

ION-EXCHANGE PAPER CHROMATOGRAPHY OF LANTHANIDE IONS

I. ANION EXCHANGE OF LANTHANIDE CITRATE COMPLEXES

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The method of paper partition chromatography has been applied to the separation of lanthanide ions by several workers, notably POLLARD, McOMIE AND STEVENS¹, LEDERER², and DANON AND LEVI³. While these investigations have been to some extent successful, the separation factors obtained have been low and separation of adjacent lanthanides has not been achieved except in the case of lanthanum and cerium^{2d}. In one of the most successful experiments LEDERER^{2d} obtained a practical separation factor (ratio of distances moved) of 1.3 between the next-but-one neighbours europium and promethium after five days elution with a mixture of ethanol and dilute hydrochloric acid.

A considerably greater extent of separation is obtained in the well-known chromatographic method using a column of cation-exchange resin and eluting with a solution of a complexing agent. For example MAYER AND FREILING⁴ using a column of Dowex 50 obtained, in less than 8 h, a practical separation factor of 3.5 between the next-but-one neighbours terbium and europium, using EDTA solution as eluent. Using citric acid for the elution the corresponding separation factor was 1.6.

In view of the simplicity and convenience of paper chromatography and the superior separating power of the ion-exchange method, it seemed desirable to investigate the use of the ion-exchange papers now available. Some preliminary work on the separation of rare earths using cellulosic cation-exchange papers has been reported by WELLS⁵. Separation of lanthanum, cerium and yttrium on paper impregnated with Dowex 50 was achieved by LEDERER⁶ using citric acid as eluent.

In the work reported here cellulosic anion-exchange resins have been used together with citric acid solutions for the elution.

EXPERIMENTAL

Whatman anion-exchange papers were used. There are three types: diethylaminoethyl-cellulose; aminoethyl-cellulose, and "ecteola" cellulose. The first mentioned was used most extensively.

The lanthanides, were in the form of radio-tracers, the following nuclides being

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used: ^{144}Ce (carrier-free), ^{147}Pm , $^{152} + ^{154}\text{Eu}$ (100 mC/g) and ^{160}Tb (initially 50 mC/g). Solutions of these (obtained from the Radiochemical Centre, Amersham) were diluted to concentrations of 5–50 $\mu\text{C/ml}$, 0.01–0.04 ml of the diluted solutions being taken for each chromatogram.

Chromatography was carried out on strips about 3 cm wide using downward flow of eluent. Convenient and simple holders for the paper and solvent were made from ordinary 4 oz. poly(ethylene) bottles. The lower half of the bottle was cut off and the resulting cylindrical pot provided on opposite sides with two horizontal slits about 4 cm long and 0.5 cm high, through which the paper strips could be inserted. These slits were made by cutting the sides and upper length of the rectangle and then bending the resulting strip outwards over a hot glass rod. This produced a protruding lower lip which kept the paper away from the sides of the bottle and this prevented siphoning. The vessel was closed with a stopper through which passed a thistle funnel whose stem passed almost to the bottom of the vessel. The polythene vessel was held in the neck of a gas-jar by means of a larger stopper. This apparatus has the advantage, apart from its negligible cost, that the paper may be placed in position and aligned with the holder empty; the solvent may then be added at any convenient time through the thistle funnel.

The paper strips were pretreated with the eluent to be used and were then air-dried before adding the tracer solution. Chromatograms were evaluated by cutting the dried strips of paper into 1 cm sections and measuring the activity of each section with a Geiger-Müller counter. Strictly therefore, the resulting chromatograms should be drawn as histograms, but for convenience they were drawn as smoothed curves. In most cases chromatograms were run with cerium and one other lanthanide. To confirm the identity of a particular peak, the counts were often repeated with the interposition of an aluminium absorber just thick enough to absorb the β -particles of the lanthanide giving the less energetic β -particles—in practice the one other than cerium (*cf. ref. 7*).

RESULTS

(i) Diethylaminoethyl-cellulose (DEAC)

Examples of the chromatograms obtained with this paper are shown in Figs. 1 and 2. It will be seen that the R_F value decreases with increasing atomic number of the lanthanide. This is to be expected, since retention depends on the formation of anionic citrate complexes whose stability should increase with decreasing size of the lanthanide ion.

Chromatograms of this type were carried out using a number of different citric acid concentrations and the effects of adding ethanol to the solvent and of lowering the pH by adding HCl were also investigated. The most convenient eluent was found to be a 0.026 M (0.5 %) solution of citric acid in water; the pH of this solution is 2.4.

The results are summarised in Table I.

In order to produce measurable separations it was necessary to choose conditions where R_F values are low, and to continue eluting long after the solvent front had reached the end of the paper. This means that direct observation of the R_F values was not generally possible, and the values reported are based on the estimated "position" of the solvent front obtained by extrapolating time-distance curves for the movement of the solvent front in the early stages of the experiments. (The rate of movement

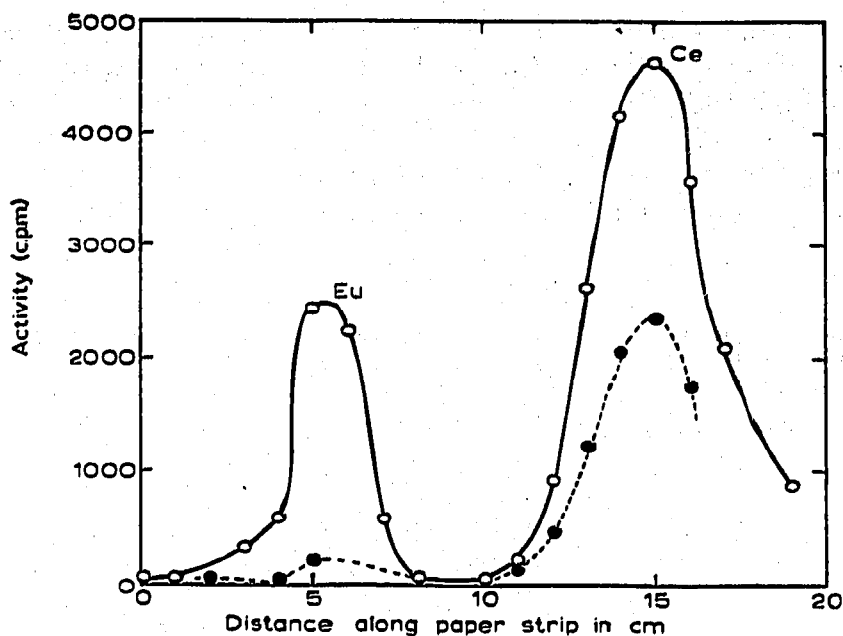


Fig. 1. Separation of ^{144}Ce and $^{152} + ^{154}\text{Eu}$ on DEAC paper by elution with 0.026 *M* citric acid. The dotted curve shows the activity measured through an aluminium absorber of thickness 248 mg/cm^2 which absorbs most of the emission from europium. Elution time 5 h.

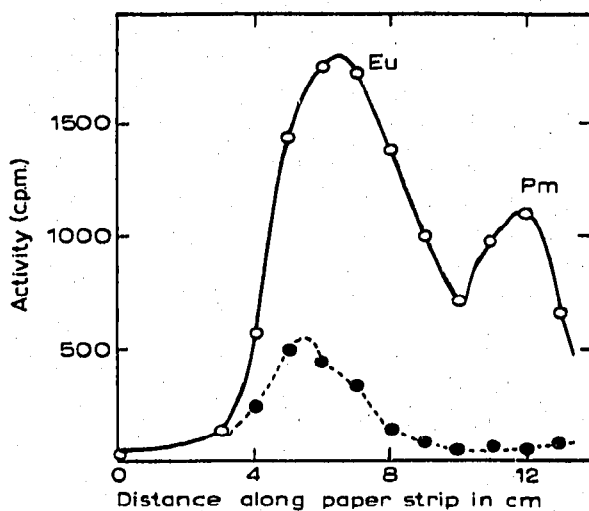


Fig. 2. Separation of ^{147}Pm and $^{152} + ^{154}\text{Eu}$ on DEAC paper by elution with 0.026 *M* citric acid solution containing 40% of ethanol. The dotted curve shows the activity measured through an aluminium absorber of thickness 41 mg/cm^2 which absorbs all of the emission from promethium. Elution time 30 h.

down the paper is not constant but tends to be faster in the initial stages.) In view of this R_F values are reported for cerium only, but values of apparent separation factors for cerium are given for the other ions used, since the distances moved by the peaks can be measured directly.

It will be seen that the R_F value is increased by increasing the citric acid concentration or by addition of HCl. These may be regarded as two different methods of

TABLE I
SEPARATIONS ON DEAC PAPER WITH CITRIC ACID SOLUTION AS ELUENT

Composition of eluent			$(R_F)_{Ce}$	d_{Ce}/d_{Eu}^*	d_{Ce}/d_{Tb}	d_{Ce}/d_{Pm}
Citric acid molarity	HCl molarity	Ethanol % v/v				
0.026	—	—	0.17	2.6	2.6	2.2
0.010	—	—	0.06		2.2-3.4	
0.0026	—	—	0.006	3		
0.026	—	10		2.4-3.4	2.9	
0.026	—	20	0.04	3.2-3.6		
0.2	—	60	0.03	2.2-3.8		
0.5	—	60	0.4	1.5		
0.010	—	20	0.02	3.2		
0.026	0.026	—		2.0		
0.026	0.04	—	0.6	1.4		
0.026	0.026	20	0.25	1.8		

* The apparent separation factor, (e.g. d_{Ce}/d_{Eu}), is the ratio of the distance moved by one ion (e.g. Ce^{3+}) to that moved by the other (e.g. Eu^{3+}).

lowering the pH and thereby reducing the concentration of anionic complexes. Addition of ethanol on the other hand lowers the R_F value to a marked extent. The apparent separation factors seem generally to be increased by those factors which reduce the R_F values. This makes it advantageous to use eluents containing ethanol. This is shown in the separation factor of 1.8 between the next-but-one neighbours Pm and Eu (Fig. 2) obtained using 0.026 M citric acid in 40% ethanol; in absence of the ethanol the separation factor was 1.3 determined directly, or only 1.2 calculated indirectly from measurements against Ce. On the other hand eluents containing ethanol often gave erratic and unreliable results.

(ii) Aminoethyl-cellulose paper (AEC)

Retention of rare earth-citrate complexes on this ion-exchange paper is greater than that of the DEAC paper discussed above. Thus using 0.026 M citric acid, the R_F value for cerium is about 0.006 for AEC paper as compared with the value of 0.17 for DEAC paper. Separations were produced on this paper but these required rather long times (40-70 h) and gave apparent separation factors similar to those found for DEAC paper, i.e. $d_{Ce}/d_{Tb} \approx 3$. The R_F values could be increased and the time shortened by using higher citric acid concentrations, but this lowered the separation factors.

(iii) "Ecteola" paper

This anion-exchange paper gave very high R_F values with the eluents used for the other papers. These values could be reduced by addition of ethanol or by lowering the citric acid concentration. No satisfactory results were obtained on this paper, however. The peaks obtained were very broad and in many cases irregular, as if a variety of small peaks were superimposed upon the main peaks.

DISCUSSION

HUFFMAN AND OSWALT⁷ investigated the separation of tracer quantities of rare earths on a column of anion-exchange resin (Dowex A-1) using a 0.0125 *M* solution of citric acid acidified to pH 2.1 with HCl. They report a chromatogram for Eu and Pm which shows an apparent separation factor of 1.3; this is identical with our value using aqueous citric acid and DEAC paper; their separation is nevertheless superior even to that shown in Fig. 2—where the separation factor is 1.8—owing to the greater sharpness of the peaks. Other workers^{8,9} have reported separations of lanthanide ions on anion-exchange columns with citric acid as eluent.

The apparent separation factor is of course not a fundamental property of the system. According to simple chromatographic theory (see, *e.g.*, ref.¹⁰):

$$(R_F)_A = \frac{1}{D_A + 1} \quad (1)$$

where D_A is the distribution ratio of the constituent A between the stationary and the mobile phases. The true separation factor for two constituents A and B is equal to the ratio of their distribution ratios; in ion-exchange terminology this is usually called the selectivity coefficient K_{B^A} , so that we may write:

$$K_{B^A} = D_A/D_B \quad (2)$$

It may readily be shown by combining eqns. (1) and (2) that the practical separation factor is given by the following equation:

$$\frac{d_A}{d_B} = (R_F)_A/(R_F)_B = (R_F)_A (1 - K_{A^B}) + K_{A^B} \quad (3)$$

When the concentration and pH of the eluent changes the separate R_F values of the two constituents change, but it is possible for their ratio, *i.e.* K_{B^A} , to remain constant. This is the case for rare earth elutions where only one type of complex ion is formed; MAYER AND FREILING⁴ have pointed out that in this case the true separation factor for two ions is equal to the ratio of the formation constants of the corresponding complex ions.

If this is the case here and $K_{Ce^{Eu}}$ is a constant, eqn. (3) predicts that a graph of practical separation factor against the R_F value for cerium should be a straight line of intercept $K_{Ce^{Eu}}$ and slope $(1 - K_{Ce^{Eu}})$. The results of Table I are plotted in this way in Fig. 3. It will be seen that there is no support for the hypothesis of a constant selectivity coefficient. At low R_F values a value of 3.2 for $K_{Ce^{Eu}}$ fits the

results best, but at higher R_F values $K_{Ce}^{Eu} = 2.1$ gives a better fit. Hence the selectivity is reduced by addition of HCl or by using high concentrations of citric acid.

Many studies have been made¹¹ of the separation of rare earths on cation-exchange columns by elution with citric acid solutions, mostly at pH values close to 3.

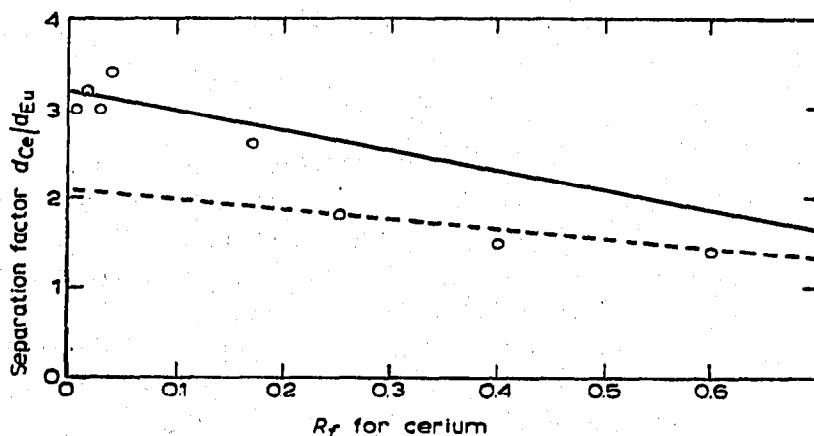
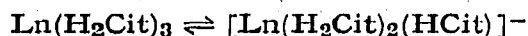


Fig. 3. Test of eqn. (3). Theoretical line for $K_{Ce}^{Eu} = 3.2$ drawn continuous. Theoretical line for $K_{Ce}^{Eu} = 2.1$ drawn dotted.

According to TOMPKINS AND MAYER¹² the complex ions produced are of the type: $La(H_2Cit)_3$, and only at pH values above 3.5 are appreciable amounts of anionic complexes formed. The work described here, and that of other investigators⁷⁻⁹ shows, however, that on anion exchangers strong adsorption from citrate solutions occurs even at pH values around 2, so that some type of dissociation of the neutral complexes, e.g.:



must be strongly favoured by the anion-exchange resin.

The equilibrium studies of TOMPKINS AND MAYER predict a separation factor of 7.2 between terbium and cerium at pH 2.88 on a cation-exchange resin. This is far higher than the value of about 3 found in the present work on anion exchange. Consistent with this, TOMPKINS AND MAYER found lower separation factors at higher pH values and attributed this to the formation of the anionic complexes which are essential in the present work.

The practical separation factors obtained^{11,13} in separations on cation-exchange columns using citric acid are generally somewhat higher than those found in the present work, but not as high as those predicted by the equilibrium studies of TOMPKINS AND MAYER. It is possible therefore that anion exchange using citrate complexes might prove practically useful, particularly in any case where it would be convenient to have the usual elution order for the lanthanides reversed.

ACKNOWLEDGEMENT

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SUMMARY

The application of cellulosic anion-exchange papers to the separation of tracer amounts of rare earths has been investigated, using citric acid solutions as eluents. It was found most satisfactory to use diethylaminoethyl-cellulose paper with 0.026 *M* citric acid (pH 2.4) as eluent. Under these conditions a practical separation factor of 2.6 between europium and cerium was obtained. Slightly higher separation factors could be obtained by adding ethanol to the citric acid solutions.

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