

## SEPARATION OF HEAVY RARE EARTHS BY REVERSED-PHASE PARTITION CHROMATOGRAPHY

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In our previous paper<sup>1</sup> it was shown that small amounts of some light rare earths can be clearly separated by means of reversed-phase partition chromatography, using tributyl phosphate (TBP) as the stationary phase and  $\text{HNO}_3$  as the mobile phase. The separation of heavy rare earths by this method appears to be more difficult, since their separation factors are generally smaller than those of the light rare earths<sup>2,3</sup>. Nevertheless, it seems that the effect of the smaller separation factors can be outweighed by using columns of better separating power. The present paper describes the results obtained with the heavy rare earths from Tb to Lu using  $\text{HNO}_3$  and HCl as eluting agents.

### EXPERIMENTAL

The radioactive rare earths were prepared by irradiation of the appropriate oxides in the Polish reactor "EWA".

The columns used in the course of this work were of the same size as previously described<sup>1</sup> and were prepared by the same method. Special attention was paid to the packing of the beds in order to obtain columns with the highest separating power. The flow rate was 4 drops per minute or  $0.4 \text{ ml.cm}^{-2}.\text{min}^{-1}$ . The total amount of each of the rare earths introduced into the column was less than 0.01 mg, and the volume of the radioactive solution was 0.04 ml.

### RESULTS AND DISCUSSION

#### *Elution with $\text{HNO}_3$*

The separation of Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu with 11.5 M  $\text{HNO}_3$  as eluting agent is shown in Fig. 1. With this concentration of  $\text{HNO}_3$  there is only slight overlapping of the Tb and Dy curves. Better separation can be achieved with 12.3 M  $\text{HNO}_3$  (Fig. 2), and still better with 13.0 M  $\text{HNO}_3$  (Fig. 3), but in the latter case the time needed for elution of all the heavy rare earths is too long, since the partition coefficients are too high. The positions of the maxima of heavy rare earths, when eluted with 12.3 M  $\text{HNO}_3$ , relative to the position of Tb, and the partition coefficients at the same acid concentration relative to the partition coefficient of Tb are given in Table I. The partition coefficients with 12.3 M  $\text{HNO}_3$  were taken from the paper published by HESFORD *et al.*<sup>3</sup>. Since in the calculation of the position of

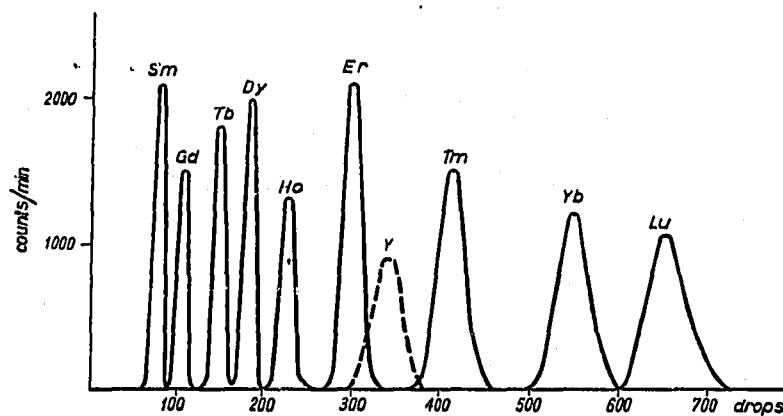


Fig. 1. Separation of Sm-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu with 11.5  $M$   $HNO_3$ .

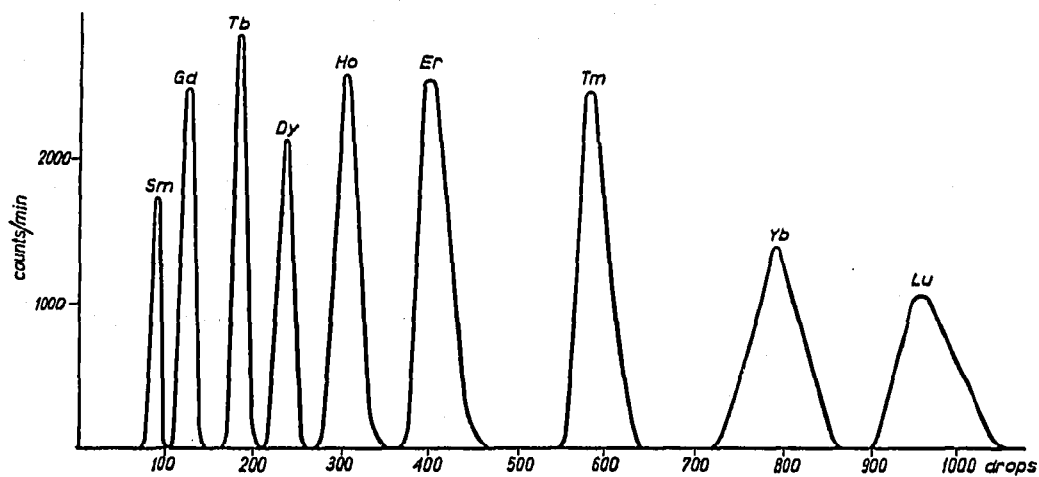


Fig. 2. Separation of Sm-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu with 12.3  $M$   $HNO_3$ .

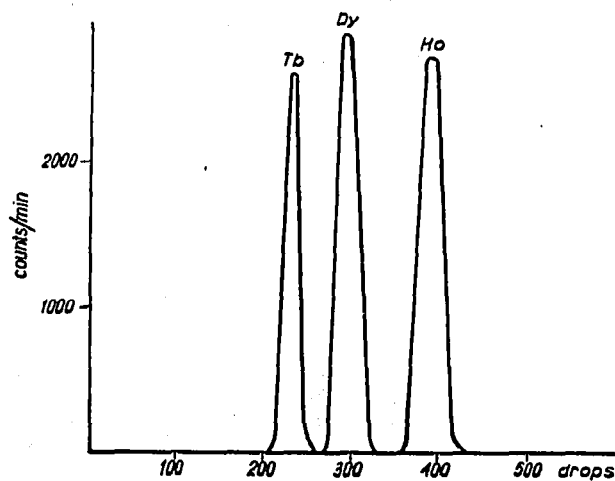


Fig. 3. Separation of Tb-Dy-Ho with 13  $M$   $HNO_3$ .

the maximum, the first free volume was always subtracted, the two sets of values can be directly compared. This comparison shows that the differences between the values obtained by dynamic and static methods are not great and can be caused by experimental errors occurring in both methods. The separation factor defined as the

TABLE I  
POSITIONS OF THE MAXIMA  
AND THE PARTITION COEFFICIENTS OF HEAVY RARE EARTHS RELATIVE TO THOSE OF Tb  
Eluting agent: 12.3 M HNO<sub>3</sub>.

	Tb	Dy	Ho	Er	Tm	Yb	Lu
Position of the maximum	1.0	1.5	2.0	2.8	4.3	6.0	7.4
Partition coefficient	1.0	1.6	2.1	2.9	4.4	5.9	7.2

ratio of the positions of the two maxima is given in Table II. It appears from these data, that the separation factor for the Yb-Lu pair is exceptionally small and that this pair plays the same role among the heavy rare earths as the Eu-Gd pair does among the light rare earths. The position of Y when eluted with 11.5 M HNO<sub>3</sub> is between Er and Tm (see Fig. 1).

TABLE II  
SEPARATION FACTORS OF PAIRS OF NEIGHBOURING HEAVY RARE EARTHS  
Eluting agent: 12.3 M HNO<sub>3</sub>.

Tb-Dy	Dy-Ho	Ho-Er	Er-Tm	Tm-Yb	Yb-Lu
1.5	1.33	1.4	1.53	1.4	1.23

#### Elution with HCl

It has been shown by PEPPARD *et al.*<sup>4</sup>, that rare earths are extracted by TBP from HCl solutions. It therefore seemed worthwhile to find out whether HCl can be used as eluting agent instead of HNO<sub>3</sub>. In Figs. 4 and 5 two examples of elution of some

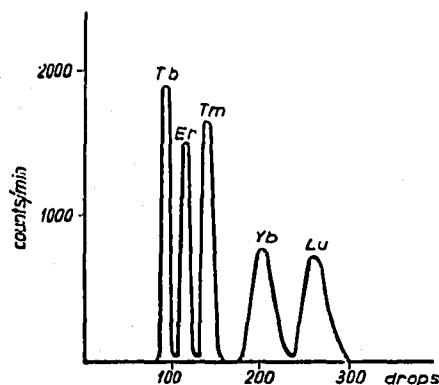


Fig. 4. Separation of Tb-Er-Tm-Yb-Lu with 11.8 M HCl.

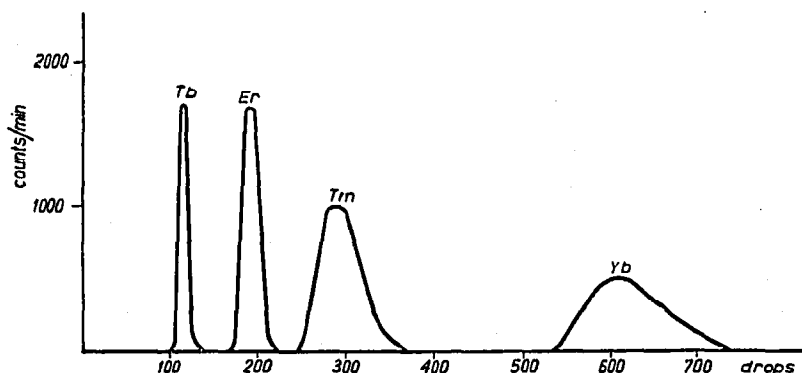


Fig. 5. Separation of Tb-Er-Tm-Yb with 12.3 M HCl.

heavy rare earths with 11.8 M and 12.3 M HCl are shown. As can be readily seen the elution curves are not much less favourable than those obtained with HNO<sub>3</sub> as eluting agent. The separation factor in the system HCl-TBP calculated from the positions of the maxima (see Tables III and IV) is even greater than in the system HNO<sub>3</sub>-TBP. Nevertheless, only the heaviest rare earths can be separated by elution

TABLE III

POSITIONS OF THE MAXIMA OF SOME HEAVY RARE EARTHS RELATIVE TO THE POSITION OF THAT OF Tb  
Eluting agent: HCl.

Concentration of HCl M	Tb	Er	Tm	Yb	Lu
11.8	1.0	2.0	3.2	6.2	9.2
12.3	1.0	2.9	5.4	13.6	—

TABLE IV

SEPARATION FACTORS OF SOME PAIRS OF HEAVY RARE EARTHS  
Eluting agent: HCl.

Concentration of HCl M	Tb-Er	Er-Tm	Tm-Yb	Yb-Lu
11.8	2.0	1.6	1.94	1.48
12.3	2.9	1.86	2.52	—

with HCl, since the partition coefficients for lighter rare earths are too small even in the most concentrated solutions of HCl available. It should be noted that the influence of the HCl concentration on the positions of the maxima is very strong, and that the separation factor for the Yb-Lu pair is smaller than that for the Tm-Yb pair, as in the case of HNO<sub>3</sub> as eluting agent.

*The effect of the amount of rare earth and of the volume of the solution introduced into the column*

It has been observed in the course of the work with light rare earths that the shape of the elution curve of gadolinium and the position of its maximum depend on the amount of gadolinium introduced into the column. In order to examine this effect more closely two sets of experiments with the Tb-Tm pair were carried out. In the first set of experiments the amount of Tm was kept constant and very small (below 0.01 mg) and the amount of Tb was gradually increased up to 0.8 mg. In the presence of more than about 0.1 mg of Tb carrier a change in the shape of the elution curve of Tb was noted. The curve became broad and asymmetric and the position of its maximum was shifted towards the left. This effect increased with the amount of added carrier. The influence on the elution curve of Tm was less pronounced, although

a broadening of the curve and the formation of a tail were also observed. In the second set of experiments the amount of Tb was kept small and constant, and increasing amounts of Tm up to 0.4 mg were successively added. In that case the position and shape of the elution curve of Tb did not change, but the elution curve of Tm was shifted towards the left, so that the initial separation factor of 3.3 for small amounts of both rare earths with 10.6 M HNO<sub>3</sub> decreased to 1.85 when the amount of Tm was increased to 0.4 mg. The shape of the elution curve of Tm was changed too, the curve becoming very asymmetric and broad. The experiments described above show that the addition of carrier does change the position and shape of its own curve. The effect on the curve of another substance present in the system in microamounts depends on whether the partition coefficient of this substance is smaller or greater than that of the substance added, the effect being greater in the second case.

The effect of the volume of the radioactive solution introduced into the column on the shape of the curve was investigated. No effect was observed with volumes smaller than 0.07 ml. With larger volumes the curves became broad, but the position of the maximum did not change.

#### SUMMARY

Reversed-phase partition chromatography with tributyl phosphate as the stationary phase was applied to the separation of heavy rare earths from Gd to Lu. As eluting agent 11.5 M, 12.3 M and 13.0 M HNO<sub>3</sub> were used. The heaviest rare earths can also be separated with HCl as eluting agent. The influence of the amount of the rare earth introduced into the column on the shape of the elution curve was investigated.

#### REFERENCES

- <sup>1</sup> S. SIEKIERSKI AND I. FIDELIS, *J. Chromatog.*, 4 (1960) 60.
- <sup>2</sup> D. F. PEPPARD, W. J. DRISCOLL, R. I. SIRONEN AND S. McCARTY, *J. Inorg. & Nuclear Chem.*, 4 (1957) 326.
- <sup>3</sup> E. HESFORD, E. E. JACKSON AND H. A. C. MCKAY, *J. Inorg. & Nuclear Chem.*, 9 (1959) 279.
- <sup>4</sup> D. F. PEPPARD, I. P. FARIS, P. R. GRAY AND G. W. MASON, *J. Phys. Chem.*, 57 (1953) 294.

*J. Chromatog.*, 5 (1961) 161-165