REVERSED-PHASE PARTITION CHROMATOGRAPHY WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID AS THE STATIONARY PHASE

PART I. SEPARATION OF RARE EARTHS

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It has been shown in previous papers from this Department that reversed-phase partition chromatography with tributyl phosphate (TBP) as the stationary phase can be applied to the separation of rare earths[1,2] and other ions[3-8]. Although the separation of adjacent rare earths including such a difficult separable pair as Eu–Gd is very satisfactory even on a 10 cm long column at room temperature, the application of TBP for that purpose has, nevertheless, two disadvantages. The first is the very high concentration of nitric acid, which is required for the separation of light rare earths and the second is the rather small mean separation factor. Although the latter is small the separation of adjacent rare earths is possible when in tracer amounts, because of the very small height equivalent of the theoretical plate (0.2 mm). An extracting agent with a higher separation factor would nevertheless be desirable especially in the case of widely differing amounts of the rare earths to be separated. The need for a better extracting agent than TBP was soon recognised by many authors, and in the past three years several papers have appeared[9-16] dealing with the application of di-(2-ethylhexyl) orthophosphoric acid (HDEHP) to reversed phase partition chromatography. But in the opinion of the present authors the advantages of the higher separation factor of HDEHP were nearly offset by the use of columns of very small separating power. The height of the plate of the columns used by PIERCE AND PECK[9,10] is 2 mm at 60° and at a flow rate of 0.5 ml·cm⁻²·min⁻¹. This value is about 10 times greater than that for columns with TBP retained on siliconized kieselguhr and operated at room temperature. The height of the plate of the columns used by CERRAI, TESTA AND TRIULZI[12] is 4 mm at 45° and decreases to 1 mm at 75°. These results seem to indicate that Corvic, cellulose powder and Kel-F are not such good supporting materials for the stationary phase as siliconized kieselguhr. Consequently, the separation of some adjacent rare earths (Ce–Pr–Nd, Eu–Gd, Dy–Ho, Yb–Lu) was not complete when these supporting materials were used, even at elevated temperatures and with the use of the gradient elution technique. On the other hand, good separation of all rare earths at 70° by the gradient elution technique was reported by WINCHESTER[13], who used siliconized kieselguhr as supporting material.

Work on the application of HDEHP retained on kieselguhr to the separation

of rare earths has been also carried out in this Department. This paper and another which follows, present the main results obtained with special emphasis on several new factors that have not been reported by previous authors.

EXPERIMENTAL

Column material and column preparation

Kieselguhr "Hyflo Supercel" was used as the solid support for HDEHP. The kieselguhr was fractionated by the sedimentation method. After drying, each fraction of the kieselguhr was treated with vapours of dimethyldichlorosilane and dried again for 1–2 h at 200°. Adequate treatment of the kieselguhr with dimethyldichlorosilane is essential for obtaining columns with good separating properties. Columns can be prepared by one of two methods. In the first method, the silicone treated kieselguhr is introduced in small portions into a glass tube and gently pressed with a glass rod after each portion. Afterwards an appropriate amount of HDEHP, alone or in a diluent, is introduced and the column eluted with dilute acid under pressure to remove air. In the second method the silicone-treated kieselguhr is mixed with HDEHP and with a volatile solvent, e.g., hexane. Nearly all the solvent is then evaporated at room temperature. The rest of the solvent is removed under reduced pressure. The dry powder obtained in this way is put into the column as described in the first method. There is no difference in the quality of columns obtained by the two methods, nevertheless the second method is to be preferred, since removal of air from the column is less troublesome. Unless otherwise stated the length of the bed was 10 cm and the diameter about 3 mm. Columns of such dimensions contained about 0.40 g of kieselguhr.

Stability of the columns and reproducibility of the results

The stability of the columns prepared by one of the two methods described above depends mainly on the content of HDEHP retained on the support. Columns used in the course of this work, containing 10 % of HDEHP (relative to the weight of kieselguhr) were perfectly stable and did not change their properties even after more than 20 runs.

The position of a peak in runs on the same column with low HDEHP content was found to vary by about 3 %.

The quality of a column is best measured by H—the effective height of the theoretical plate (later referred to simply as the height of the plate). To determine H, the number of plates was calculated from the equation given by GLUECKAUF[17]:

$$N = \frac{8V^2{}_{max}}{W^2}$$

where V_{max} is the volume of the eluate at the peak maximum and W is the width of the elution peak at $1/e$ of the maximum solute concentration. The height of the plate for the columns prepared from different batches of the same fraction of column material was found to vary by less than 15 % at constant flow rate and temperature. The mean value calculated from the elution of europium with HNO_3 at a flow rate of 0.75 ml·cm^{-2}·min^{-1} is about 0.33 mm for the specific fraction of kieselguhr used in the course of this work.

Reagent and radiotracers

HDEHP, supplied by Light and Co, was carefully purified by the method described by STEWART AND CRANDALL[18]. The content of the monoderivative was less than 0.2 %.

Most of the radioisotopes used were prepared by irradiation of appropriate targets in the Polish reactor "EWA". Some radioisotopes were obtained from the Radiochemical Centre, Amersham.

Unless otherwise stated the amount of rare-earths carrier was below 0.001 mg.

Elution

Elutions were carried out at room temperature using acids of appropriate concentration pre-equilibrated with HDEHP. Drops of the eluate were collected, dried and their activity assayed by means of an end window G.M. counter. The flow rate was 0.75 ml·cm^{-2}·min^{-1} or about 2 drops/min.

The volume of the sample introduced into the column was about 0.03 ml.

<center>RESULTS AND DISCUSSION</center>

The effect of the grain size, amount of HDEHP and of diluent on the height of the plate

The height of the plate depends on the grain size of the kieselguhr. In the present study the fraction which settled within 10 min in a 20 cm high beaker was used. Using this fraction columns could be easily prepared where the height of the plate is about 0.33 mm. This value was thought to be fairly satisfactory for work with HDEHP because of its high separation factor. It is nevertheless possible to prepare columns with a plate height of less than 0.2 mm. For the latter purpose the fraction of kieselguhr settling between 20 and 30 min should be used.

The height of the plate is affected by the amount of HDEHP retained on the kieselguhr in the column. This is illustrated by the data quoted in Table I. The height

<center>TABLE I</center>

<center>THE EFFECT OF THE AMOUNT OF HDEHP ON THE HEIGHT OF THE PLATE</center>

mg of HDEHP per 1 g of kieselguhr	*50*	*65*	*75*	*100*	*150*	*200*	*250*	*500*
H in mm	0.34	0.33	0.33	0.35	0.59	0.96	1.0	1.95

of the plate was calculated from the position and width of the europium peak. Elution was carried out with HCl at a flow rate of 0.75 ml·cm^{-2}·min^{-1}. An increase in the amount of HDEHP from 5 % to 10 % (relative to the amount of kieselguhr) does not change the height of the plate. A further increase from 10 % to 50 % increases the height of the plate several times. Unless otherwise indicated the ratio of HDEHP to kieselguhr chosen for further work was 1:10.

Some experiments were carried out on the columns with solutions of HDEHP in kerosene or TBP as diluent. The presence of a diluent does not improve the height of the plate.

Separation of microamounts of rare earths

Typical examples of the separation of tracer amounts of rare earths in HNO_3 as eluting agent are shown in Figs. 1, 2, 3 and 4. The values of the separation factors (β) for adjacent rare earths in HNO_3 and HCl are quoted in Table II. The separation factor is low in both these acids for the following pairs: Ce–Pr, Pr–Nd, Eu–Gd,
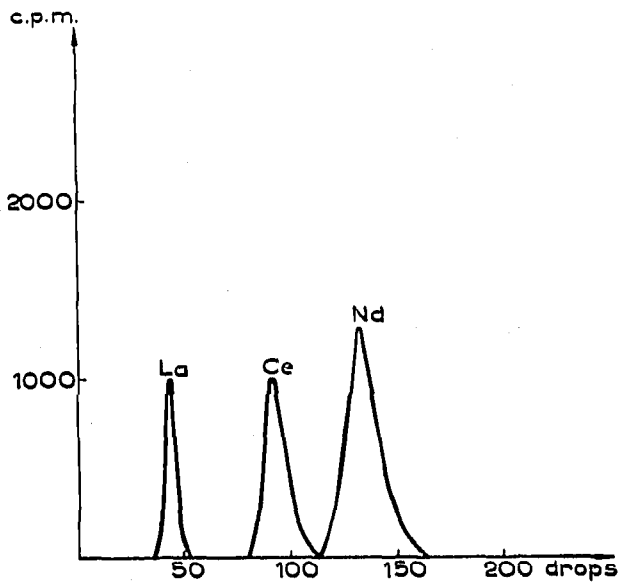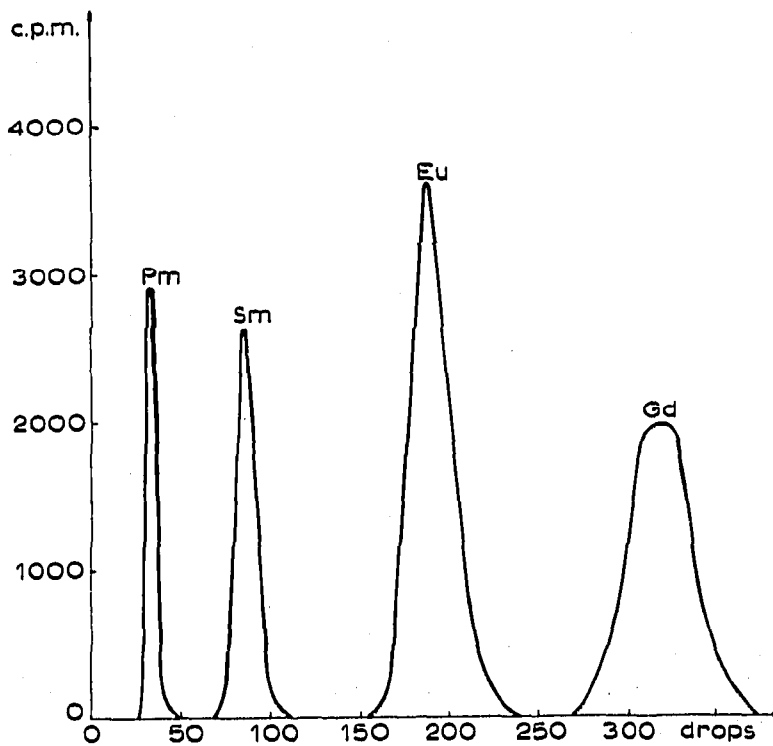

Fig. 1. Separation of La–Ce–Nd with 0.21 M HNO

Fig. 2. Separation of Pm–Sm–Eu–Gd with 0.39 M HNO$_3$.
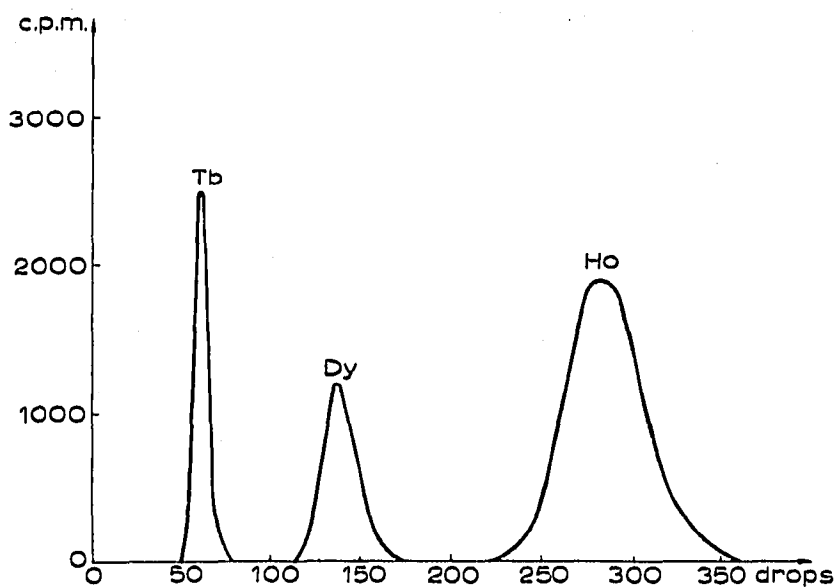
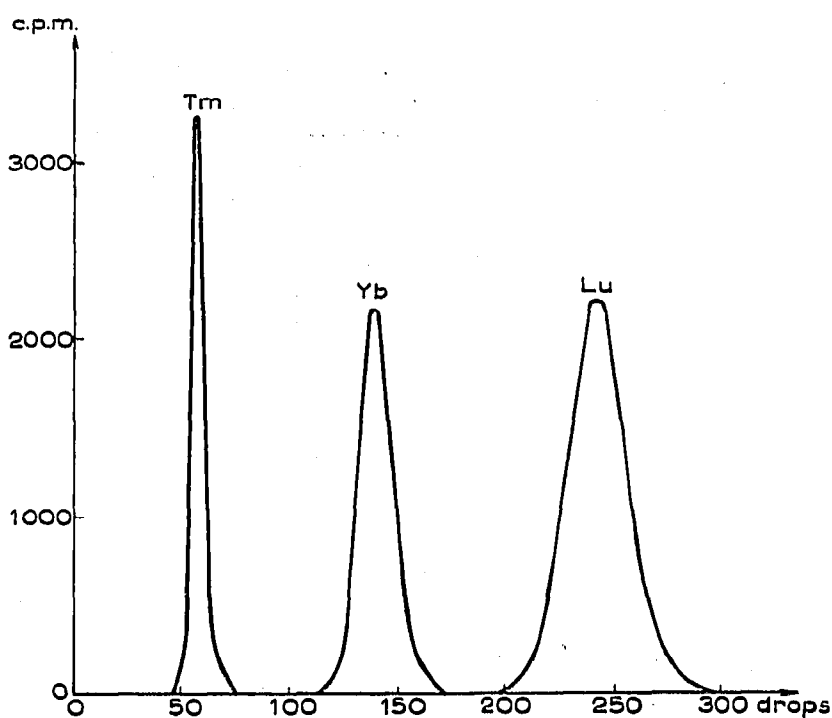Fig. 3. Separation of Tb–Dy–Ho with 1.16 M HNO$_3$.

Fig. 4. Separation of Tm–Yb–Lu with 5.12 M HNO$_3$.

Dy–Ho and Yb–Lu. Contrary to the results reported by PIERCE AND PECK no difficulty was found in separating the last three pairs. We were not able to separate Ce–Pr–Nd using 10 cm long columns and HNO$_3$ as eluting agent, but with HCl as eluting agent the separation proved quite satisfactory (Fig. 5). Generally, the separation factor for the light rare earths is a little more favorable in HCl than in HNO$_3$.

TABLE II

SEPARATION FACTORS FOR ADJACENT RARE EARTHS

	La-Ce	Ce-Pr	Pr-Nd	Nd-Pm	Pm-Sm	Sm-Eu	Eu-Gd	Gd-Tb	Tb-Dy	Dy-Ho	Ho-Er	Er-Tm	Tm-Yb	Yb-Lu
HCl	2.8	1.5	1.3	2.7	3.2	2.2	1.5	5.0	2.6	2.1	2.8	3.4	2.8	1.9
HNO$_3$	2.7	*Ce-Nd* 1.55		2.1	2.7	2.1	1.7	5.5	3.0	2.2	2.7	3.5	3.1	1.9

It is difficult to give a reasonable explanation for this difference, since according to PEPPARD et al.[19], the light rare earths are only very slightly complexed at low concentrations of both these acids. The mean (geometric) separation factor is 2.41 in both HCl and HNO$_3$. This value is substantially greater than those reported by PIERCE, PECK AND HOBBS[16] for HCl and HClO$_4$ as eluants. The probable reason for the higher separation factor reported in the present work is the lower temperature at which the experiments were performed. That an increase in temperature decreases the separation factor was shown by CERRAI, TESTA AND TRIULZI[12].
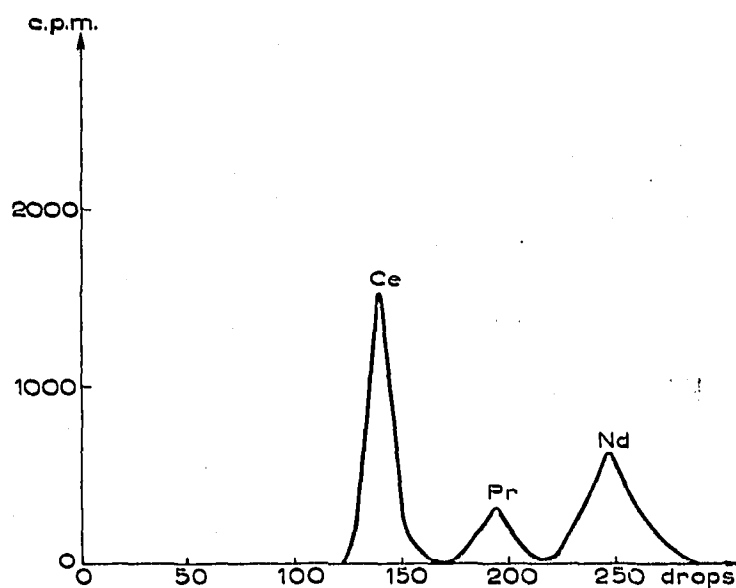

Fig. 5. Separation of Ce–Pr–Nd with 0.14 M HCl.

The separation factors in HCl and HNO$_3$ do not differ substantially for the heavy rare earths, but a new effect can be observed which rules out HCl as an eluant at room temperature. It can be seen that the height of the plate determined from the position and width of the peak of a heavy rare earth element is several times higher with HCl than with HNO$_3$ as eluant. The effect of the acid is best illustrated by comparison of Figs. 4 and 6. The peaks of Tm and Lu eluted with HCl are so broad that there is no space between them for Yb. This effect of acid was probably not noticed by earlier authors working on the same systems because it disappears at higher temperatures. The effect of acid, temperature and flow rate on the height of the plate will be discussed in detail in Part II of this series.
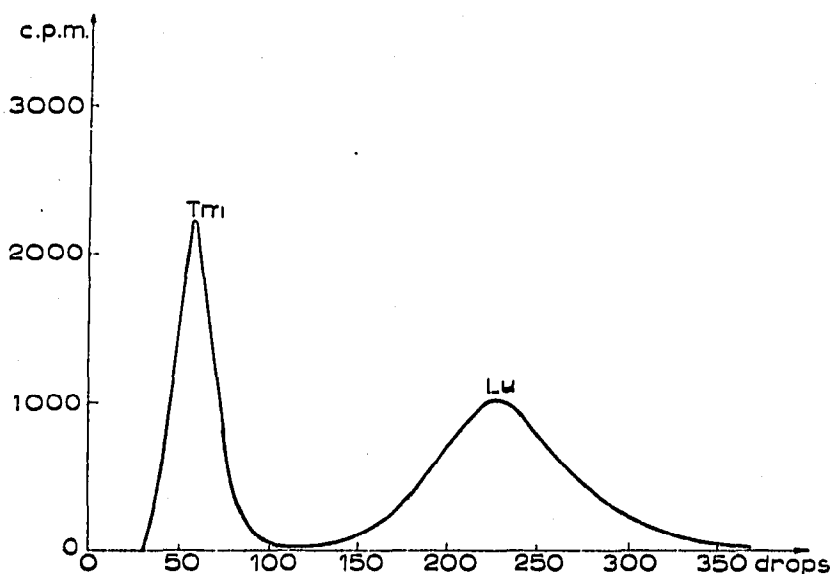
Fig. 6. Elution of Tm and Lu with 2.95 M HCl.

Separation of microamounts of Tb from macroamounts of Er

The amounts of the rare earths used in all previous experiments were below 0.001 mg. For many practical purposes such as isotope production, or studying nuclear reactions, the separation of microamounts of one element from a macroamount of another element which was used as a target is more important than the separation of tracer amounts of elements. To study the applicability of HDEHP retained on the kieselguhr to this problem the pair of elements Tb–Er was chosen. In the series of experiments the amount of Tb was kept constant (below 0.001 mg) and the amount of Er was
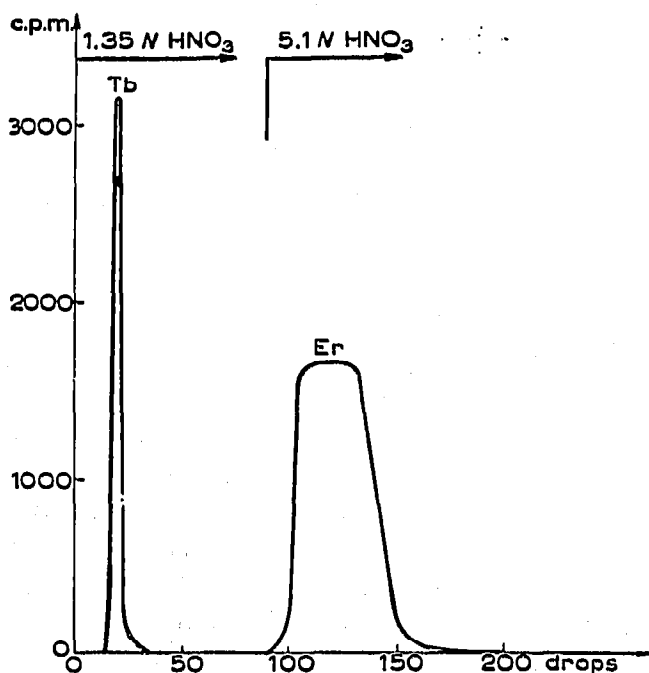

Fig. 7. Separation of microamounts of Tb from 22.6 mg of Er.

TABLE III

SEPARATION OF MICROAMOUNTS OF Tb FROM MACROAMOUNTS OF Er

Column	Length of the bed (mm)	Diameter of the tube (mm)	Amount of kieselguhr (g)	Amount of HDEHP (g)	Concn. of Er (M/l)	Max. amount of Er (mg)	Molar ratio HDEHP/Er	Mequiv. of Er/1 g of HDEHP	Mequiv. of Er/1 g of column material
I	90	2.9	0.350	0.142	0.27	22.6	3.24	2.86	0.83
II	100	7.0	1.76	0.709	0.19	110	3.32	2.78	0.80

gradually increased. In this manner the maximum amount of Er which does not affect the separation was determined. HNO_3 of low concentration was employed for the elution, so that as much as possible of the theoretical column exchange capacity was available. Only after the Tb was completely eluted was more concentrated acid applied to speed up the elution of Er. Two columns differing in size were used. Both of them contained 40 % HDEHP. The results are shown in Table III and in Figs. 7 and 8.
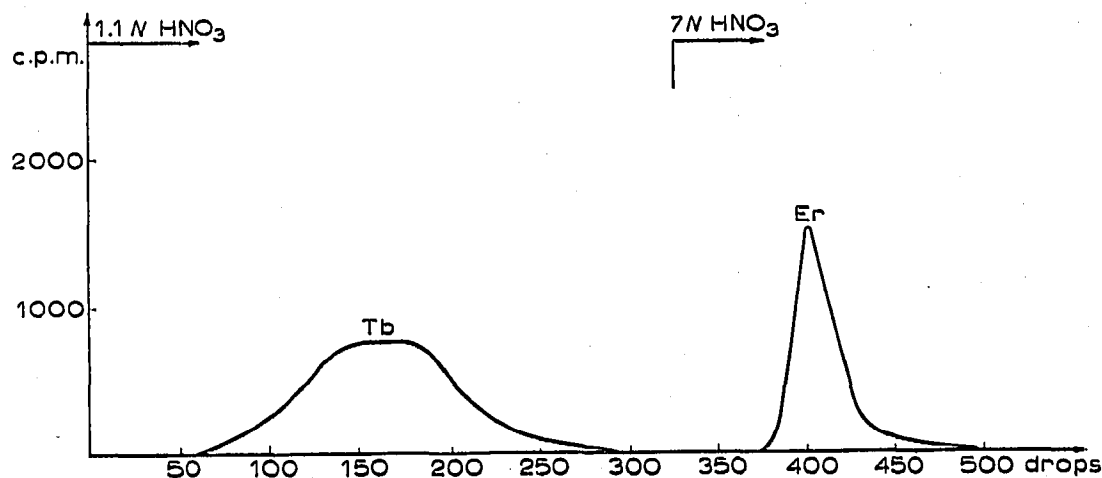

Fig. 8. Separation of microamounts of Tb from 110 mg of Er.

CONCLUSIONS

The ratio of HDEHP to Me in the extracted complex is equal to 3 with a high loading of the organic phase.

When the separation factor between two rare earths is $\geqslant 17$ (the value of β for the Tb–Er pair), practically the whole exchange capacity of the column can be made available without affecting the separation of the microamount of the lighter element from the macroamount of heavier.

There is a linear proportionality between the maximum amount of the rare earth elements retained on the column and the amount of HDEHP. This makes it possible to predict suitable dimensions for a column, according to the amount of the macrocomponent in the mixture.

SUMMARY

Reversed phase partition chromatography with HDEHP retained on kieselguhr as the stationary phase was applied to the separation of rare earths. The influence of the amount of HDEHP on the height of the plate has been studied. Up to 10 % of HDEHP (with respect to the amount of kieselguhr) the height of the plate is about 0.33 mm which makes possible very clear separations of adjacent rare earths at room temperature. No gradient elution technique was found necessary for the separation. The height of the plate can be decreased to less than 0.2 mm by using a specially selected fraction of kieselguhr.

Microamounts of Tb were separated from macroamounts of Er. The amount of Er retained on the column and separated from Tb was found to be proportional to the amount of HDEHP.

It was found that the width of the elution peak of heavy rare earths is much greater with HCl than with HNO_3 as eluting agent.

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