

## SEPARATION OF SEVERAL RARE EARTHS BY EXTRACTION CHROMATOGRAPHY USING BIFUNCTIONAL PHOSPHINE OXIDES\*

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The separation of the rare earth and other ions by extraction chromatography on paper impregnated with methylenebis(di-*n*-hexylphosphine oxide), MHDPO, and methylenebis[di-(2-ethylhexyl)-phosphine oxide], MEHDPO, was reported in previous papers from this Laboratory<sup>1-4</sup>. The separation of milligram amounts of rare earth salts on short columns packed with various inert supports impregnated with MHDPO and MEHDPO is reported in the present paper.

SIEKIERSKI AND FIDELIS have reported the partition chromatographic separation of the rare earths using tri-*n*-butyl phosphate, TBP<sup>5,6</sup>, and 2-ethylhexylphenylphosphonic acid, HEHØP<sup>7</sup>, supported on kieselguhr as the stationary phases. SOCHACKA AND SIEKIERSKI<sup>8,9</sup>, WANTANABE<sup>10</sup>, WINCHESTER<sup>11</sup>, and GROSSE-RUYKEN AND BOSHOLM<sup>12</sup> studied the separation of the rare earths where di-(2-ethylhexyl) orthophosphoric acid, HDEHP, (also supported on kieselguhr) was used as the stationary phase. CERRAI *et al.*<sup>13</sup> reported the separation of the rare earths on columns packed with cellulose powder treated with HDEHP. PIERCE *et al.*<sup>14,15</sup> also reported the column separation of the rare earths using HDEHP and Corvic [a poly-(vinyl chloride-vinyl acetate) copolymer].

Two factors are of importance for an effective column separation. These are the separation factor,  $\beta$ , defined as the ratio of the partition coefficients, and the height equivalent to a theoretical plate, HETP. SOCHACKA AND SIEKIERSKI<sup>8</sup> reported a mean value for HETP, based on the elution of europium with nitric acid, of only 0.33 mm for HDEHP-kieselguhr columns. The latter authors<sup>9</sup> also studied the effect of flow rate, the eluting acid and the temperature on HETP and explained the higher plate heights which were observed by other workers with HDEHP on the basis of the faster flow rates or the larger particle size of the supporting material employed. FIDELIS AND SIEKIERSKI<sup>7</sup> found HEHØP gave somewhat larger separation factors than HDEHP and made the observation that minimum values of HETP with either of these acidic extractants, HDEHP or HEHØP, were significantly greater than the minimum values observed with neutral extractants such as TBP or tri-*n*-octylphosphine oxide, TOPO. They found that the TBP-kieselguhr columns were less sensitive to the amount of carrier but concluded that the acidic compounds were superior stationary phases because of the considerably larger separation factors and the lower acid concentration required for the mobile phase.

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Although the separation factors (based on paper chromatographic data<sup>3,4</sup>) for the neutral bifunctional phosphine oxides, MHDPO and MEHDPO, appeared to be intermediate between those reported for the TBP and acidic extractants such as HDEHP and HEHØP, the possibility of smaller plate heights with the neutral compounds suggested that these extractants were worth investigating as stationary phases for column separations.

#### EXPERIMENTAL

The MHDPO, MEHDPO and the Chlorophosphonazo III which was used as the chromogenic reagent were synthesized by procedures reported previously<sup>4,10,17</sup>. The solid supports used were Kel-F powder (molding powder Grade 300, 60–80 mesh, 3 M Company, St. Paul, Minn., U.S.A.), Plaskon (3200 Powder, 200 mesh fraction, Allied Chemical, Morristown, N.J., U.S.A.) and Hyflow Super Cel (Fisher Scientific Company, Chicago, Ill., U.S.A.). The fraction of the kieselguhr (Hyflow Super Cel) which was used was that which passed a 200-mesh screen (particle size less than 0.074 mm) and settled from water in 10 min. This is essentially the same fraction as used by SIEKIERSKI AND FIDELIS<sup>5</sup>. Initially, the kieselguhr was treated with dichlorodimethylsilane<sup>5,8,11</sup> but in the case of MHDPO and MEHDPO, column performance was as good or better without this step and in subsequent work it was omitted.

The supporting material was added to a solution of the appropriate extractant in acetone to give a slurry, and the acetone was evaporated by heating the slurry gently while stirring vigorously. The final dry product was thoroughly mixed. The amount of extractant on the kieselguhr was always 10 % by weight while it was 20 % in the case of Plaskon and 10 % or 33 % with the Kel-F.

The columns employed were 0.9 cm in diameter, and the bed height was 19–31 cm. The columns were packed by the addition of small portions of the dry (extractant–kieselguhr) mixture which was firmly pressed into place with a glass rod after each addition. Approximately 0.5 g of the solid material was required for each centimeter of bed height.

The effluent from the column was transferred to the proper tube in the fraction collector by 2-mm polyethylene tubing. The total volume from the bottom of the column to the end of the polyethylene tubing was less than 0.5 ml. Provision was made for pressurizing the top of the column. The column was conditioned by passing several column volumes of eluent through the column.

Fifty-microliter amounts (unless specifically stated otherwise) of 0.1 *M* solutions of each of the rare earths (in 0.1 *M* acid) used for any run were added to the top of the column. The sample solution was slowly forced onto the column bed by carefully pressurizing the column head. Several small amounts of eluent were likewise added and allowed to move onto the bed to make certain the entire sample was fixed on the bed and to prevent mixing in the top of the column prior to elution. The eluent, supplied to the column from a reservoir kept under the same pressure, was then allowed to drip into the top of the column. The effluent was collected using a Research Specialties Company Automatic Fraction Collector and the timed-flow system. It was found that the flow rate was sensibly constant after several column volumes of the eluting acid had passed through the column and this was frequently verified by determination of the volume of selected fractions. The reservoir was held under a

constant pressure of 2 to 15 p.s.i., depending on the desired flow rate, by means of a Johnson Air Regulator. A flow rate of approximately 0.31 ml/cm<sup>2</sup>/min (the usual rate) was obtained with a pressure of approximately 4 to 5 p.s.i.

The rare earths in the effluent were determined spectrophotometrically using Chlorophosphonazo III as the chromogenic reagent. The rare earth complex with the latter reagent develops in strongly acidic solution and it was usually only necessary to dilute the fraction collected with a constant amount of water and add the chromogenic reagent. In several instances where large fractions were collected, it was necessary to evaporate the excess acid.

## RESULTS AND DISCUSSION

### *Terminology and treatment of column data*

The terminology and treatment of column data in the present paper follows that used by GLUECKAUF<sup>18</sup>. The partition coefficient,  $K_D$ , is defined by:

$$K_D = a - \alpha \quad (1)$$

where  $\alpha$  is the void fraction of the column and  $a$  is given by:

$$a = \frac{V}{X} \quad (2)$$

The  $V$  term is the peak elution volume and  $X$ , the "free column volume". Actually,  $X'$ , the empty column volume,  $X$ , diminished by one-half the volume of the initial band should be used. In the present paper the initial band volume was considered negligible in comparison to  $X$  and it was assumed  $X = X'$ . The number of plates on the column,  $N$ , was calculated from:

$$N = 8 \left( \frac{V}{W} \right)^2 \quad (3)$$

where  $W$  is the width of the elution peak at a solute concentration in the effluent of 1/e times its maximum value. The height equivalent to a theoretical plate (HETP) is the bed height divided by  $N$ .

The void fraction,  $\alpha$ , was determined in two ways. The weight of the packed column was determined when dry and then after filling with water. The difference divided by the empty column volume,  $X$ , was taken as  $\alpha$ . The peak elution volume required to elute some salt which is supposedly not retained by the column (potassium chloride) divided by the empty column volume,  $X$ , should also give  $\alpha$ . For tightly packed columns, significantly different values for  $\alpha$  were obtained by these two methods with the latter value always the larger. The former method gave  $\alpha$  values which resulted in more rational values of  $K_D$  for the lighter rare earths and gave separation factors,  $\beta$ , in much better agreement with those obtained by paper techniques<sup>3,4</sup>. The choice of  $\alpha$  values used is obviously of little significance except in cases where  $K_D$  is small. It should be noted that  $K_D$  is a column parameter and is defined by GLUECKAUF<sup>18</sup> as the ratio of the amount of solute on the stationary phase

TABLE I

 $K_D$  DATA FOR 33% MHDPO-KEL-F, COLUMN IBed height = 31 cm;  $X = 19.5 \text{ cm}^3$ ; flow rate =  $0.20 \text{ ml/cm}^2/\text{min}$ ;  $\alpha = 0.64$ .

Rare earth	9 M HNO <sub>3</sub>	12 M HNO <sub>3</sub>	16 M HNO <sub>3</sub>
La	1.76 (1)*	—	0.18 (6)
Pr	—	2.18 (2)	1.26 (5), 1.00 (6)
Nd	7.86 (1)	—	2.03 (4)
Sm	—	10.26 (2)	7.91 (3)
Eu	24.56 (1)	—	11.46 (5)
Gd	—	17.36 (2)	15.36 (6)
Tb	—	—	29.6 (6)
Dy	—	—	33.36 (7)
Ho	—	40.36 (2)	—
Er	—	66.76 (2)	56.36 (7)
Lu	—	—	98.16 (7)

\* Numbers between parentheses indicate run number.

in  $1 \text{ cm}^3$  of column volume divided by the amount of solute in  $1 \text{ cm}^3$  of mobile phase. Larger values of  $K_D$  would be expected for the same solute on more tightly packed columns or columns with a greater amount of extractant on the inert supporting material.

*MHDPO columns*

The separation of small amounts of calcium and magnesium from major amounts of yttrium on MHDPO-Kel-F columns had been previously investigated<sup>2</sup>, and the initial studies on the separation of the rare earths were made using a similar column which was 33% by weight in MHDPO. Data obtained with this column

TABLE II

 $K_D$  DATA FOR 10% MHDPO-HYFLOW SUPER CEL, COLUMN IIBed height = 20.8 cm;  $X = 14.30 \text{ cm}^3$ ; flow rate =  $0.20 \text{ ml/cm}^2/\text{min}$ ;  $\alpha = 0.74$ ; mobile phase = 16 M HNO<sub>3</sub>.

Rare earth	$K_D$
La	0.28 (3)*
Pr	0.48 (1), 0.47 (3)
Nd	0.52 (3)
Sm	2.02 (1)
Eu	2.30 (2)
Gd	3.03 (2)
Tb	6.06 (2)
Dy	7.51 (4)
Ho	10.26 (2)
Er	11.56 (4)
Tm	16.46 (5)
Yb	26.86 (4)
Lu	23.76 (5)

\* Numbers between parentheses indicate run number.

TABLE III  
HETP VALUES ON 10% AND 33% MHDPO COLUMNS

33% MHDPO on 60-80 mesh Kel-F			10% MHDPO on Hyflow Super Cel		
HETP (mm)	Acid (M)	Rare earth present	HETP (mm)	Acid (M)	Rare earth present
3.2 (Nd)	9	La, Nd, Eu	0.42 (Pr)	16	Pr, Sm
3.9 (Eu)	9	La, Nd, Eu	0.37 (Sm)	16	Pr, Sm
4.3 (Eu)	12	Pr, Nd, Eu, Gd, Dy, Er	0.79 (Eu)	16	Eu, Gd, Tb, Ho
3.4 (Dy)	12	Pr, Nd, Eu, Gd, Dy, Er	0.89 (Gd)	16	Eu, Gd, Tb, Ho
0.98 (Nd)	16	Nd, Eu	0.98 (Tb)	16	Eu, Gd, Tb, Ho
2.4 (Eu)	16	Nd, Eu	0.95 (Ho)	16	Eu, Gd, Tb, Ho

(Column I) are shown in Table I. The partition coefficient is seen to decrease and the separation factor to increase with increasing acid concentration of the mobile phase, as was previously observed in the case of paper chromatography<sup>3</sup>. Except in the case of the light rare earths, the  $K_D$  values were so large that column separations are not really feasible except with 16 M nitric acid. Even in this case the separation of the heavy rare earths required an unreasonably long time.

The data obtained for the column separation of the rare earths using kieselguhr (Hyflow Super Cel) treated with dichlorodimethylsilane and loaded with only 10 wt. % MHDPO (Column II) are shown in Table II. As expected the  $K_D$  values are lower, but the separation factors are not significantly different. The plate heights are significantly lower, however, as shown in Table III.

Although there is some indication that HETP increases with  $K_D$  (as might be expected because of the diffusion effect<sup>9</sup>), significantly lower plate heights were observed with Column II even when the HETP values are calculated for elements

TABLE IV

$K_D$  DATA FOR RARE EARTH NITRATES ON MEHDPO-HYFLOW SUPER CEL, COLUMN III  
Bed height = 20.8 cm; flow rate = 0.27 ml/cm<sup>2</sup>/min;  $X = 13.23$ ;  $\alpha = 0.60$ .

Rare earth	Nitric acid concentration (M)						
	3.0	6.0	7.5	9.0	10.5	12	14
La	0.58	—	—	—	—	—	—
Pr	1.44	—	—	—	—	—	—
Nd	1.82	0.5	—	0.5	—	—	0.5
Sm	—	—	—	—	—	—	—
Eu	4.71	1.0	0.87	0.90*	0.98	1.21	4.10
Gd	—	—	—	0.83	—	—	—
Tb	—	2.8	2.14	2.12*	2.72	4.12	—
Dy	—	—	—	2.80	—	—	—
Ho	—	—	—	4.20*	—	—	—
Er	—	—	—	7.70	—	—	—
Tm	—	—	—	16.4	—	—	—
Yb	—	—	—	25.1	—	—	—

\* Average values for several different runs.

with similar  $K_D$  values. For example, HETP values of 0.98 mm (Nd) and 0.37 mm (Sm) were obtained on the 33% and 10% columns, respectively, using 16 *M* nitric acid as the eluting agent. The  $K_D$  values for these two elements were 2.03 (Table I) and 2.02 (Table II). Likewise, HETP values of 2.4 mm (Eu) and 0.95 mm (Ho) were obtained on the 33% and 10% columns, respectively, where the  $K_D$  values were 11.46 (33% MHDPO) and 10.26 (10% MHDPO). The lower values for HETP were anticipated on the basis of the smaller particle size and lighter loading of extractant on the kieselguhr. The somewhat higher plate heights for the four heavier rare earths on Column II (Table III), probably reflect the higher  $K_D$  values and greater load on the column.

#### MEHDPO columns

$K_D$  data obtained from elution curves for several rare earth nitrates on a column packed with 10% MEHDPO on Hyflow Super Cel (Column III) are shown in Table IV. The Hyflow Super Cel used in this column was treated with dichlorodimethylsilane. All elutions with this column were carried out at ambient room temperature of 25°. The flow rate was 0.27 ml/cm<sup>2</sup>/min for the data given in Table IV. At a flow rate of 0.71 ml/cm<sup>2</sup>/min the  $K_D$  values (not shown in Table IV) for europium and terbium were 0.95 and 2.38 as compared with values of 0.80 and 2.22 at a flow rate of 0.16 ml/cm<sup>2</sup>/min. The separation factor was 2.50 at the higher flow rate and 2.76 at the lower rate.

In agreement with paper chromatographic data<sup>4</sup>, minimum values for  $K_D$  are obtained with 7.5 to 9 *M* nitric acid (see  $K_D$  values for europium and terbium in Table IV). The separation factors for the heavy rare earth couples are larger with MEHDPO (with 9 *M* nitric acid) than with MHDPO at any acid concentration. A comparison of the values obtained for the separation factors,  $\beta$ , for several rare earth couples by the column and paper techniques is shown in Table V. The plate heights calculated for various elution curves for Column III were approximately 1.0 mm.

The effect of the temperature and flow rate on  $K_D$ ,  $\beta$ , and HETP for gadolinium and terbium is shown in Table VI. This column was prepared using kieselguhr which was not treated with dimethyldichlorosilane and will be referred to as Column IV.

$K_D$  and  $\beta$  values appear to be relatively insensitive to both the temperature

TABLE V

SEPARATION FACTORS FOR SEVERAL RARE EARTH COUPLES ON MEHDPO-HYFLOW SUPER CEL, COLUMN III

Eluent = 9 *M* nitric acid.

Rare earth couple	$\beta$ (column)	$\beta$ (paper)*
Gd-Tb	2.60	3.42
Tb-Dy	1.30	1.51
Dy-Ho	1.47	1.43
Ho-Er	1.84	1.87
Er-Tm	2.14	1.61
Tm-Yb	1.53	1.58

\* Taken from Ref. 4.

TABLE VI

ELUTION BEHAVIOR OF GADOLINIUM AND TERBIUM, COLUMN IV

Bed height = 21.0 cm;  $X = 12.48 \text{ cm}^3$ ;  $\alpha = 0.6$ .

Run No.	Temp. (°C)	Flow rate (ml/cm <sup>2</sup> /min)	$K_D$		HETP (mm)		$\beta$
			Gd	Tb	Gd	Tb	
1*	25	0.27	1.01	—	0.77	—	—
2	25	0.27	1.12	2.63	1.09	1.04	2.35
3	35	0.33	1.05	2.32	1.10	0.92	2.26
4	35	0.60	1.09	2.41	1.58	1.39	2.21
5	45	0.71	0.98	2.34	2.10	1.83	2.38
6	45	0.35	1.05	2.31	1.34	1.32	2.20
7	25	0.57	0.99	2.42	1.68	1.51	2.44
8	20	0.27	1.04	2.53	1.75	1.30	2.44
9	25	0.27	1.00	2.40	1.59	1.25	2.40
10	25	0.28	1.03	—	1.20	—	—
11**	25	0.28	0.97	—	1.77	—	—

\* Only Gd was placed on the column where no data for Tb are shown.

\*\* 25  $\mu$ moles of Gd placed on column in this one run.

and flow rate. The relative standard deviation for the  $K_D$  values for terbium is 4.5 % which is within the expected experimental error. The plate height appears to increase slightly with use (compare HETP for runs 2 and 9). Slightly larger plate heights were also observed at the fastest flow rate (run 5) and for the largest solute load (run 11).

Some data obtained on a slightly more tightly packed column with a void fraction,  $\alpha$ , equal to 0.5 are shown in Table VII. Significantly lower values for HETP were observed (runs 1–3) than for the less tightly packed Column IV. The terbium concentration in run 2 (where 20  $\mu$ moles of terbium were placed on the column) exceeded the useful range of the spectrophotometric method employed and the HETP value was not determined.

The acid concentration of the eluent was then dropped to 3  $M$  and 0.5  $M$  (runs 4 and 5 respectively) to study the separation of the lighter rare earths. As indicated by the  $K_D$  values, lanthanum can be easily separated from praseodymium and neodymium, but the elution curves for the latter couple were not resolved.

The plate heights for subsequent runs (6 and 7), again using 9  $M$  nitric acid, were much larger (than for runs 1–3). Run 7 (repeat of run 1) confirmed the fact that the column performance had deteriorated. Possibly the changes in the acid concentration of the eluent caused channeling. The data on runs 6 and 7 are included because of the significantly larger separation factors observed for terbium, dysprosium and holmium (run 6) on this more tightly packed column. Despite the increase in plate height, the elution curves were still completely resolved.

It seemed entirely possible that the lower values for HETP using Hyflow Super Cel as a support for the extractant than those obtained when Kel-F-300 was used were primarily due to the smaller particle size of the former (< 200 mesh) as compared with the Kel-F (60–80 mesh). The authors' small supply of Kel-F-300 did not yield a sufficient amount of material which would pass a 200-mesh screen to examine this possibility. Furthermore, the manufacture of this material has been discontinued and the replacement products (KF-6051 and KF-6061, 3M Company, St. Paul, Minn., U.S.A.) were reported to be of little use as supporting materials<sup>10</sup>.

TABLE VII

DATA FOR MEHDPO-HYFLOW SUPER CEL, COLUMN V

Bed height = 21 cm; flow rate = 0.22 ml/cm<sup>2</sup>/min;  $X = 13.48$  ml;  $\alpha = 0.5$ .

Run No.	$K_D$					HETP				
	9 M HNO <sub>3</sub>					9 M HNO <sub>3</sub>				
	Gd	Tb	Dy	Ho	Er	Gd	Tb	Dy	Ho	Er
1	1.37					0.32				
2	1.35	2.64				0.38	??			
3			4.80		12.00			0.74		0.53
6		2.41	4.40	6.98			3.00	2.00	2.00	
7	1.37					2.30				
	3 M HNO <sub>3</sub>			3 M HNO <sub>3</sub>						
	La	Pr	Nd	La	Pr	Nd				
4	0.61	1.16	1.29	0.67	??	??				
	0.5 M HNO <sub>3</sub>			0.5 M HNO <sub>3</sub>						
	La	Pr	Nd	La	Pr	Nd				
5	3.50	9.75	10.00	0.99	??	??				

\* 1  $\mu$ mole of Gd and 20  $\mu$ moles Tb on column for run 2. In all other cases, 5  $\mu$ moles of each element. HETP for terbium not calculated (see text).

\*\* Elution curves not resolved.

TABLE VIII

DATA FOR MEHDPO-PLASKON COLUMNS

Bed height = 21 cm (VI) and 19 cm (VII); flow rate = 0.31 ml/cm<sup>2</sup>/min;  $X = 13.35$  cm<sup>3</sup> (VI) and 12.07 cm<sup>3</sup> (VII);  $\alpha = 0.6$  (VI) and 0.5 (VII); mobile phase = 9 M HNO<sub>3</sub>.

Rare earth	$K_D$		HETP (mm)	
	Column VI	Column VII	Column VI	Column VII
Nd	0.46	—	—	—
Sm	1.08	—	—	—
Eu	1.54	—	—	—
Gd	1.77	—	0.94	—
Tb	4.67	6.38	0.63	1.1
Dy	7.93	10.7	0.73	1.0
Ho	11.45	16.1	0.75	1.0
Er	—	37.6	—	—
Tm	—	57.5	—	—
Yb	—	93.1	—	—



It was recently brought to the authors' attention that Kel-F-300 is still available from Applied Science Laboratories, Inc. (State College, Pa., U.S.A.), but this was not known at the time the present work was done. HUFF<sup>10</sup> had suggested that Plaskon was an adequate substitute for Kel-F-300. A sample portion of Plaskon was screened and the portion which passed a 200-mesh screen was used as a supporting phase for MEHDPO.

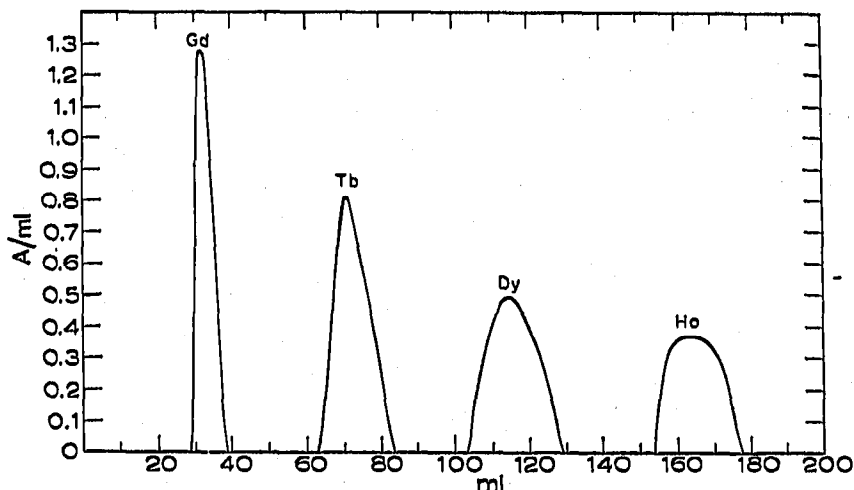


Fig. 1. Elution curves for several rare earth nitrates. Column VI. Column: 20% MEHDPO on Plaskon; mobile phase: 9 M HNO<sub>3</sub>.

$K_D$  and HETP data for the separation of several rare earths on the MEHDPO-Plaskon columns (Columns VI and VII) are presented in Table VIII. Column VII was more tightly packed and as expected the  $K_D$  values obtained are somewhat larger. The plate heights are somewhat larger than the best values obtained on the kieselguhr columns (Table VII) but quite comparable with the average values. Elution curves for the separation of the heavy rare earths on Column VI are shown in Fig. 1.

Some difficulty was encountered in the spectrophotometric determination of the rare earths with large  $K_D$  values (greater than 30). Larger fractions were collected and it was necessary to concentrate the rare earth by evaporation of the excess acid. This resulted in the concentration of any organophosphorus compound eluted from the column. Apparently the organophosphorus compound interferes to some extent with the spectrophotometric determination of the rare earths and the plate heights could not be determined in these cases.

The data presented show that MHDPO and MEHDPO are useful stationary phases for the separation of milligram amounts of a number of the rare earths on small columns. The data also suggest that Plaskon and perhaps Kel-F are as useful as kieselguhr as supporting materials when the particle sizes of the various supports are comparable. The more inert nature of the fluorocarbon materials is a definite advantage over kieselguhr.

The plate heights reported in the present work are somewhat larger than those reported by SOCHACKA AND SIEKIERSKI<sup>8</sup> for HDEHP. The latter authors used tracer techniques, however, and the amount of rare earth carrier was "below 0.001 mg". In the present work approximately 1 mg of each rare earth was used.

## SUMMARY

Data are presented on the separation of various rare earth ions by extraction chromatography using methylenebis(di-*n*-hexylphosphine oxide), MHDPO, and methylenebis[di-(2-ethylhexyl)-phosphine oxide], MEHDPO, supported on kieselguhr, Kel-F, or Plaskon as stationary phases. The data suggest the particular support used for the extractant has little effect on HETP provided the particle size of the supporting material is the same.

The observed  $K_D$  and HETP values are shown to be relatively insensitive to moderate changes in the flow rate and temperature. Average values of HETP of approximately 1 mm were observed but values less than half that large were obtained in some cases. Elution curves for the separation of four adjacent rare earths (milligram amounts of gadolinium, terbium, dysprosium and holmium) are shown.

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