THE PREPARATION OF CARRIER-FREE [115]In
BY A REVERSE PHASE PARTITION TECHNIQUE

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INTRODUCTION

The preparation of carrier-free tracers by the separation of a daughter element from its parent, has frequently necessitated complicated chemical procedures, but in a number of cases the method has been considerably simplified by the use of ion exchange techniques, which have allowed selective elution of the tracer required. Recently it has been shown that solutions of chelating agents in organic solvents may be retained on a solid supporting medium[1], and providing that the stabilities of the complexes formed by the chelating agent with parent and daughter differ sufficiently, it should be possible to carry out separation by selective elution in a manner exactly similar to that of the ion exchange technique.

Since the most convenient type of separation is that provided by elution of the daughter, the metal to be eluted should partition in favour of the eluting solvent, giving an R_F value approaching 1, whilst the parent should be retained by the support with an R_F value of near 0. This ensures that the minimum volume of eluting agent is required to effect the separation, and that contamination of the effluent by the parent is precluded.

This type of method has been used to separate carrier-free [115]In from parent [115]Cd, a procedure previously involving either a precipitation technique[2] or solvent extraction[3], since the greater stability of the complex of cadmium with dithizone (diphenyl thiocarbazone) enables the indium to be eluted preferentially from a dithizone column which initially contains both metals.

The dithizone column was made up as previously described[1] by retaining a solution of dithizone in an organic solvent on silica gel. In order to carry out column operation under conditions which approach equilibrium as nearly as possible, the organic solvent should favour quick reaction between metal and chelating agent. Chloroform and carbon tetrachloride are the two solvents most widely used for dithizone, and whilst carbon tetrachloride solutions tend, in general, to react more quickly with metals in acid solution[4] the greater solubility of dithizone in chloroform enables a support of higher capacity to be prepared. Consequently in these investigations, experiments were carried out using both chloroform and carbon tetrachloride as organic solvent.

Silica gel, 85–120 mesh, was prepared from sodium silicate by precipitation with 10 N hydrochloric acid and, after sieving, was purified by washing, first with successive volumes of concentrated hydrochloric acid until the acid remained colourless, and then with a strong ethylenediaminetetraacetic acid solution of pH 5. The gel was finally washed with water, alcohol and ether, and dried at 110°.[1]

A solution of purified dithizone[5] in organic solvent was added to the silica gel, and after thoroughly stirring the mixture, solvent was evaporated off with compressed air until a freely running powder was obtained. This powder was stored in a desiccator over organic solvent in the dark, and before use was always air dried to allow any surplus solvent to evaporate. The support was slurried with a N sodium acetate–hydrochloric acid buffer pH 5 and the column made up in the usual way.

The cadmium–indium mixture was retained as a thin band at the top of the column when the metals, in pH 5 buffer, were added as influent to the column.

After washing with pH 5 buffer the column was eluted with $N/500$ perchloric acid and the effluent from the column monitored for activity. In all cases the column size was 2.4 cm^2 × 4 cm and the flow rate was 0.15 ml/cm^2/min. The aqueous phases were presaturated with the organic solvent used on the silica gel.

The dithizone content of a given weight of support was determined by shaking the support with successive volumes of dilute aqueous ammonia until all the dithizone had been transferred into the aqueous phase, acidifying the combined aqueous extracts, and dissolving precipitated dithizone in carbon tetrachloride.

The optical density of the organic layer was measured and, using a value of $34.6 \cdot 10^3$ for the extinction coefficient of dithizone in carbon tetrachloride[6], the dithizone content of the column material calculated.

The behaviour of a metal M^{n+}, which forms a chelate in the aqueous phase of a two-phase system with a chelating agent HL according to the equation:

$$M^{n+} + n\text{HL} \rightleftharpoons \text{ML}_n + n\text{H}^+ \qquad (1)$$

has been shown to be given by[7]:

$$\frac{[\text{ML}_n]_o}{[\text{M}^{n+}]} = K \frac{P_c}{P_r{}^n} \frac{[\text{HL}]_o^n}{[\text{H}^+]^n} = K' \frac{[\text{HL}]_o^n}{[\text{H}^+]^n} \qquad (2)$$

where P_c and P_r are the partition coefficients of the chelate and chelating agent respectively, such that:

$$P_c = \frac{[\text{ML}_n]_o}{[\text{ML}_n]} \text{ and } P_r = \frac{[\text{HL}]_o}{[\text{HL}]}$$

and K is the equilibrium constant for eqn. (1). Square brackets represent concentra-

tions, which are used in place of activities for solutions of constant ionic strength, and the subscript o denotes species present in the organic phase. It is assumed that no intermediate chelate species are formed and that other complexes are absent. Under these circumstances $[ML_n]_o/[M^{n+}]$ may be identified with the fraction of metal extracted.

In the case of non-extractable complexes being formed in the aqueous phase between the metal and another anion, the fraction extracted E, where:
$E = \Sigma[M]_o/\Sigma[M]$ is now given by

$$E = K'' \frac{[HL]_o^n}{[H^+]^n} \qquad (2a)$$

but K'' now refers to a given anion concentration in the aqueous phase.

If, during the chromatographic elution of a metal, partitioning between a stationary phase and a mobile liquid, d_m and d_s are the distances travelled by metal and solvent front respectively, d_m will be proportional to the solubility of the metal in the mobile solvent whilst $d_s—d_m$ will be proportional to the solubility of the metal in the stationary phase[8].

Thus:

$$\frac{d_m}{d_s—d_m} = \frac{k}{E} \qquad (3)$$

where k is a constant accounting for the ratio of the cross-section of the moving and stationary phases.

Now

$$R_F = \frac{d_m}{d_s} \qquad (4)$$

so by combining eqns. (2a), (3) and (4):

$$\frac{1}{R_F} = 1 + \frac{K''}{k} \frac{[HL]_o^n}{[H^+]^n} \qquad (5)$$

provided eqn. (2a) represents the behaviour of a chelating agent retained on a solid support material.

From eqn. (5) it follows that an increase in R_F would result from either an increase in the hydrogen ion concentration, or a decrease in the ligand acid concentration. A high value of $[HL]_o$ will be required to provide a column with as large a capacity as possible, consequently the R_F value may be most conveniently varied either by alteration of the hydrogen ion concentration or by the use of water-soluble complexing agents which form non-extractable competitive complexes with the metal, and result in the lowering of the value of K''. For the separation of two metals, conditions must be chosen so that one metal can be eluted without contamination by the other, and it was found that indium could be selectively removed from a cadmium–indium mixture, retained on a dithizone column, with $N/500$ perchloric acid. Fig. 1 gives a plot of the activity of the effluent against effluent volume for the cases where carbon tetrachloride (curve A) and chloroform (curve B) were used as organic solvents. γ-Ray spectrometry and half-life determinations showed that the activity was due solely to 4.5 h [115]In and no trace of cadmium could be detected.

The peak effluent volume is smaller when carbon tetrachloride is used on the silica gel, but curve B more nearly approaches the "bell-shaped curves" expected for Gaussian distribution. The higher value of $[HL]_0$ attained with chloroform as solvent ($6.08 \cdot 10^{-3}$ mols dithizone per kg of support as opposed to $1.6 \cdot 10^{-3}$ mols/kg)
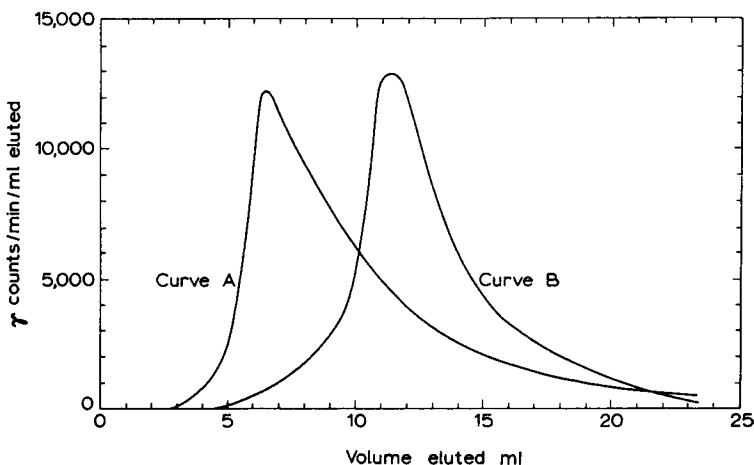

Fig. 1. Plot of activity against effluent volume for the elution of indium with perchloric acid. For curve A the organic solvent was carbon tetrachloride, for curve B, chloroform.

would be expected to favour a linear extraction isotherm and also to offset any increase in the value of K' that might occur if the chloroform was replaced by carbon tetrachloride. The dependence of the extraction process upon the presence of dithizone was verified by passing the cadmium-indium mixture in pH 5 buffer down a column of silica gel which had been treated with organic solvent but no dithizone. Under these conditions the metals were not retained by the column but passed through with the mobile phase and appeared in the effluent as soon as the liquid retained in the column had been displaced.

SUMMARY

A column of a solution of a chelating agent (dithizone) retained on silica gel, has been used to separate [115]In from the parent cadmium. The higher stability of the complex of cadmium with dithizone enables the indium to be preferentially eluted with dilute perchloric acid, whilst the cadmium, which remains complexed under these conditions, stays on the column.

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