

THE USE OF TRI-ISO-OCTYLAMINE AS AN ANION EXCHANGER FOR PARTITION CHROMATOGRAPHY

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INTRODUCTION

The application of reversed phase partition chromatography to inorganic separations has recently received considerable attention, and selective column materials have been prepared by immobilising extractants of the type commonly employed for solvent extraction, upon a solid carrier. The resulting solid phase, when packed into a column, can often combine the selectivity of the reagent with the technical advantages of chromatographic operation, and by varying the composition of the stationary and mobile phases, separation of a very wide range of elements can be achieved¹. Particular interest has been centred on the separation of the rare earths from each other by elution with aqueous acid from columns retaining di-(2-ethyl-hexyl) hydrogen phosphate, and a number of separation schemes have been reported²⁻⁶. However, the scope of the technique can quite clearly be extended by varying the complexing agent providing the stationary phase, and we report here experiments which have been carried out to examine the behaviour of an anion exchange material prepared by retaining a high molecular weight amine on a polymeric support.

The use of high molecular weight amines as the stationary phase in partition chromatography has already been described using paper^{7,8}, cellulose⁹, sintered polymers¹⁰ and a fluorinated polymer¹¹ as carriers. For the work reported here Corvic R51/83, a poly-(vinyl chloride/vinyl acetate) copolymer, already used to retain organic extractants for partition chromatography¹² was used as carrier; tri-iso-octylamine (TIOA) was chosen as the extracting amine since in spite of being an isomeric mixture, it has found useful application to analytical separations by virtue of the good separation factors that can be achieved for many mixtures, its cheapness, low aqueous solubility and high solubility in organic diluents¹³. Zinc tracer was used initially to assess the behaviour of the solid phase but subsequently a number of elements were extracted from hydrochloric acid by TIOA-Corvic.

EXPERIMENTAL

Preparation of Corvic retaining TIOA

In previous work an organic reagent was added to Corvic in a volume of organic solvent which was less than the maximum the solid could take up², and distribution of the reagent throughout the solid was obtained by stirring the mixture vigorously

during both the addition of the solution to the polymer, and the subsequent evaporation of the volatile organic solvent. This method was used for the amine, together with a second method which consisted of dissolving the reagent in more organic solvent than the polymer could sorb, and adding this larger volume of solution to the carrier. Again a current of air was employed to evaporate off organic solvents before use. Distribution ratios, found by batch extraction techniques for material made up by both these methods, showed that lower, but constant values were, obtained when excess of solvent was used. Material made up with excess solvent was prepared from 20 g of Corvic R51/83 (100-150 mesh) and 1 g TIOA dissolved initially in 10 ml of toluene and 20 ml of chloroform, while for solvent deficient conditions the quantities of Corvic and TIOA were the same but only 8 ml of toluene and 12 ml of chloroform were used.

Since relatively small volumes of amine were employed for some of the work reported in this paper, it was felt that the reagent would be more uniformly distributed throughout the solid if excess of solvent was used, and therefore this method was finally employed, although evaporation of the organic solvent took longer. The usual technique was to dissolve the required amount of TIOA in 10 ml of toluene and 20 ml of chloroform, add the solution to 20 g Corvic, and finally evaporate off the solvents in an air stream, with continuous stirring.

For some experiments Corvic was prepared retaining the amine salt rather than the free amine. After the amine had been added to the Corvic as described above and the organic solvent evaporated off, the loaded powder was stirred with concentrated hydrochloric acid for 15 minutes. The solid phase was then freed from acid by filtration on a glass sinter and finally stored in a vacuum desiccator until required.

Experimental techniques

Batch extractions have already been used to obtain distribution data for a reversed phase system¹⁴. A number of preliminary experiments indicated that batch extractions were also feasible with TIOA retained on Corvic, and therefore this method of obtaining distribution ratios was adopted. Usual quantities of the two phases employed for the extractions were 1 g of the solid and 20 ml of the aqueous phase. The temperature of the extraction could be thermostatically controlled if required.

Radiotracers were generally obtained by irradiating "Specpure" chemicals in a thermal neutron flux of 10^{12} n/sq.cm/sec but in a few cases radioactive materials were obtained from The Radiochemical Centre, Amersham, Bucks. The purity of the tracers was assessed before use by γ -ray spectroscopy and half-life determinations, and interference from impurities, avoided by careful choice of irradiation and decay times, by the use of γ -ray spectroscopy or by chemical separations.

Chromatographic separations were carried out at room temperatures on columns 18 cm long \times 0.6 cm diameter. Radiotracers were used to follow the elution, and the effluent from the column was collected in fractions by means of an automatic fraction collector actuated either by a drop counter or by timing pulses. The radioactivity of individual fractions was measured with a well-type scintillation counter and the activity over the peak identified by means of a 3 in. \times 3 in. NaI (Tl) crystal connected to a 512-channel analyser system.

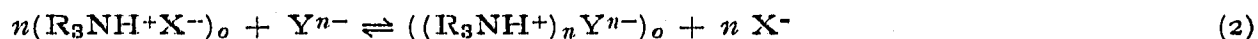
RESULTS AND DISCUSSION

High molecular weight amines have been extensively used for the extraction of metal ions in liquid-liquid systems¹⁵, and in many cases the extraction behaviour of the amine has been found to bear a resemblance to that of solid anion exchange resins.

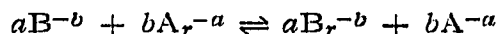
A free base high molecular weight tertiary amine can extract acid from aqueous solution to form an amine salt, *e.g.*



where R_3N represents a tertiary amine, and X^- the anion of a simple acid or complex metal acid, and the subscript o denotes species present in the non-aqueous phase. Metal extraction from an aqueous acid phase by this amine salt can therefore take place according to the equation:



where Y^{n-} is the anion containing the element to be extracted. Clearly equation (2) is similar to the general exchange equilibrium for an anion exchange resin:



where A and B are the exchanging anions and the subscript r denotes species present in the resin phase. Thus a column material for partition chromatography consisting of an amine retained on an inert carrier could be expected to bear at least a superficial resemblance to an anion exchange resin, although the dissimilar nature of the non-aqueous phases in the two cases will result in differences being apparent between the partition and resin systems. Further as the structure of the amine and the nature of the organic diluent are found to affect distribution ratios in liquid-liquid systems, it should be possible to prepare column materials with different exchange characteristics by varying the composition of the immobilised phase. However, as large quantities of organic diluent retained on the solid phase will increase the likelihood of the retained phase stripping from the carrier during chromatographic elution, or batch extraction, the quantity of organic diluent on the solid was kept as small as possible in these experiments by exposing the solid to a current of air before use. Previous experience with partition systems, involving a solid extractant (*e.g.* dithi-zone) retained on a carrier indicated that the presence of organic solvent on the carrier improved the rate of reaction between a solute dissolved in an aqueous phase and the immobilised extractant, but with the liquid amine retention of large quantities of solvent proved unnecessary.

The extraction of zinc from aqueous hydrochloric acid by TIOA

The extraction of many elements from aqueous solution by high molecular weight amines has been studied and summarised elsewhere¹⁵ but it has been customary to use the amine dissolved in an organic diluent. For the experiments reported here organic diluents were evaporated off the column material before use, and in order to compare the shape of the extraction curve provided by TIOA retained on

Corvic, with that found when TIOA was dissolved in a diluent, zinc was extracted from aqueous hydrochloric acid by 0.1 % w/v TIOA in toluene and by 5 % w/w TIOA on Corvic. The results are presented in Fig. 1 and in both cases show curves with maxima, maximum extraction occurring at an aqueous acidity 3.5 *M* for the liquid-liquid system, and at rather lower acidity when the amine was retained on Corvic.

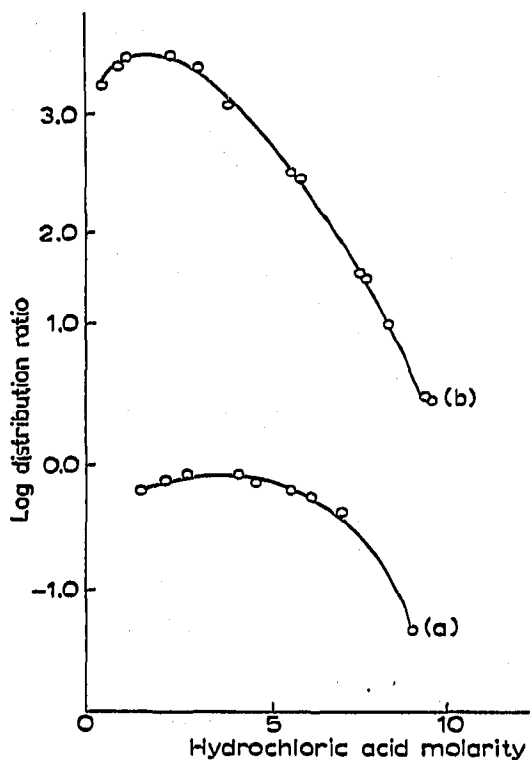


Fig. 1. Extraction of zinc from hydrochloric acid by (a) = 0.1 % w/v TIOA in toluene and (b) = 5 % w/w TIOA-Corvic.

The extraction of zinc from aqueous hydrochloric acid into a solution of methyl dioctylamine in trichlorethylene has already been reported and the results compared with those found for the extraction of zinc from hydrochloric acid by Dowex 1¹⁶. Experimental extraction curves showing maxima at aqueous acid strengths of 2.3 *M* were obtained, and possible mechanisms leading to this shape of extraction curve were discussed.

The wide range of distribution ratios that can be achieved with zinc in the TIOA-Corvic system (Fig. 1) permit the element to be either extracted by or eluted from a column of the material if the correct aqueous acidity is chosen while the actual value of the distribution ratio at any acidity may be altered by varying the reagent loading of the solid phase. Results for 2.5, 5, 10, 20 and 25 % w/w TIOA-Corvic provided a family of extraction curves of generally similar shape, but with the most heavily loaded material exhibiting strongest extraction of zinc.

The amine hydrochloride retained on Corvic gave similar extraction curves to the free base amine, and in addition showed rather better stability when the column material was kept for long periods, but over a period of two or three weeks, the normal time required to use a batch of TIOA-Corvic, there was insufficient deterioration

of the free base amine to warrant the longer preparation procedure required for the amine salt.

Extraction isotherm

As a concentration wave of solute passes down a chromatographic column during elution analysis, the solute loading of the solid phase at any particular point in the column will first increase, pass through a maximum and then decrease again. In order to reduce the distortion of peak shape caused by different concentrations of

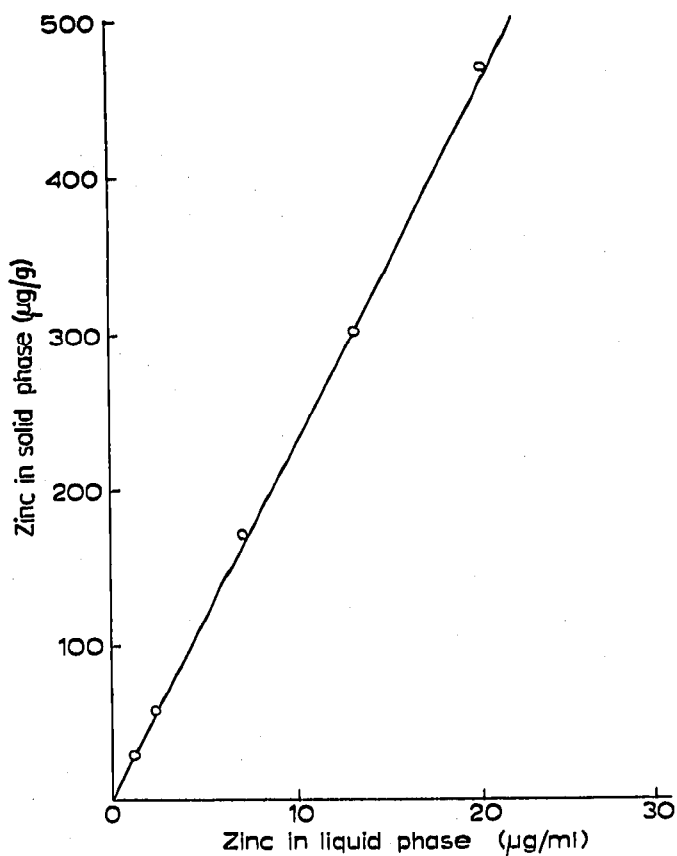


Fig. 2. Extraction isotherm for the extraction of zinc from hydrochloric acid by 5% w/w TIOA-Corvic.

solute travelling at different velocities, the distribution ratio of solute should remain constant over a wide range of solute loadings. An extraction isotherm obtained for the extraction of zinc from aqueous hydrochloric acid by 5% w/w TIOA-Corvic is given in Fig. 2 and shows that a good linear dependency is maintained between the concentration of zinc on the polymer and in the hydrochloric acid solution over a wide range of zinc concentrations. In all cases equilibrium was approached from one direction only, that of a metal-rich aqueous phase, and no equilibrations were carried out when net mass-transfer was from the solid to the liquid phase.

Extraction behaviour of individual elements

Schemes for chromatographic separation can be conveniently designed from batch extraction data if this provides a reliable basis for calculating separation fac-

tors, and extensive information is available for the extraction of many elements from hydrochloric acid into solutions of high-molecular weight amines¹⁵. For the specific case of TIOA the extraction of more than 60 elements has been recorded¹⁷. However, when amines have been employed for solvent extraction, they have usually been dissolved in organic diluent, whereas in these experiments as much solvent as possible was removed from the Corvic before use; therefore in view of the importance of solvent in amine extractions, batch extractions were carried out to examine the distribution of a number of elements between aqueous hydrochloric acid and 5 % w/w TIOA-Corvic. Results are presented in Fig. 3 in the manner originally used for anion exchange resins¹⁸, and indicated a general pattern of extraction which is similar to that found for TIOA in solution, although the actual distribution ratios are dependent upon the TIOA loading of the solid phase.

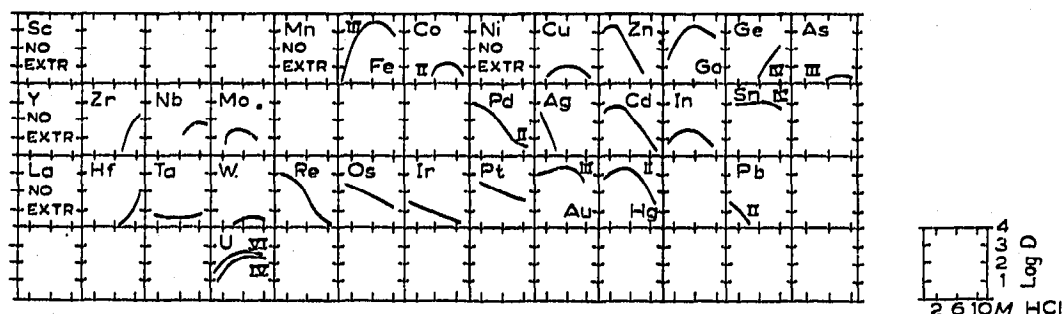


Fig. 3. Extraction of a number of elements from aqueous hydrochloric acid by TIOA-Corvic. D = distribution ratio.

The use of diagrams of the form of Fig. 3 for devising separation schemes has been discussed by KRAUS AND NELSON¹⁸ and will not be reconsidered here. However, the most satisfactory separations will be achieved when there is a large difference in the relative mobilities of the migrating species and when extremely careful control of column conditions is unnecessary. For many applications the most convenient separations are those in which separate solutes are removed from the column with different eluting solutions. Unfortunately even when separation factors are large and distribution ratios can be controlled to give high or low extraction, satisfactory separations may still be impossible to achieve if peak shapes are poor, or if solutes exhibit serious tailing. Although linear isotherms obtained from batch experiments, suggest that good peaks should be obtained at equilibrium, slow mass transfer across the phase boundary might result in distorted peak shapes. Consequently columns of TIOA-Corvic were made up and used for a number of separations, suitable conditions being devised with the aid of data presented in Fig. 3.

Separations

The relatively simple separation of arsenic, germanium and indium was used to evaluate the behaviour of TIOA-Corvic during actual separation and the result of the elution is shown in Fig. 4. The effluent was collected in one-minute fractions, and the acid strengths that are given on the graphs refer to the acidity of the influent whilst a given effluent fraction was being collected. It can be seen that the peak shapes obtained by elution of the solutes from a TIOA-Corvic column are good and

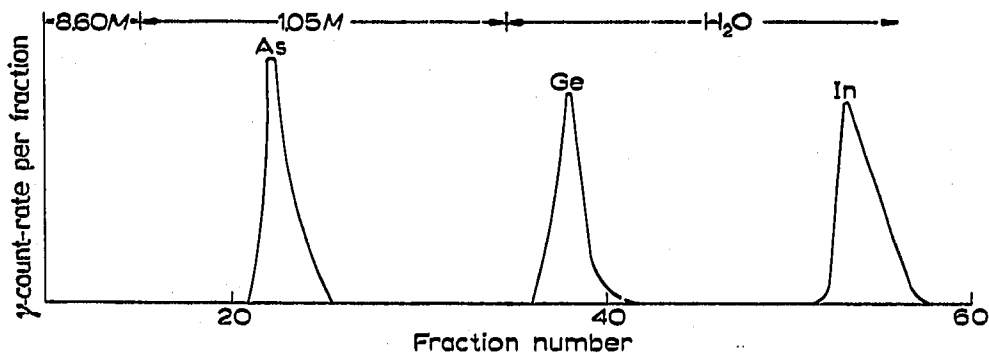


Fig. 4. Separation of As, Ge and In by elution with hydrochloric acid from columns of TIOA-Corvic.

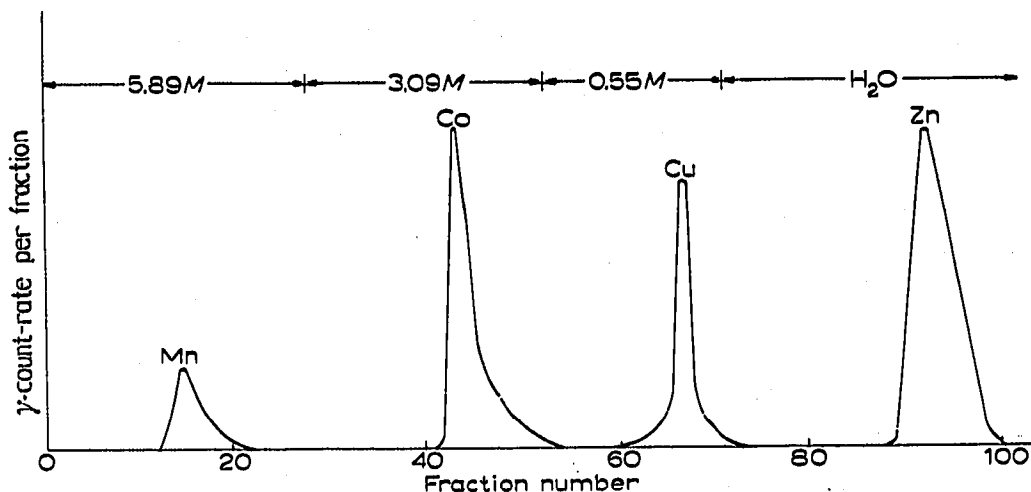


Fig. 5. Separation of Mn, Co, Cu and Zn by elution with hydrochloric acid from columns of TIOA-Corvic.

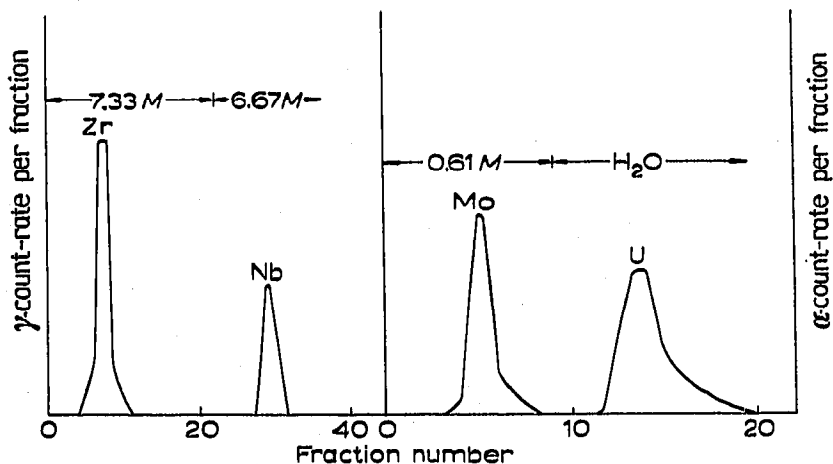


Fig. 6. Separation of Zr from Nb and Mo from U on columns of TIOA-Corvic. Nb eluted with 6.67 N sulphuric acid.

show relatively little tailing. The separation of manganese, cobalt, copper and zinc is shown in Fig. 5; as for the separation of the elements on a column of anion exchange resin by elution with hydrochloric acid¹⁰ manganese is eluted first, in this case with 5.89 *M* hydrochloric acid, cobalt is eluted next with 3.09 *M* hydrochloric acid whilst zinc, which is most firmly extracted by TIOA-Corvic is removed from the column with water after the copper has been eluted with 0.55 *M* hydrochloric acid.

Further examples, typical of the separation that can be achieved with TIOA-Corvic are shown in Fig. 6 for two pairs of elements. Again sharp peaks are obtained (a characteristic already noted for other amine columns⁹) which gives good solute disengagement and permits TIOA-Corvic to be used for the satisfactory separation of a wide range of elements.

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SUMMARY

A column material for partition chromatography has been prepared by retaining tri-iso-octylamine on an inert carrier. The behaviour of the material has been examined by batch extraction techniques, and a number of separations have been carried out.

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