

THE SEPARATION OF THE RARE EARTHS BY PARTITION  
CHROMATOGRAPHY WITH REVERSED PHASESPART II. BEHAVIOUR OF INDIVIDUAL ELEMENTS ON  
HDEHP-CORVIC COLUMNS

T. B. PIERCE, P. F. PECK AND R. S. HOBBS

*Analytical Chemistry Branch, Atomic Energy Research Establishment,  
Harwell, Didcot, Berks. (Great Britain)*

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In Part I of this series<sup>1</sup> it was suggested that a useful separation of the rare earths might be achieved if the properties of certain complexing agents, known to provide large separation factors for adjacent lanthanides in liquid-liquid systems, (*e.g.* di-(2-ethylhexyl) orthophosphoric acid, HDEHP) were exploited by chromatographic elution<sup>1</sup>. A system was therefore developed in which HDEHP was retained on a poly-(vinyl chloride/vinyl acetate) copolymer (Corvic) and the resulting solid used in columns for chromatographic determinations. It was found that this column material could be conveniently prepared with reproducible elution characteristics and that sharp elution peaks could be obtained if columns were run at 60°. A third power dependency of  $(1/R_F - 1)$  upon the hydrogen ion concentration of the eluting phase showed that the behaviour of HDEHP retained on Corvic had some similarities with that when the reagent was dissolved in an organic diluent such as toluene. This system is known to give good separation factors for adjacent lanthanides<sup>2</sup>, but a wider assessment of the potentialities of HDEHP-Corvic columns for the chromatographic separation of the rare earths would be possible only if the separation factors of all elements of the series, achieved by elution from these columns, were investigated. Consequently, to determine the effect of transferring HDEHP from a liquid to a solid phase, a number of elutions and liquid-liquid extractions of all the elements from lanthanum to lutetium were carried out.

## EXPERIMENTAL

The chromatographic apparatus, reagents and techniques were similar to those already described<sup>1</sup>, the columns being run at temperatures of 60°. HDEHP-Corvic mixtures as made up, were found to have a capacity of 0.32 mequiv./g by saturation with metal and were used for elutions between 1 and 10 days after preparation.

For solvent extraction 20% v/v solutions of purified HDEHP in redistilled toluene were used and equilibrations carried out at 25° ± 0.1°. Each of the two phases contacted during the extraction process was pre-equilibrated with the other at this temperature and 10 ml of both solutions were pipetted into a thermostated centrifuge tube. After active lanthanide tracer had been added in not more than 0.01 ml of

solution, the phases were mixed by stirring briskly for 20 min and then separated by centrifugation. To confirm that equilibrium had been attained organic phases containing extracted tracer were re-equilibrated with fresh perchloric acid to enable equilibrium to be reached from conditions of metal deficient as well as metal rich aqueous phase. No attempt was made to maintain the ionic strength of the aqueous phase constant and acid solutions were made up by diluting concentrated acid to the appropriate value.

2 ml of each solution were carefully pipetted off to enable the distribution of radioactivity to be assayed and the acid strength of the aqueous phase obtained by titration against standard alkali. Experimental results were plotted on a graph of  $\log$  of the distribution ratio ( $\log D$ ) versus  $\log$  of the hydrogen ion concentration of the aqueous phase for liquid-liquid determinations, and a graph of  $R_M = \log (1/R_F - 1)$  versus  $\log$  of the hydrogen ion concentration of the eluting phase for elutions. The best straight lines through the points for each individual element were found by the method of least squares, and slopes and intercepts were calculated.

## RESULTS

### Perchlorate system

Since aqueous phases were made up by dilution of concentrated acid with water, an increase in the hydrogen ion concentration of the aqueous phase was associated with an increase in the concentration of the anion of the acid. In order to reduce the effect of complexes that might be formed between the rare earths and this anion, a series of elutions was carried out using perchloric acid as aqueous phase. As in Part I of this series<sup>1</sup> it was considered that batch extraction methods might be unsuitable for determining distribution ratios when HDEHP-Corvic mixtures were employed as solid phase, since shaking might cause the complexing agent to strip from the polymer. The results obtained for the elution of all the lanthanides from HDEHP-Corvic columns by aqueous perchloric acid are presented on a plot of  $R_M$  against the  $\log$  of the hydrogen ion concentration of the eluting phase in Fig. 1. It can be seen that in

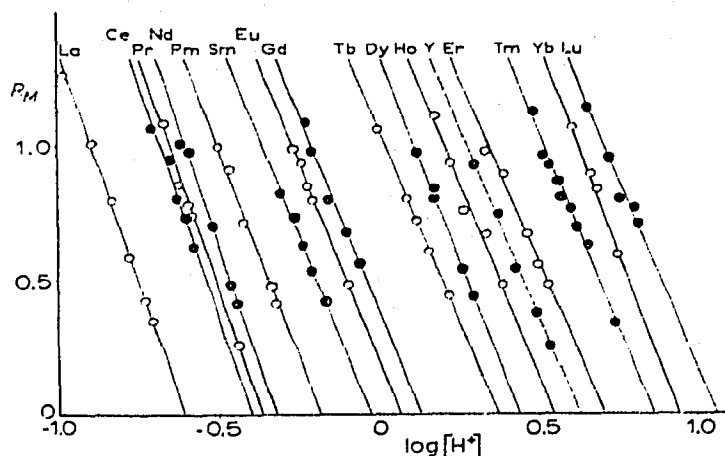


Fig. 1. Elution of the lanthanides from HDEHP-Corvic columns with perchloric acid.

all cases a linear relationship is found, the average slopes of all the lines being  $-3.13 \pm 0.29$ , which is close to the expected value<sup>2</sup> of  $-3.0$ . Experimental results for yttrium are also included. If it is assumed that the elution of the rare earths from

columns of a complexing agent immobilised on a solid support is accounted<sup>1</sup> for by the following equation:

$$R_M = \log A_s/A_m + \log K^{11} + n \log [\text{HL}]_0 - n \log [\text{H}^+] \quad (1)$$

it can be seen that for the elution of two elements from columns of similar characteristics (*i.e.* columns for which  $A_s$ ,  $A_m$  and  $[\text{HL}]_0$  are the same) at a given  $R_M$  value:

$$\log K_1^{11} - \log K_2^{11} = n \log [\text{H}^+]_1 - n \log [\text{H}^+]_2$$

subscripts 1 and 2 referring to the values obtained for the two different elements. A plot of  $3 \log [\text{H}^+]$  at  $R_M = 1.0$  is shown for the rare earths in Fig. 2 from which it can be seen that the value of the intercept increases linearly with the atomic number of the elements eluted, the slope of the line corresponding to an average separation factor for adjacent rare earths of  $2.44 \pm 1.15$ .

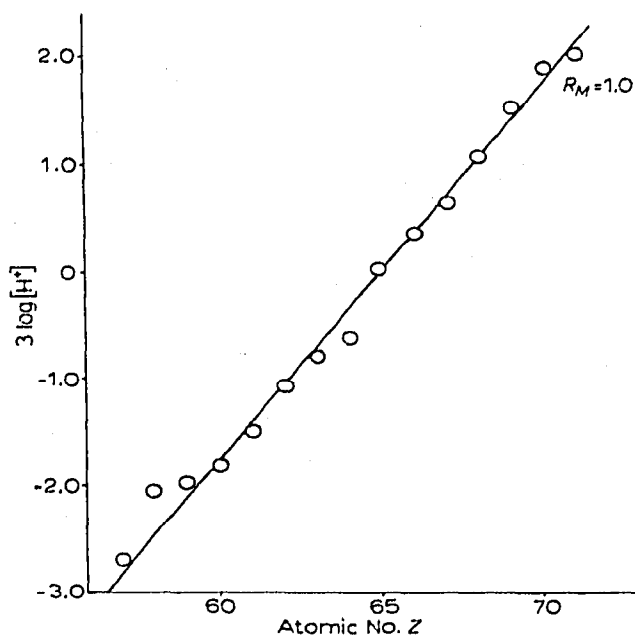


Fig. 2. Plot of  $3 \log [\text{H}^+]$  at  $R_M = 1.0$  against atomic number for perchlorate elutions.

This compares well with the average value of  $2.40 \pm 0.87$  found for the extraction of rare earths from aqueous perchloric acid, by a solution of HDEHP in toluene<sup>3</sup>, but clearly separation factors for adjacent pairs vary considerably throughout the series.

#### *Hydrochloric acid*

Hydrochloric acid was used in place of perchloric acid as aqueous phase for a series of elutions, since the chloride systems could prove more acceptable than the perchlorate for a number of practical separations. Results of the hydrochloric acid elutions are given in Fig. 3 from which it can be seen, once more, that consistent results are obtained, the average slope of the best straight lines through the points being  $-2.73 \pm 0.37$ . Again, however, the aqueous phase was made up from concentrated acid by dilution with water, and therefore the chloride ion concentration increased as the acidity of the aqueous phase was increased.

For comparison the rare earths were extracted from aqueous hydrochloric acid into a solution of HDEHP in toluene at 25°, and the results of these extractions are given in Fig. 4, on a plot of  $\log D$ , (log of the distribution ratio), against the log of the

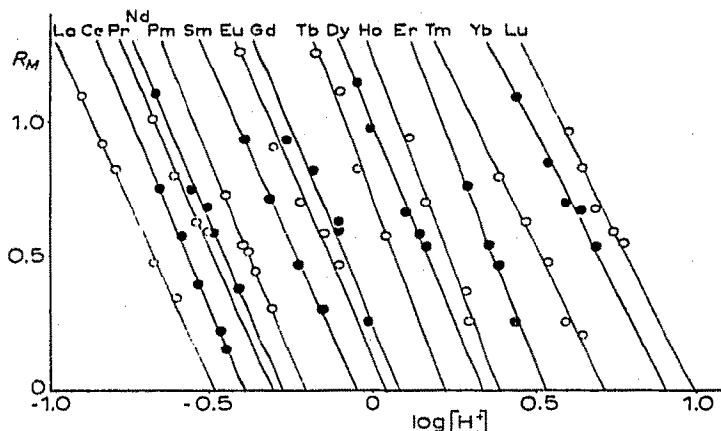


Fig. 3. Elution of the lanthanides from HDEHP-Corvic columns with hydrochloric acid.

hydrogen ion concentration of the aqueous phase, the average slope of the lines being  $-3.57 \pm 0.25$ .

Since the equation, equivalent to eqn. (1) for liquid-liquid extractions when phases of the same volumes are used is:

$$\log D = \log K_L + n \log [HL]_0 - n \log [H^+]$$

where  $K_L$  is a constant and the subscript 0 refers to species present in the organic phase, a graph of  $3 \log [H^+]$  at a given value of  $\log D$ , against atomic number for the rare earths should give a measure of the separation factors for adjacent elements. This is shown in Fig. 5, together with the value of  $3 \log [H^+]$  at which  $R_M = 1$  in the

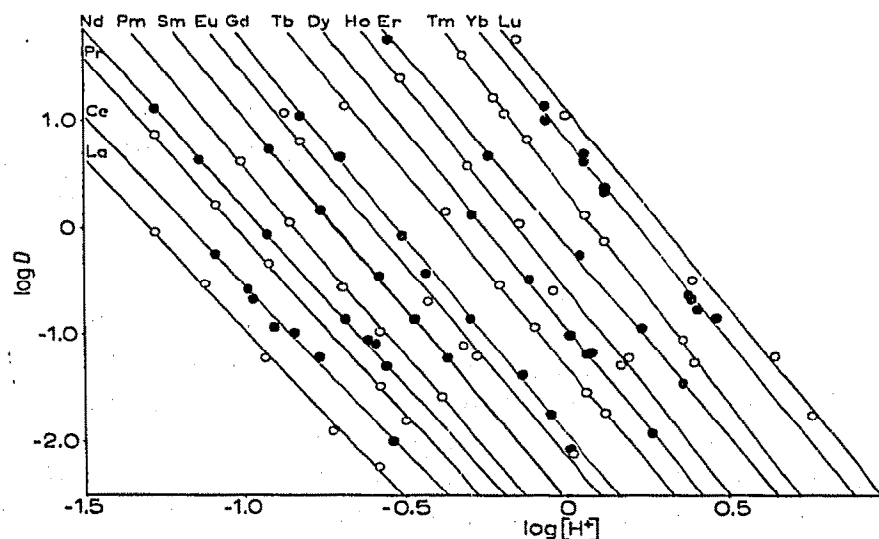


Fig. 4. Distribution of the lanthanides between aqueous hydrochloric acid and a solution of HDEHP in toluene.

chloride system. The average separation factors for the liquid-liquid and liquid-solid systems are  $2.24 \pm 0.42$  and  $2.11 \pm 0.57$  respectively.

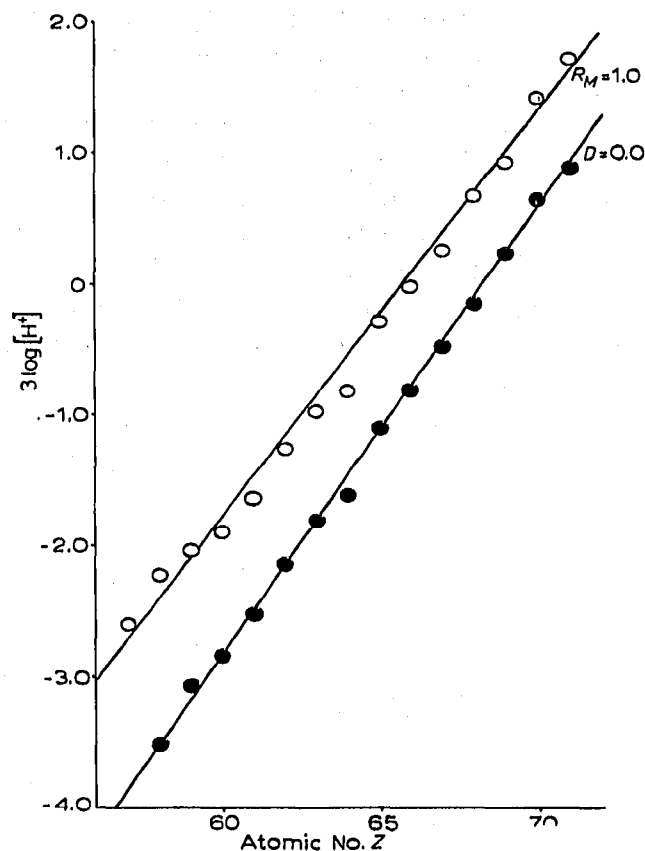


Fig. 5. Plot of  $3 \log [H^+]$  at  $R_M = 1.0$  and  $\log D = 0$  against atomic number for hydrochloric acid elutions and extractions. ● refers to extractions and O to elutions.

#### DISCUSSION

HDEHP-Corvic mixtures were developed as a column material, suitable for chromatographic operation, since it was hoped that the good separation factors, found for adjacent rare earths in liquid-liquid systems when the alkyl-phosphoric acid was dissolved in an organic diluent such as toluene, would be unaltered when the HDEHP was immobilised on a solid supporting material. For this to occur, the effect of the other constituents of the non-aqueous phase upon HDEHP-rare earth equilibria must be small, or at least produce systematic differences in the  $K^{11}$  values when the complexing agent is transferred from a liquid to a solid phase, so that the ratios of the  $K^{11}$  values of the elements, (the separation factors) do not vary. The average separation factor for adjacent members of the rare earth series, calculated from perchlorate elutions, is in fact very near to that found for the liquid-liquid perchlorate system ( $2.44 \pm 1.15$  compared with  $2.40 \pm 0.87$ ) thus indicating that transference of the HDEHP from a liquid to a solid phase does not diminish the possibility of obtaining good rare earth separations with the reagent. Rigorous comparison between liquid-liquid and liquid-solid results quoted in this paper and elsewhere<sup>3</sup> for the same aqueous phase is not possible, since, in order to obtain sharp elution peaks, chromato-

graphic elutions were carried out at 60° whereas the more convenient temperature of 25° was used for liquid-liquid extractions and the acid ranges over which both series of experiments were carried out for the same element were different, thus resulting in different acid anion concentration in the two cases. However, if varying the concentration of the perchlorate ion in the aqueous phase has little effect on the distribution of the rare earths between the aqueous and non-aqueous phase, and the effect of temperature on the extraction of the rare earths is either small or similar for all the elements, then the individual separation factors for adjacent pairs of elements should be nearly equal for the liquid-liquid, and for the liquid-solid systems, provided that the alkyl phosphoric acid behaves in the same manner in both cases.

In Fig. 6 the values of  $3 \log [H^+]$  at  $R_M = 1.0$  for perchlorate elutions are plotted against atomic number for all the elements from lanthanum to lutetium as in Fig. 2, together with the values of  $3 \log [H^+]$  at which  $\log D = 0$  in the liquid-liquid system,

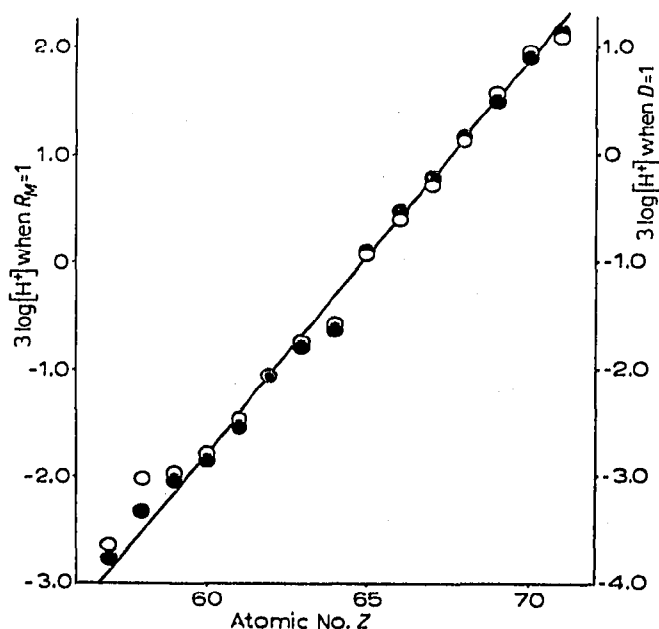


Fig. 6. Comparison of separation factors found from perchlorate extractions and elutions. ● refers to liquid-liquid results and O to liquid-solid results.

with the scale displaced by the average difference between  $3 \log [H^+]$  when  $R_M = 1.0$  and  $3 \log [H^+]$  when  $\log D = 0$  for each element. From this it can be seen that the relative positions of the points derived from solvent extraction results, correspond well with those taken from elution measurements, the largest difference occurring in the case of cerium, which shows a smaller separation from praseodymium in the liquid-solid than in the liquid-liquid system. Thus, generally, similar separation factors are obtained in the two systems, which is of interest, since liquid-liquid measurements are derived from equilibrium determinations with the HDEHP dissolved in toluene, whereas for elutions, the aqueous phase flowed past the reagent which was immobilised on a solid.

Further, the results suggest that it should be possible to predict the behaviour of elements on these columns from liquid-liquid results, if the position of the elution maximum for one element is known at a given acidity, together with the liquid extraction data for this and the other elements to be eluted.

The linear relationship between  $3 \log [H^+]$  at  $R_M = 1.0$  and atomic number indicates that a mixture of all the elements from lanthanum to lutetium could be separated by elution from HDEHP-Corvic columns, and that elements would be eluted in the order of increasing atomic number, that is to say in the order which is the reverse of that found in conventional cation-exchanger-aqueous complexing agent procedures. Yttrium, if it were to fall on the line shown in Fig. 2, would have to have an atomic number of 67.4 which is in good agreement with the value of 67.5 found for the liquid-liquid system<sup>3</sup>.

When hydrochloric acid is used in place of perchloric acid, any chloro-complexes formed in the aqueous phase would be expected to favour a decrease in the distribution of the rare earths into the organic phase, and this effect, if appreciable, would be apparent in determinations, such as those quoted in Figs. 3 and 4, where the chloride concentration of the aqueous phase was changing. Plots of  $R_M$  and  $\log D$  against  $3 \log [H^+]$  were found to be linear, within the limits of experimental error, over the acid ranges used for each element, but separation factors were generally smaller when chloride, as opposed to perchlorate was the anion of the acid, the average separation factors being  $2.24 \pm 0.42$  and  $2.11 \pm 0.57$  for the liquid-liquid and liquid-solid systems respectively. This compares with the values of  $2.40 \pm 0.87$  and  $2.44 \pm 1.15$  quoted above for the equivalent values in the perchlorate system, and the value of 2.5 found for the chloride system at constant chloride concentration<sup>2</sup>.

The separation factors for adjacent pairs of rare earths calculated from the elution data presented in Figs. 1 and 3 are given in Table I, together with values found for liquid-liquid systems (Fig. 4 and ref. 3) and for ion-exchange elutions<sup>4</sup>.

It can be seen that the most difficult mixtures of elements to separate from one another by elution from HDEHP-Corvic columns will be cerium-praseodymium-neodymium, and europium-gadolinium, and this has already been found to be the case in practice<sup>5</sup>. With the exception of the cerium-praseodymium separation, and perhaps the praseodymium-neodymium separation, separation factors found when

TABLE I

SEPARATION FACTORS FOR THE RARE EARTHS IN SOME HDEHP AND ION-EXCHANGE SYSTEMS

Separation	HDEHP				Dowex 50		
	Perchlorate system		Chloride system		Glycolate at 87°	$\alpha$ -Hydroxyisobutyrate at 87°	Lactate at 20°
	Elutions	Extractions	Elutions	Extractions			
La-Ce	4.7	3.0	2.4	2.4	2.6	2.2	2.1
Ce-Pr	1.3	2.1	1.5	2.8	1.5	1.6	2.04
Pr-Nd	1.4	1.4	1.4	1.7	1.4	1.57	1.38
Nd-Pm	2.1	2.2	1.9	2.1	1.26	1.61	1.35
Pm-Sm	2.6	3.1	2.3	2.4	1.29	1.82	1.32
Sm-Eu	1.8	1.9	2.0	2.2	1.22	1.6	1.20
Eu-Gd	1.5	1.4	1.4	1.6	1.06	1.4	1.04
Gd-Tb	5.2	5.0	3.3	3.2	1.3	2.2	1.50
Tb-Dy	1.9	2.1	1.9	2.0	1.39	1.88	1.65
Dy-Ho	1.8	1.9	1.9	2.1	1.2	1.63	1.43
Ho-Er	2.7	2.3	2.7	2.1	1.5	1.23	1.60
Er-Tm	3.3	2.5	1.8	2.5	1.4	1.30	1.54
Tm-Yb	2.2	3.1	3.1	2.5	1.5	1.33	1.54
Yb-Lu	1.8	1.9	2.0	1.8	1.32	1.36	1.40
Average	2.4	2.4	2.1	2.2	1.43	1.62	1.51

HDEHP is immobilised on Corvic, are not appreciably worse than the best figure given in Table I for ion-exchange separations, and in most cases are very much better.

Separation factors given in Table I derived for elutions and extractions of pairs of elements by the same acid suggest that the effect that immobilising the complexing agent on Corvic has on the relative positions of the rare earth-HDEHP equilibria is small, and it is therefore likely that similar figures to those quoted above would be obtained in reversed phase systems where the HDEHP was retained on another inert support. Separation factors have been reported for a number of pairs of rare earths after elution by hydrochloric acid from columns of HDEHP retained on cellulose powder<sup>6</sup>. The values obtained, (La-Ce 2.35; Nd-Pm 2.10; Eu-Gd 1.65; Gd-Tb 3.85; Tm-Yb 3.33), cannot be compared exactly with the figures given in Table I because of a difference in operating conditions but are clearly similar to them.

A disadvantage of the reversed phase system described in this paper compared with conventional ion-exchangers for the separation of macro quantities of rare earths is provided by the relatively low capacity of HDEHP-Corvic columns for the extraction of metals. Whilst it has been found that the capacity of the column material used in these determinations (0.32 mequiv./g) could be considerably improved by adding more phosphoric acid to the polymer<sup>1</sup> and it is possible that higher loadings could be achieved with other support materials<sup>7</sup>, the acid-base binding capacity of ~ 3 mequiv./g indicates that even under the most favourable conditions the capacity of HDEHP mixtures cannot equal that of suitable ion-exchangers (~ 5 mequiv./g). Nevertheless, the reliability of the system, the order of elution of the elements, the simplicity of the eluting phase and the generally higher separation factors for adjacent elements has resulted in the reversed phase partition technique providing a more satisfactory means for the routine separation of rare earths, prior to analytical determination, in several cases.

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#### SUMMARY

The elements lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium have been eluted by perchloric and hydrochloric acid of different strengths from columns of di-(2-ethylhexyl) orthophosphoric acid retained on a poly-(vinyl chloride/vinyl acetate) copolymer. From these results separation factors have been calculated and these are compared with values obtained from solvent extraction determinations with the alkyl-phosphoric acid dissolved in toluene.

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