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EXPERIMENTAL DETERMINATION OF ELUTION REQUIREMENTS  
IN DISPLACEMENT ION EXCHANGE\*

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## SUMMARY

It is clear that the progress of separation of any number of lanthanons by displacement ion-exchange elution can be predicted by expressions derived from the basic equilibria involved. The computation process can be reversed so that separation factors are obtained from boundary movement diagrams.

## INTRODUCTION

Separation theory pertinent to resolution of lanthanide (and other) mixtures *via* chelate formation and displacement cation-chromatography has evolved gradually from an approach suggested by POWELL AND SPEDDING in 1959<sup>1</sup>. Since then, noteworthy contributions have been made regarding the treatment of ternary<sup>2, 3</sup> and more general multicomponent mixtures<sup>4, 5</sup>. The treatment herein is intended to paraphrase the general elegant development of HELFFERICH AND JAMES<sup>5</sup>, and to illustrate that not only can boundary movement diagrams be constructed (and elution requirements be determined) from a prior knowledge of mixture composition and separation factors but, conversely, that practical separation factors can be established from experimentally determined boundary movements.

## THEORY

Imagine a quantity of multicomponent mixture of lanthanides deposited non-selectively on a cation-exchange bed, forming a loaded zone in which the mole fraction  $\bar{X}_1$  of each component is uniform throughout. The charge is to be eluted under conditions promoting displacement chromatographic elution, *i.e.*, so that small increments of the material sorbed in the load zone are continually displaced from the stationary phase at the rear (upstream boundary) of the zone, percolated in dilute solution in

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the mobile aqueous phase through the rest of the sorbed mixture, and redeposited on the stationary phase at the front (downstream edge) of the load zone. Such behavior is promoted by employing a dilute solution of ammonium salt of a strongly chelating anion (such as the EDTA or HEDTA anion) as the eluant and having the cation-exchange bed ahead of the load zone charged with a cationic species that forms a more stable complex with the chelating agent than does any component of the mixture being separated. If the chelant is selective in the degree to which it complexes individual lanthanons (and/or the resin itself manifests selectivity), the system exhibits a series of separation factors ( $\alpha_i^1$ ) between the first (most easily eluted) lanthanon and the other components of the mixture. The individual separation factors relative to component 1 may be represented generally as

$$\alpha_i^1 = (X_1/X_i) / (\bar{X}_1/\bar{X}_i) \quad (i = 1 \text{ through } n) \quad (1)$$

where  $X_i$  and  $\bar{X}_i$  are the mole fractions of the  $i$ th component existing in the solution and resin phases, respectively, when the components of the two phases are at equilibrium. From this definition of the separation factors involved, and the stipulation that  $X_1 + X_2 + \dots + X_n = 1$ ,

$$\frac{X_1\bar{X}_1}{\alpha_1^1\bar{X}_1} + \frac{X_1\bar{X}_2}{\alpha_2^1\bar{X}_1} + \dots + \frac{X_1\bar{X}_n}{\alpha_n^1\bar{X}_1} = 1 = (X_1/\bar{X}_1) \sum_{i=1}^n (\bar{X}_i/\alpha_i^1) \quad (2)$$

Since  $(X_1/\bar{X}_1)$  equals  $\alpha_j^1(X_j/\bar{X}_j)$  under equilibrium conditions, it is seen that the mole fraction of any solution component at equilibrium with a sorbed mixture is defined by the expression

$$X_j = \bar{X}_j / \left( \alpha_j^1 \sum_{i=1}^n (\bar{X}_i/\alpha_i^1) \right) \quad (3)$$

Under these conditions, from the moment elution is initiated until the load is displaced sufficiently to effect disengagement of components 1 and  $n$ , two series of concentration subzones (plateaus) of decreasing multiplicity develop (one series downstream and one upstream from the diminishing residual  $n$ -component zone). Each developing subzone, as well as the diminishing zone of original mixture, is defined at its extremities by recognizable boundaries (actually narrow concentration gradient regions between concentration plateaus) associated with successive disappearance, one at a time, of individual components ( $n$  through 1 downstream, and 1 through  $n$  upstream). That is, until components 1 and  $n$  disengage from each other, the individual chromatographic subzones (from the downstream end to the upstream end of the load zone) contain the components 1; 1,2; 1,2,3; ...; 1,2,3, ...,  $n$ ; 2,3,4, ...,  $n$ ; ...;  $n - 1$ ,  $n$ ;  $n$ , respectively.

The rate of movement of the boundary which separates the front of the  $n$ -component subzone from the rear of the downstream ( $n - 1$ )-component subzone (devoid of component  $n$ ) is determined by the circumstance that the  $n$ -component zone contains  $\bar{X}_n$  moles of component  $n$  per mole of mixture, and the fact that equilibrium considerations dictate a net transport, rearward across the  $n$ -component zone, amounting to  $(\bar{X}_n - X_n)$  moles of component  $n$  per mole of load displacement. It is obvious from this that the rate at which this boundary progresses down the system

amounts to  $(1 - (\bar{X}_n - X_n)/\bar{X}_n)$  or simply  $(X_n/\bar{X}_n)$  moles per mole of load displaced by elution. By similar lines of reasoning, one concludes that the upstream boundary of the  $n$ -component residual zone progresses downstream on the resin bed system at a rate of  $(1 + (X_1 - \bar{X}_1)/\bar{X}_1)$  or  $(X_1/\bar{X}_1)$  moles per mole of load displacement. In fact, it is clear that each boundary between consecutive subzone mixtures of decreasing multiplicity (both downstream and upstream) moves at a rate (moles per mole of load displacement) fixed simply by the ratio of mole fractions (in solution and on the resin) of the singular component which is missing on one side of the concentration gradient region which comprises the boundary. The composition of each uniform mixture comprising a downstream subzone, therefore, depends directly on the composition of the mixture of next higher multiplicity situated immediately upstream.

Let  $d$  be the integral order number for the position of a particular subzone mixture (numbered downstream from the residual  $n$ -component mixture), so that  $n - d$  denotes both the multiplicity of the mixture and the sequential elution order number of the singular component (present only on the upstream side of the gradient region dividing the  $d$  and  $d + 1$  subzones). Then the mole fractions ( ${}_{d+1}X_j$  and  ${}_{d+1}\bar{X}_j$ ) in solution and on the resin of the  $j$ th component present in the  $d + 1$  subzone are related to the mole fractions ( ${}_dX_j$  and  ${}_d\bar{X}_j$ ) of that element and the mole fractions ( ${}_dX_{n-d}$  and  ${}_d\bar{X}_{n-d}$ ) of the slowest-moving component ( $n - d$ ) present in the  $d$  subzones as follows:

$$({}_{d+1}X_j - {}_dX_j) / ({}_{d+1}\bar{X}_j - {}_d\bar{X}_j) = {}_dX_{n-d} / {}_d\bar{X}_{n-d} \quad (4)$$

Since requirements for equilibrium (eqn. 3) are such that

$${}_dX_j = {}_d\bar{X}_j / \left( \alpha_j^1 \sum_{i=1}^{n-d} ({}_d\bar{X}_i / \alpha_i^1) \right) \quad (5)$$

$${}_dX_{n-d} = {}_d\bar{X}_{n-d} / \left( \alpha_{n-d}^1 \sum_{i=1}^{n-d} ({}_d\bar{X}_i / \alpha_i^1) \right) \quad (6)$$

$${}_{d+1}X_j = {}_{d+1}\bar{X}_j / \left( \alpha_j^1 \sum_{i=1}^{n-d-1} ({}_{d+1}\bar{X}_i / \alpha_i^1) \right) \quad (7)$$

it is readily deduced that

$${}_{d+1}\bar{X}_j = \frac{{}_d\bar{X}_j(1 - \alpha_{n-d}^j)}{1 - \alpha_{n-d}^j(D/D')} \quad (8)$$

and since  $\sum_{j=1}^{n-d-1} ({}_{d+1}\bar{X}_j) = 1$ , that

$$\sum_{j=1}^{n-d-1} \frac{{}_d\bar{X}_j(1 - \alpha_{n-d}^j)}{1 - \alpha_{n-d}^j(D/D')} = 1 \quad (9)$$

where  $D$  equals  $\sum_{i=1}^{n-d} ({}_d\bar{X}_i / \alpha_i^1)$ , a predetermined quantity, and  $D'$  equals  $\sum_{i=1}^{n-d-1} ({}_d\bar{X}_i / \alpha_i^1)$ ,

an unknown involving the (as yet undetermined) mole fractions of the  $n-d-1$  components in the  $d + 1$  subzone.

After expanding the condensed eqn. 9 and substituting the various known  ${}^a\bar{X}_j$  and  $\alpha_{n-d}^j$  values, as well as the (from these) predetermined  $D$  term,  $D'$  is found by solving the resulting polynomial (quadratic when  $n-d-1$  equals 2, cubic when  $n-d-1$  equals 3, etc.). Since  $D < D' < 1$ , the polynomial in  $D'$  is readily obtained by successive approximations utilizing an appropriately programmed electronic computer. After finding  $D'$ , it is a simple matter to establish the individual  ${}^{a+1}\bar{X}_j$  values by means of eqn. 8. It is thus seen to be a straightforward although laborious, algebraic exercise to compute the compositions (mole fractions of each component) of the uniform mixtures in every downstream subzone, one after the other, from a knowledge of the initial composition of the  $n$ -component residual mixture from which subzones are successively generated.

The situation upstream from the  $n$ -component residual mixture is very similar to that existing downstream. The composition of each subzone is generated by equilibrium and transport phenomena from the preceding subzone containing one more component. If  $u$  is used to denote the order number upstream from the  $n$ -component mixture of a particular subzone, so that  $u+1$  describes the sequential elution order number of the fastest moving component in that subzone, the mole fractions ( ${}^{u+1}X_j$  and  ${}^{u+1}\bar{X}_j$ ) of component  $j$  in the next ( $u+1$ ) subzone are related to the mole fractions ( ${}^uX_j$  and  ${}^u\bar{X}_j$ ) of that element and to the mole fractions ( ${}^uX_{u+1}$  and  ${}^u\bar{X}_{u+1}$ ) of the fastest moving component of the  $u$  subzone, as follows:

$$({}^{u+1}X_j - {}^uX_j) / ({}^{u+1}\bar{X}_j - {}^u\bar{X}_j) = {}^uX_{u+1} / {}^u\bar{X}_{u+1} \quad (10)$$

where equilibrium considerations dictate that

$${}^uX_j = {}^u\bar{X}_j / \left( \alpha_j^{u+1} \sum_{i=u+1}^n ({}^u\bar{X}_i / \alpha_i^{u+1}) \right) \quad (11)$$

$${}^uX_{u+1} = {}^u\bar{X}_{u+1} / \left( \sum_{i=u+1}^n ({}^u\bar{X}_i / \alpha_i^{u+1}) \right) \quad (12)$$

$${}^{u+1}X_j = {}^{u+1}\bar{X}_j / \left( \alpha_j^{u+2} \sum_{i=u+2}^n ({}^{u+1}\bar{X}_i / \alpha_i^{u+2}) \right) \quad (13)$$

Thus, for adjacent subzones,  $u$  and  $u+1$  (numbered upstream), prior to the time that components 1 and  $n$  disengage from each other,

$${}^{u+1}\bar{X}_j = \frac{{}^u\bar{X}_j(1 - 1/\alpha_j^{u+1})}{1 - U/(\alpha_j^{u+2}U')} \quad (14)$$

and

$$\sum_{j=u+2}^n \frac{{}^u\bar{X}_j(1 - 1/\alpha_j^{u+1})}{1 - U/(\alpha_j^{u+2}U')} = 1 \quad (15)$$

where  $U$  is the known quantity  $\sum_{i=u+1}^n ({}^u\bar{X}_i / \alpha_i^{u+1})$  and  $U'$  is the unknown

$\sum_{i=u+2}^n ({}^{u+1}\bar{X}_i / \alpha_i^{u+2})$ . The polynomial in  $U'$  obtained by expanding eqn. 15 is solved for

$U'$  in exactly the same way that the polynomial from eqn. 9 was solved for  $D'$ . Then the values of  ${}^{u+1}\bar{X}_j$  are obtained from eqn. 14.

After components 1 and  $n$  have disengaged, a second generation subzone (comprised of elements 2 through  $n - 1$ ) begins to form from the first generation upstream and downstream subzones (comprised of components 2 through  $n$  and 1 through  $n - 1$ , respectively). As other fast moving and slow moving components disengage, additional subzones form and disappear until the original mixture is separated into  $n$  unicomponent regions. The pattern and parentage of individual subzones is indicated in Fig. 1. It is seen that many of the subzones indicated form at the expense of two parent subzones; however, one needs only to know the composition of one parent to

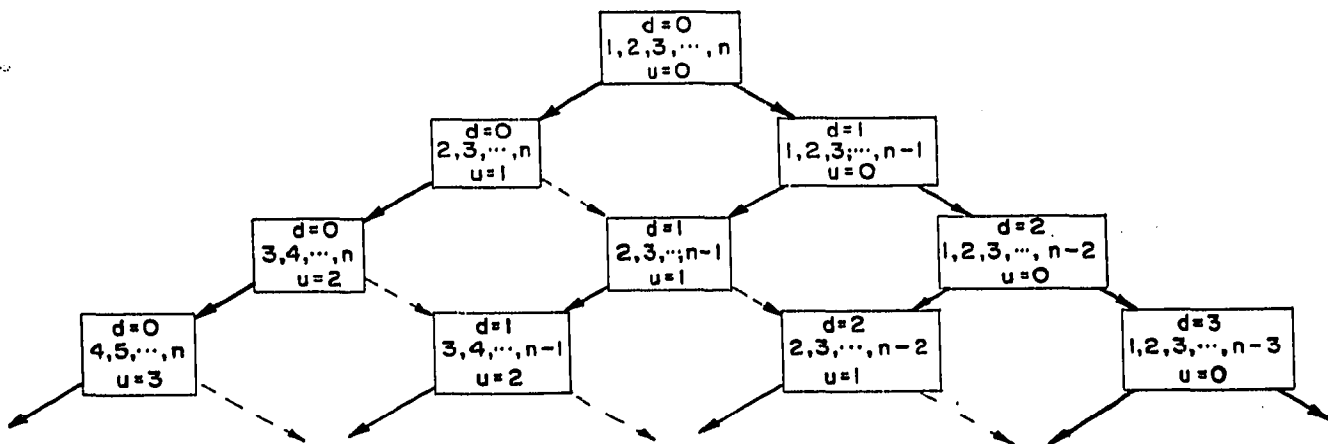


Fig. 1. Hierarchy of plateaus and subzones in an ion-exchange displacement separation.

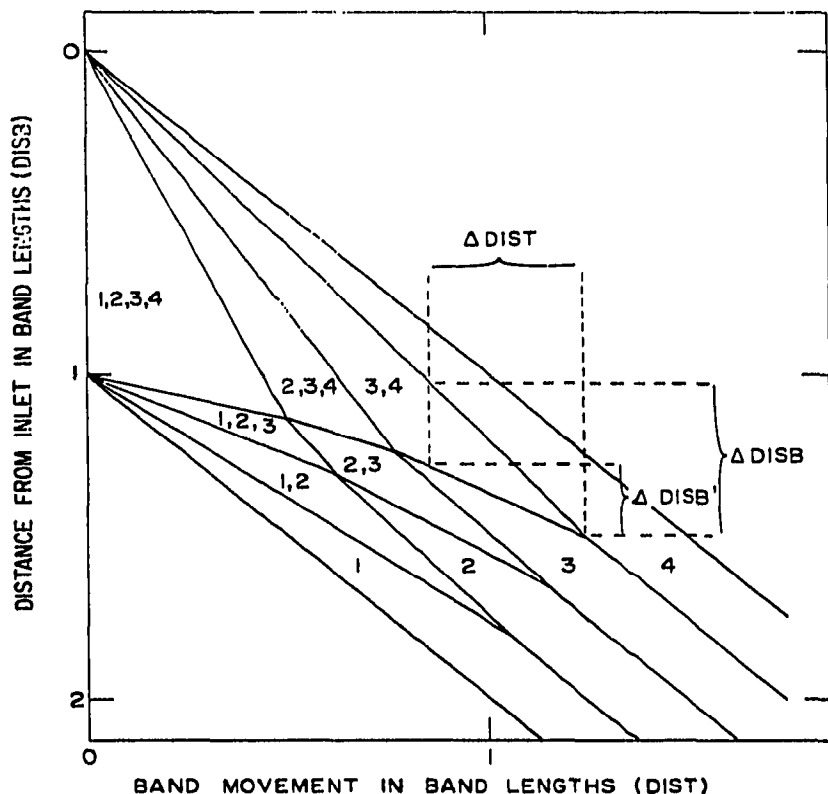


Fig. 2. Boundary movement diagram for a four element separation.

ascertain the composition of a dependent zone. That is, just as the composition of each mixture along the upper lefthand diagonal (Fig. 1) may be computed, one after the other, from the composition of the original mixture, the composition of each mixture along subsequent left-sloping sets can be determined from the composition of less and less complex mixtures computed down the upper righthand diagonal (see computational sequences indicated by the arrows in Fig. 1).

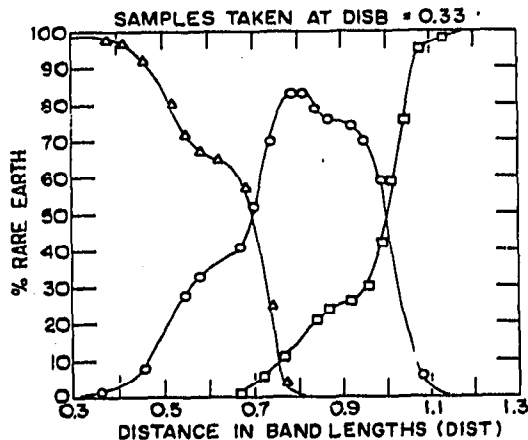
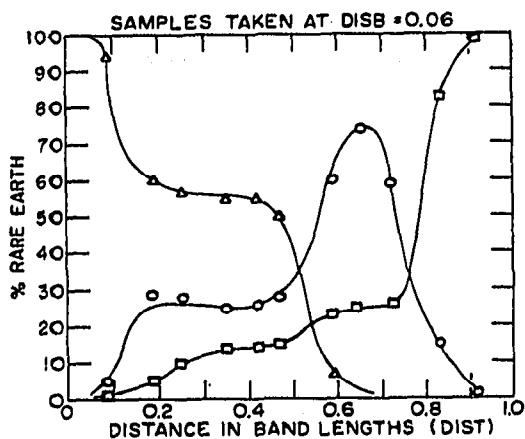
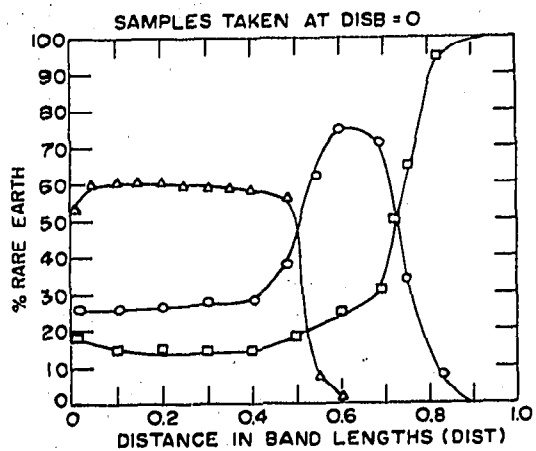


Fig. 3. Successive band profiles of a thulium, ytterbium, erbium separation.

Knowledge of the various  $(X_j/\bar{X}_j)$  values corresponding to specific subzone mixtures enables one to construct boundary movement diagrams (point-slope-intersection plots) in which line segment intersections determine the elution distances required to achieve disengagement of specific pairs. Conversely, if the individual separation factors are not known in advance, boundary movement diagrams can be constructed by interpreting analytical profiles taken at a number of fixed points along the bed system during the elution of a mixture. These diagrams can then be used to assess the various  $\alpha_k^j$  values operative during the elution (see Fig. 2). The slopes  $(\Delta\text{DISB}/\Delta\text{DIST})$  and  $(\Delta\text{DISB}'/\Delta\text{DIST})$  of pairs of converging line segments

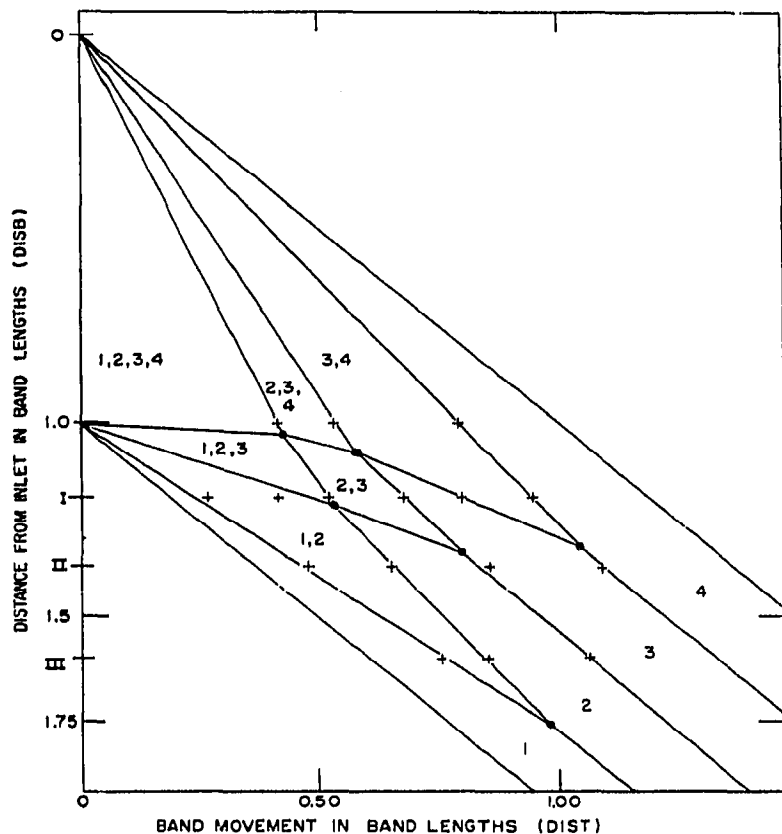


Fig. 4. Boundary movement diagram for an erbium, holmium, dysprosium, terbium separation.

(which represent rates of progress of the upstream and downstream boundaries of diminishing mixtures) define the ratios  $(X_j/\bar{X}_j)$  and  $(X_k/\bar{X}_k)$ , where the subscripts  $j$  and  $k$  denote the elution order numbers of the unique components (present in the subzone under consideration but absent from the next upstream and next downstream subzones, respectively). Consequently,

$$\alpha_k^j = (X_j/\bar{X}_j)/(X_k/\bar{X}_k) = \Delta\text{DISB}/\Delta\text{DISB}' \quad (16)$$

#### EXPERIMENTAL

The cation-exchange beds used in this work were comprised of 40-50 mesh spheres of Dowex 50 X8 packed in 2-in. I.D. Pyrex glass columns, fitted with Saran

cloth bed supports, neoprene gaskets and Plexiglass end closures. The bed systems generally consisted of a load zone section followed by a series of shorter appendages allow convenient withdrawal of analytical samples from the aqueous phase at pre-determined points along the system as the elution progressed. In all experiments the eluant was 0.014 *M* ammonium EDTA solution adjusted to pH 8.4. The retaining bed (in the short appendages) was initially charged with a  $\text{Cu}^{2+}$ - $\text{H}^{+}$  mixture by passing a 1 *M*  $\text{CuSO}_4$ -1 *M*  $\text{H}_2\text{SO}_4$  mixture through the appendages. The aqueous phase samples were analyzed spectrophotometrically.

### Experiment I

The load zone section was loaded to saturation with an excess of Er-Tm-Yb chloride mixture and flushed with distilled water in a backwash operation to insure uniform distribution of the components within the load zone. A series of  $\text{Cu}^{2+}$ - $\text{H}^{+}$

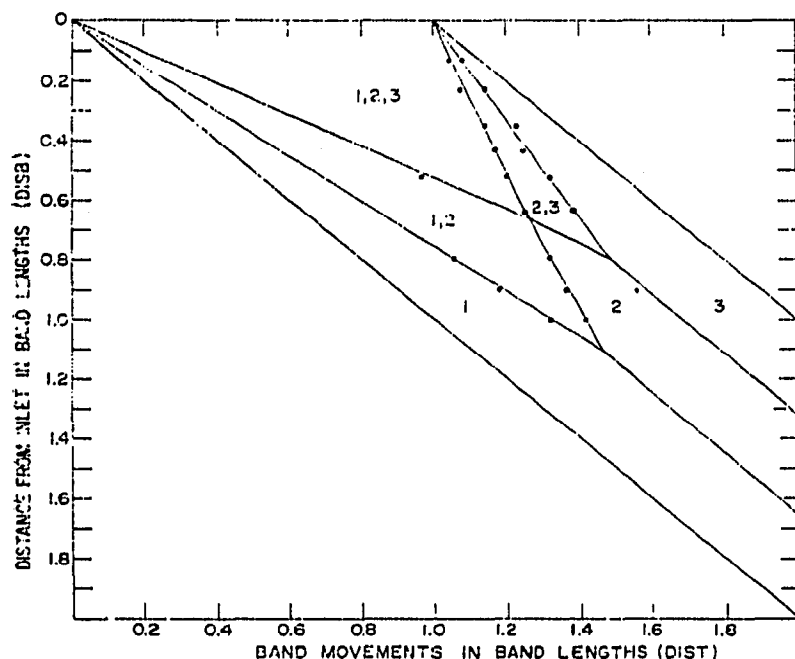


Fig. 5. Boundary movement diagram for a prechelated thulium, ytterbium, erbium separation.

beds (0.06, 0.33, 0.51, 0.68 and 1.0 times the capacity of the load zone) was appended to the load zone section, and elution was initiated at *ca.* 25° and a flow rate of 25 ml per min. Samples of the eluate passing between column segments were withdrawn periodically and analyzed carefully. Fig. 3 shows compositions observed at typical sampling points as a function of elution progress. From such plots it was ascertained when (in terms of band lengths) each subzone boundary had progressed a specified distance.

### Experiment II

An Er-Ho-Dy-Tb mixture was loaded and eluted as in the first experiment and profiled at points designated by O, I, II, and III along the ordinate of Fig. 4.



*Experiment III*

Equilibrated solutions of erbium EDTA, thulium EDTA and ytterbium EDTA obtained from a set of previous elutions were mixed and passed onto a system of retaining beds followed by ammonium EDTA eluant. The mixture was sampled periodically in transit at points corresponding to 0.13, 0.23, 0.35, 0.43, 0.52, 0.64, 0.80, 0.90 and 1.00 band lengths to construct Fig. 5.

## RESULTS AND DISCUSSION

The boundary movement diagrams obtained experimentally were used to establish separation factors and the results are compared in Table I to separation factors computed solely from literature values of lanthanide EDTA stability constants<sup>6,7</sup>. It is seen that agreement between the practical results and the predicted values (in parentheses) is fair in most instances. Hence this approach provides means for studying chelate formation under conditions not suitable for potentiometric and polarographic measurements. For example, separation factors have been established in this way at elevated temperature and used to confirm a predicted change in dentate character of the HEDTA ligand<sup>8</sup>.

TABLE I

COMPARISON OF PRACTICAL AND THEORETICAL SEPARATION FACTORS

<i>Experiment</i>	<i>R.E. pair</i>	<i>Separation factor</i>
I	Yb-Tm	2.8 (1.8)
	Tm-Er	2.3 (3.1)
	Yb-Er	6.2 (5.6)
II	Er-Ho	1.6 (1.8)
	Ho-Dy	2.7 (2.6)
	Dy-Tb	2.4 (2.3)
	Er-Dy	4.4 (4.7)
	Er-Tb	10.7 (10.1)
	Ho-Tb	6.7 (5.9)
III	Yb-Tm	2.9 (1.8)
	Tm-Er	1.9 (3.1)
	Yb-Er	5.6 (5.6)

## REFERENCES

- 1 J. E. POWELL AND F. H. SPEDDING, *Chem. Eng. Progr. Symp. Ser.*, 55, No. 24 (1959) 101.
- 2 J. E. POWELL, H. R. BURKHOLDER AND D. B. JAMES, *J. Chromatog.*, 32 (1968) 559.
- 3 D. B. JAMES, J. E. POWELL AND H. R. BURKHOLDER, *J. Chromatog.*, 35 (1968) 423.
- 4 L. G. SILLEN, *Arkiv. Kemi*, 2 (1950) 277.
- 5 F. HELFFERICH AND D. B. JAMES, *J. Chromatog.*, 46 (1970) 1.
- 6 E. J. WHEELWRIGHT, F. H. SPEDDING AND G. SWARZENBACH, *J. Am. Chem. Soc.*, 75 (1953) 4196.
- 7 J. E. POWELL, *Progress in the Science and Technology of Rare Earths*, Pergamon, Oxford, 1964, p. 62.
- 8 J. E. POWELL AND H. R. BURKHOLDER, *J. Chromatog.*, 36 (1968) 99.