON *et al.*¹ in column experiments. The same decrease of R_F values on the cellulose sulphonic acid at higher HClO₄ concentrations occurs also with Th(IV), U(VI), La(III), Y(III) and Sc(III) while these are not adsorbed by pure cellulose (Whatman No. 3MM paper). The possibility of adsorption on the network causing this "non-ideal" behaviour must hence be ruled out for these ions.

On the other hand quite considerable adsorption on pure cellulose may be observed with Pb(II), Bi(III), Ag(I) and Tl(I) and here the decrease of the R_F values on the cellulose sulphonic exchanger is of the same order of magnitude as the adsorption; thus in some instances adsorption also plays a role.

The lowering of R_F values for most of the divalent transition metals seems to be less than that observed by NELSON *et al.*¹. However, owing to the fragility of the paper we could not work with concentrations higher than 6 *N* HClO₄, which is the region where the increased adsorption seems to commence. However, the R_F values of Ga(III) do not decrease at higher HClO₄ concentrations, although a minimum around 3 *N* HClO₄ was obtained by NELSON *et al.*¹. It seems that Amberlite IR-120 (in the papers employed here) and Dowex-50 are not strictly comparable for this phenomenon.

Zr(IV) shows some hydrolysis at lower concentrations of HClO₄, which causes it to adsorb (or precipitate) on pure cellulose, and should therefore be omitted from any considerations of this mechanism.

Finally we would like to draw attention to the fact that the deviation from

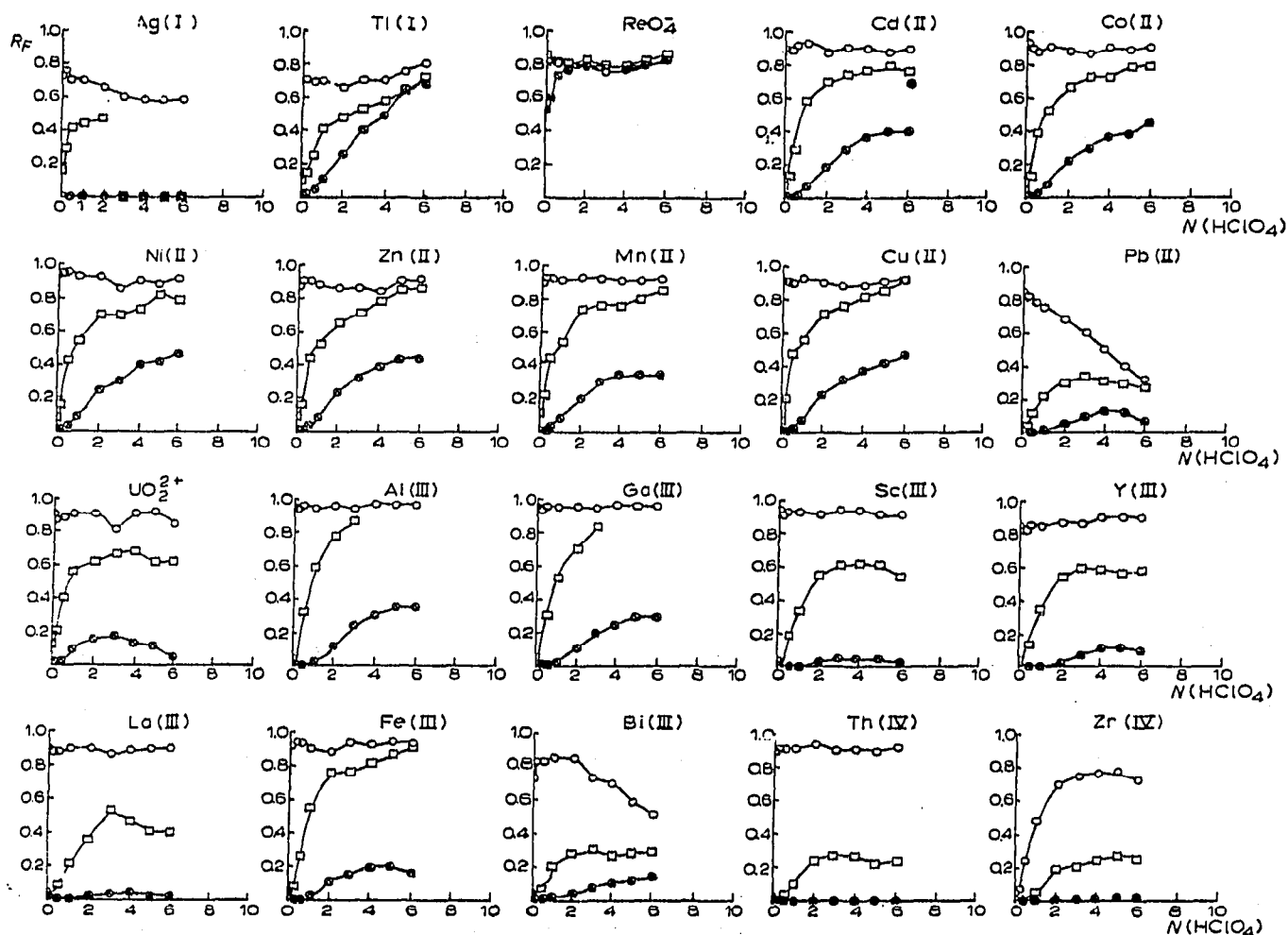


Fig. 1. R_F values of metal ions plotted against the concentration of HClO_4 for the following papers: \odot — \odot Whatman No. 3MM cellulose paper; \square — \square Macherey, Nagel & Co. stark saures Ionenaustauscherpapier (containing sulphonic acid groups attached to the cellulose); \otimes — \otimes sulphonic acid resin paper (SA-2).

“ideal” behaviour occurs in the region where the conductivity of HClO_4 reaches a maximum. We seem to reach here the gradual dehydration of HClO_4 , which may first induce the metal ion to dehydrate itself and hence adsorb more strongly on the resin.

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