

Short Communication

Chromatographic techniques using liquid ion-exchangers

Recently much attention has been given to the use of liquid ion-exchangers in chromatography (paper and column). Though the first publications^{1,2} were devoted to the use of high-molecular-weight amines, recent developments all concern di-(2-ethylhexyl) hydrogen phosphate (HDEHP) and related compounds (for reviews *cf.* refs. 3 and 4), while special emphasis has been placed upon the separation of rare earth mixtures.

The interesting separations recorded in the rapidly increasing number of publications in this branch of chemistry and, moreover, the correlation of results so obtained with those from extraction procedures and ion-exchange techniques (*cf.* the work of KRAUS AND NELSON⁵) have led us to investigate further the possible applications of chromatographic techniques using amines, the more so since most attention has hitherto been focused on the rather expensive tri-*n*-octylamine. This preliminary report describes a method in which the use of liquid ion-exchangers is successfully combined with a simple form of thin-layer chromatography.

The first experiments were carried out using Amberlite LA-1 (weakly basic secondary amine; N-dodeceny-(trialkylmethyl)-amine) and HCl, with silica gel (Fluka, Type DO (no binder)) as a support. The amine is converted into its HCl salt by equilibrating a solution in chloroform for 10 min in a separatory funnel with 3 vol. of HCl of appropriate normality (see below); the organic solution is separated, filtered on paper and dried for some hours over sodium sulphate. The amine·HCl solution so obtained is mixed with silica gel (silica gel-chloroform, 1:2, v/v) and the resulting suspension is agitated for some time.

Thin-layer plates are prepared by dipping ordinary microscope slides (2.5 cm × 7.5 cm) into the silica gel-chloroform mixture for approx. 5 sec. On leaving the glass plates for some minutes in the air, in order to evaporate off the chloroform, a thin film of amine-impregnated silica gel adheres to the slides. Using cotton wool, a margin of 1-2 mm is made along the edges of the slides in order to avoid undesirable contact with the eluting agent.

The thin-layer plates so prepared are spotted with the solution to be investigated using a 1-mm wide strip of filter paper; the resulting spot ought to have a diameter of 1-2 mm. When the spots are air-dry the thin-layer plates are put into small vessels (Hellendahl staining jars) containing the eluting agent (4-6 plates per vessel) and the chromatogram is developed for 10 min using the ascending technique. Subsequently, the plates are dried in the air and the spots are visualized using conventional techniques. The ions mentioned in Fig. 1 were detected using either H₂S gas [Pb(II), Bi(III), Hg(II) and Sb(III)], dipping with dithiooxamide in chloroform [Ni(II), Co(II) and Cu(II)] or spraying with 8-hydroxyquinoline in 80% ethanol [Al(III), Fe(III), Mn(II), Zn(II) and Cd(II)].

Preliminary investigations showed the use of 0.10 M amine·HCl solutions in

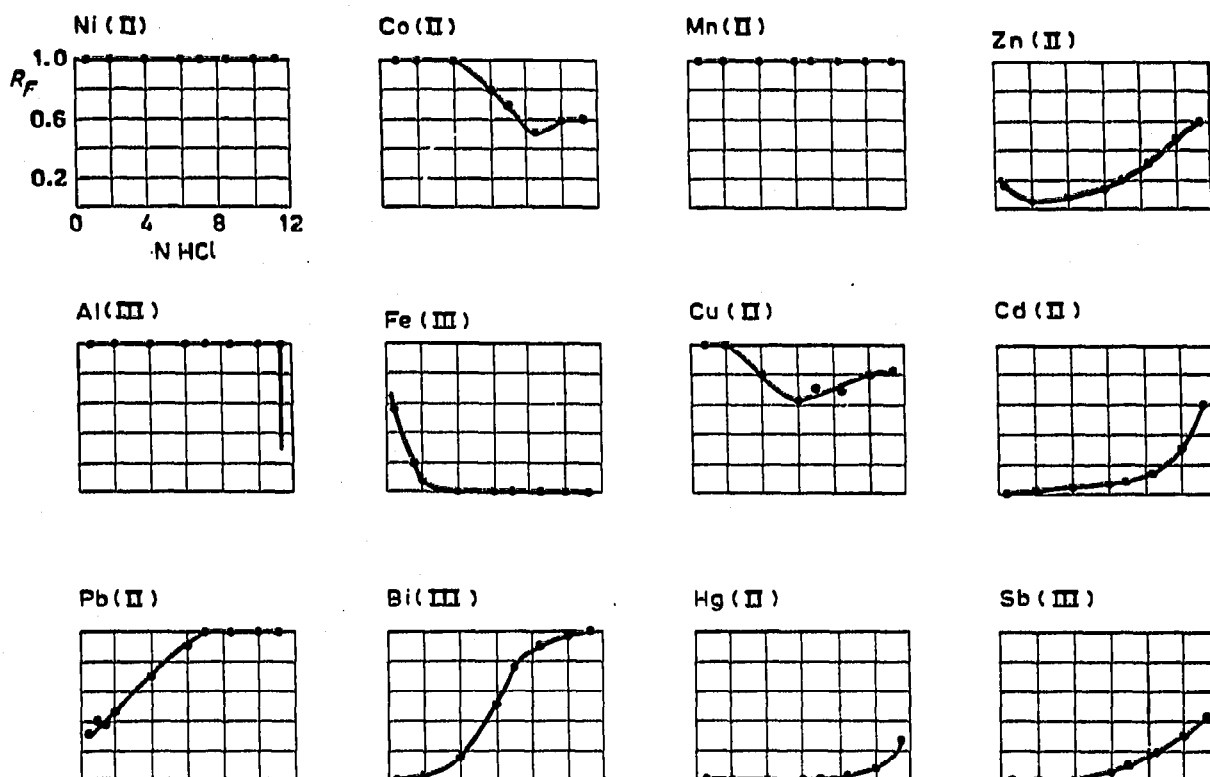


Fig. 1. R_F -spectra found for some cations in thin-layer chromatography using silica gel impregnated with Amberlite LA-1 · HCl as support and HCl of varying concentration as eluting agent.

chloroform to give excellent results. Experiments were carried out using 0.5–11.5 N HCl as eluting agent. At first, the amine was equilibrated with HCl of the same normality as that used as eluting agent, but it was shown that equilibration with 2 N HCl in all cases — irrespective of the normality of the eluting agent — made hardly any difference.

R_F -spectra for some ions are shown in Fig. 1. It is clearly seen that the results obtained — which were fairly reproducible — exhibit good agreement with the ion-exchange data of KRAUS AND NELSON⁵ and also with the results obtained in extrac-

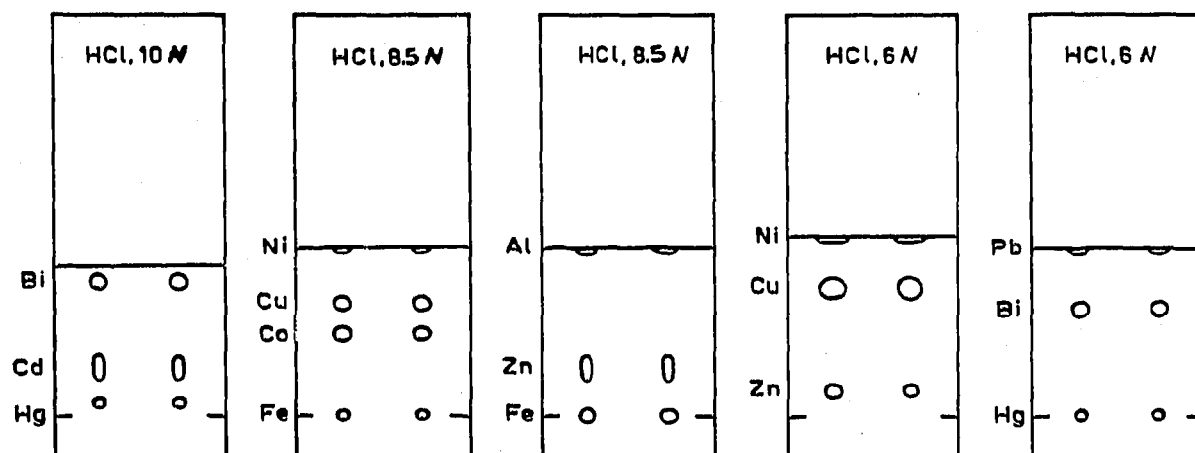


Fig. 2. Examples of qualitative separations obtained using the thin-layer technique described in this paper. For experimental details see text and figure.

tion procedures, as cited in the reviews by GREEN⁴ and by COLEMAN⁶. Our data show, moreover, that (i) many qualitative separations are easily carried out using the inexpensive amine Amberlite LA-1: some examples are given in Fig. 2; (ii) the rapidity of the separation method outlined above makes it superior to most other methods of qualitative analysis so that detailed investigation would certainly be of interest, together with its possible quantitative application (*cf.* ref. 2).

The use of the rapid thin-layer technique described here is, moreover, important in view of the reliable predictions that can sometimes be made about the results of ion-exchange or extraction procedures under comparable circumstances.

Investigations are now in progress on the use of other supports, amines and complexing agents. Attention has already been given to the use of paper-chromatographic procedures analogous to those outlined by CERRAI AND TESTA^{1,3}. It was found that good results are obtained when using 0.15 M Amberlite LA-1·HCl solutions in chloroform or benzene; Whatman No. 1 paper was used throughout. Schleicher and Schüll paper No. 2043a gave comparable results, while Schleicher and Schüll 2040a and 2045a were somewhat less satisfactory. In general, the results are comparable to those given above for the thin-layer experiments. Excellent separations can be accomplished in 3–4 h.

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1 C. TESTA, *J. Chromatog.*, 5 (1961) 236.

2 E. CERRAI AND C. TESTA, *J. Chromatog.*, 5 (1961) 442; 6 (1961) 443.

3 E. CERRAI, *Chromatographic Reviews*, Vol. 6, Elsevier, Amsterdam, 1964, p. 129.

4 H. GREEN, *Talanta*, 11 (1964) 1561.

5 K. A. KRAUS AND F. NELSON, *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, Vol. 7, p. 113.

6 C. F. COLEMAN, *Nucl. Sci. Eng.*, 17 (1963) 274.

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Notes

Thin-layer chromatographic method for the separation of rare earths

Although thin-layer chromatography (TLC) has proved to be an excellent and rapid separation technique in organic and biochemical analysis, it has found little use in inorganic separations. The technique offers many unique advantages, the most important being its rapidity and the possibility to use corrosive reagents and impregnations. The separation of some adjacent rare earths (R.E.) with a rapid chromatographic technique is interesting in view of radiochemical studies. The use of TLC

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