

SEPARATION OF SOME INORGANIC IONS BY REVERSED-PHASE PARTITION CHROMATOGRAPHY ON THIN LAYERS

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The widespread application of thin-layer chromatography to the separation of small quantities of organic material is well known and the technique has found wide acceptance by virtue of its speed, selectivity and convenience. By contrast, separation of inorganic mixtures on thin layers has received relatively little attention and the investigations that have been carried out have been primarily concerned with separations on layers of conventional adsorbents such as kieselguhr, silica gel and cellulose¹. Reversed-phase partition chromatography in which an organic extractant is retained as stationary phase on an inert carrier, has provided good separation of inorganic mixtures by column and paper chromatographic techniques², and retention of extractants on thin layers of carriers spread on glass plates is also possible^{3,4}. We have already reported rapid separation of certain rare earth mixtures by thin-layer reversed-phase partition chromatography on a polymeric layer retaining di-(2-ethylhexyl) hydrogen phosphate⁵, but in this particular case emphasis was placed on speed, rather than resolution and a relatively coarse grade of carrier was used. Subsequently, separation of a very wide range of inorganic ions has been achieved on a fine grade of carrier, employing a variety of stationary and mobile phases, and using solvent extraction data to provide a guide to the conditions required. As examples, we report in this paper a number of separations carried out with three different extractants and using two different carriers, silica gel and powdered polyvinyl chloride.

EXPERIMENTAL

Preparation of thin layers

Two carrier materials were used for these experiments, silica gel supplied commercially for thin-layer chromatography (Whatman SG 41) and granulated polyvinyl chloride (Corvic D 55/3, Imperial Chemical Industries Ltd.) A poly(vinyl chloride-vinyl acetate) copolymer (Corvic R 51/83) has been used previously as carrier for reversed-phase partition chromatography in columns⁶ or sintered sheets⁷ and even on thin layers⁵, but the particle size of this solid was much coarser than that usually employed for thin-layer chromatography, and the layers, although robust gave relatively poor resolution. Consequently a number of different polymers were assessed as carriers and Corvic D 55/3 was found to be the most satisfactory of those tried.

Neither the silica gel nor the Corvic was sufficiently free from inorganic impurities to permit their use for chromatography without chemical purification and the silica gel needed particularly thorough treatment. After passing through a 300-mesh sieve, both carriers were repeatedly washed, first with concentrated hydrochloric acid until the acid remained clear, and then with demineralised water. When tests with colour-forming reagents indicated that inorganic impurities were still present these impurities were usually removed by washing with a solution of ethylenediaminetetraacetic acid in deionised water.

Thin layers retaining an organic extractant were made by first spreading a layer of Corvic on a glass plate and subsequently allowing a solution of the extractant in a volatile organic solvent to run over it. The plate was used after evaporation of the solvent.

Standard commercial equipment was used to prepare the thin layers, but a special spreader, constructed of polymeric materials was made to reduce trace element contamination of the thin layers, and to permit the Corvic to be added to the plates in a slurry of dilute acid if required. In practice, however, thin layers could be satisfactorily prepared from a slurry of the carrier in water, with the result that use of a polymeric spreader was not essential, particularly when radiotracer techniques were used to locate the position of the migrating solutes.

After the slurry had been spread over the plates and the water on the surface allowed to evaporate, the plates were heated in an oven. The silica gel layers were heated at 110° for 30 min but the Corvic was heated at a rather lower temperature to avoid the risk of the particles sintering which caused uneven fronts, and 30 min at 70° proved satisfactory.

The stationary phase was added to the carrier by dissolving it in diethyl ether or some other volatile solvent and feeding the resulting solution to the horizontal plate by means of a paper wick. This method of allowing the solution to run over the layer was chosen in preference to dipping the plate in a solution of the reagent to avoid damaging the fragile thin layers of silica which became detached from the glass backing plates rather readily. Corvic layers were very much more robust and could be dipped in a variety of organic solutions without damage, but they were prepared in exactly the same way as the silica layers to enable direct comparison to be made. Whenever possible mobile and stationary phases were saturated with the other before use and extractants purified by standard techniques.

Ascending, descending and horizontal methods of development were tried and in all cases satisfactory results were obtained with Corvic layers. However, silica showed least tendency to come away from the glass backing plates during horizontal development and therefore this technique was always used for silica layers.

Layers were spread on standard plates 20 cm long and 20, 10 or 5 cm wide; development was usually allowed to proceed for about 10 cm.

Both radioactive and inactive solutes were spotted on to the plates and their final positions located, either by spraying the plates with a colour-forming reagent such as 8-hydroxyquinoline or diphenylthiocarbazone, or by removing portions of the thin layer and counting the radioactivity. γ -Ray spectroscopy was used whenever possible to identify the active nuclides when mixtures of radioactive elements were separated by thin-layer chromatography.

RESULTS AND DISCUSSION

An initial series of experiments was conducted to find a thickness of layer which gave satisfactory surfaces and good reversed-phase partition chromatograms for the elution of inorganic solutes. The procedure finally adopted was to move the spreader slowly over the plates with the blade set at a height of 0.25 mm above the glass backing plate.

The quantity of extractant on the thin layer was found to influence both the R_F value of the solute and the speed of elution. Increases in reagent loading of the carrier in reversed-phase partition chromatography have been shown to reduce the R_F value of inorganic ions migrating on paper⁸ and in columns⁹, and this effect was also found for partition chromatography on thin layers with solutes migrating more slowly on the more heavily loaded layers.

The rate of development was also dependent upon the reagent loading of the carrier with the most heavily loaded layers requiring the largest development time. Under the experimental conditions required for the separations reported below, the usual time necessary for the mobile phase to traverse 10 cm of the loaded thin layer was 40-50 minutes.

At high reagent loadings, particularly when di-(2-ethylhexyl) hydrogen phosphate was retained on silica, the extractant tended to strip from the carrier and was pushed ahead of the advancing aqueous phase. A suitable reagent loading of the carrier which gave adequate capacity without showing any tendency to strip was finally obtained by adding the extractant in an organic solvent as a 10% solution. The uniformity of the distribution of the stationary phase on the thin layer was assessed by placing several spots of the same radioactive element across the bottom of a number of plates and after development locating the new positions of the elements by removing and counting 0.5 cm lengths of each track of the thin layer. Positions of maximum activity were never found to vary by more than one 0.5 cm fraction on the same plate, irrespective of the point across the bottom of the plate at which the spot started and usually maximum activity occurred in the same fraction, thus indicating that the extractant was evenly spread over the plate. Similar values of R_F were obtained for the same elements eluted under similar conditions on plates of the same batch, but appreciable variations were sometimes found from batch to batch and it was customary to elute at least one standard, together with the mixture on a thin layer.

Generally, slightly sharper eluted spots were obtained on layers of silica gel than on Corvic, and small initial spots of solute were more easily formed on silica, but the robust polymer layer was easier to handle and was always preferred when conditions permitted.

Three different extractants were employed as stationary phases for these experiments, and all were liquids which had previously proved satisfactory for reversed-phase partition chromatography in column operation; they were the cation exchanger di-(2-ethylhexyl) hydrogen phosphate (HDEHP)^{6,10-14}, the anion exchanger tri-iso-octylamine (TIOA)¹⁵ and the neutral phosphorus ester tri-*n*-butyl phosphate (TBP)¹⁶⁻¹⁸.

In all cases aqueous acid was used as mobile phase and gave straight fronts when advancing over the stationary phase.

By choice of extractant and mobile phase a large number of different separations have been carried out on thin layers, but for brevity we give below only one or two typical examples of separations achieved with each extractant.

Tri-n-butyl phosphate

The use of TBP for liquid-liquid extraction has been extensively investigated and the extraction of about fifty elements from aqueous hydrochloric acid by 100% TBP has been reported¹⁰. A number of elements of the first transition series were spotted onto corvic and silica layers which had been contacted with 10% TBP in diethyl ether and developed with hydrochloric acid of different strengths. The results are shown in Fig. 1 as a plot of R_F against the normality of the developing acid and

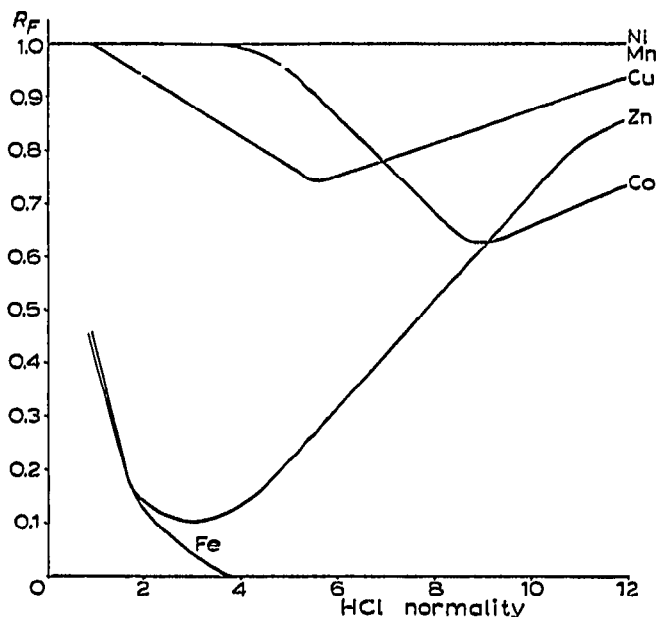


Fig. 1. Plot of R_F value against hydrochloric acid concentration for the migration of a number of elements over layers of Corvic retaining TBP.

are of the form expected from liquid-liquid extraction data, assuming that distribution ratios for the solvent extraction system are the same function of aqueous acid concentration as is the parameter $(1/R_F - 1)$ for the partition chromatographic system. Thus nickel and manganese which show relatively low extraction by 100% TBP from hydrochloric acid move with the solvent front at all acidities, while iron, which exhibits a high distribution ratio when extracted from a range of strongly acid aqueous solutions by 100% TBP stays essentially at the starting point when eluted with acids stronger than about 4 *M*. As an example of the separations that can be achieved on thin layers retaining TBP, chromatograms obtained for the elution of a number of elements with hydrochloric acid individually and as a mixture are given in Fig. 2. The spots were well defined permitting essentially complete disengagement of the different elements by this thin-layer technique.

Di-(2-ethylhexyl) hydrogen phosphate

HDEHP has been extensively used for reversed-phase partition chromatography of the rare earths because of the good separation factors that can be obtained

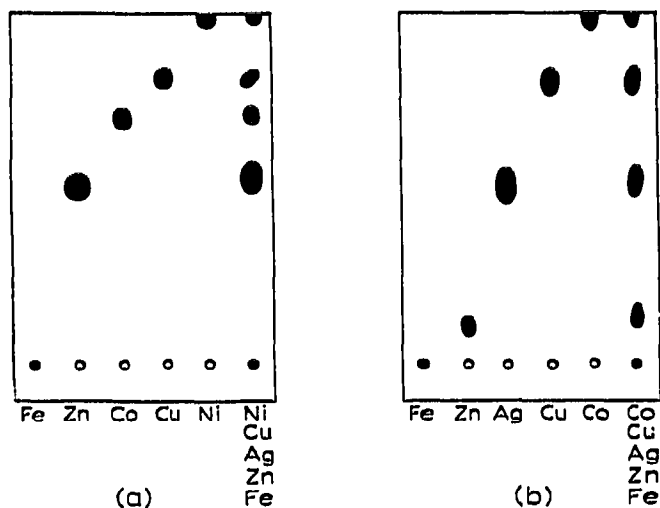


Fig. 2. Separation of a number of elements on TBP Corvic layers by elution with hydrochloric acid. Acid strength: (a) 8 *N*, (b) 4 *N*.

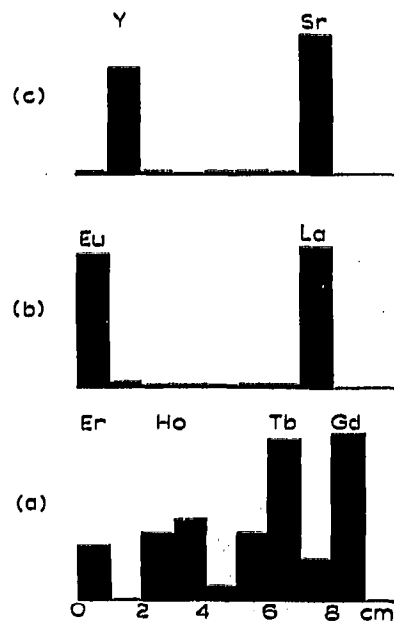


Fig. 3. Histograms of separations carried out on HDEHP-silica layers with hydrochloric acid as eluant. Acid strength: (a) 1.75 *N*, (b) 0.3 *N*, (c) 1.5 *N*.

for adjacent elements with this extractant²⁰. The rare earths are normally eluted with aqueous acid and their mobilities are found to decrease with increasing atomic number. We have already reported the rapid separation of a number of rare earths on layers of a coarse grade of Corvic retaining HDEHP⁵; for the experiments reported here the reagent was added either to silica gel, or to a finer grade of Corvic with particles of the size more usually employed for thin-layer chromatography. No attempt was made to obtain a plot of the zone migration parameter, $R_M \log (1/R_F - 1)$ against the hydrogen ion concentration of the aqueous phase as this has already been reported for the thin-layer system⁵, and instead a number of separations were attempted by eluting elements and mixtures on Corvic and silica layers retaining HDEHP as the stationary phase. An example is given in Fig. 3. Development was carried out at room temperature and not at the elevated temperatures used for some column separations. Again elements showing the highest distribution ratios in the respective liquid-liquid systems gave the lowest R_F values, and separation factors were of the order expected from column chromatography although accurate separation factors could not be calculated from histograms of the type shown in Fig. 3.

Tri-iso-octylamine

The third extractant used as stationary phase was the liquid anion exchanger TIOA. The use of high molecular weight amines for the extraction of inorganic ions has received considerable attention²¹ and distribution data for the extraction of more than sixty elements from hydrochloric acid into TIOA has been reported²². Experience with TIOA retained on a carrier as stationary phase for column chromatography indicated that the amine might also be of use for reversed-phase partition chromatography on thin layers.

The behaviour of TIOA retained on Corvic D 55/3 for thin-layer chromatography was similar to that retained on Corvic R 51/83 for column chromatography which has been described in greater detail elsewhere¹⁵ and will not be re-considered here. Examples of separations obtained on stationary phases of TIOA are shown in Fig. 4 and again the elements which migrate furthest are those which show lowest extraction in the comparable liquid-liquid system.

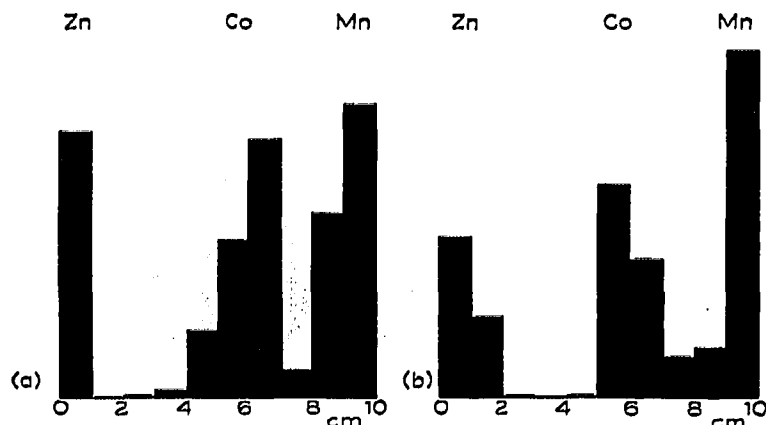


Fig. 4. Histograms of separations carried out with a stationary TIOA phase. (a) carrier: Corvic; eluant: 4 N hydrochloric acid; (b) carrier: silica; eluant: 4 N hydrochloric acid.

CONCLUSION

Reversed-phase partition chromatography employing a stationary phase of organic extractant retained on a thin layer of carrier can provide separation of a wide variety of inorganic ions, selectivity for the technique being achieved by careful choice of extractant and eluting phase.

Provided that rapid mass-transfer between the two phases is possible and the usual precautions are taken to minimise spot size good resolution can be attained.

Powdered polyvinyl chloride can be used as an alternative to the more conventional carriers used for thin-layer chromatography as it provides very robust thin layers, without requiring the addition of any binder.

SUMMARY

Separation of mixtures of inorganic ions has been obtained by elution with aqueous acid on a stationary phase of an organic extractant retained on a thin layer of a carrier. Di-(2-ethylhexyl) hydrogen phosphate, tri-iso-octylamine and tri-*n*-butyl phosphate were used as extractant and silica gel and powdered polyvinyl chloride employed as carriers.

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