

USE OF 2-ETHYLHEXYL PHENYLPHOSPHONIC ACID IN REVERSED PHASE PARTITION CHROMATOGRAPHY

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Two factors determine the separating ability of an extracting system in partition chromatography. The first is the effective height of the theoretical plate (later referred to simply as the height of the plate, H), the second is the separation factor for a pair of cations to be separated. It has been shown in previous papers from this Department^{1,2} that the height of the plate depends on the flow rate, the temperature and the amount of extracting agent in the stationary phase. A comparison of our results, obtained for di-(2-ethylhexyl) orthophosphoric acid (HDEHP) as extracting agent, with the results of other authors working with the same extractant^{3,4} shows also that the height of the plate depends on the nature of the supporting material and is lowest for silicone-treated kieselguhr. However, it is possible that this effect might not be caused by the different surface properties of the different materials, but simply by the different sizes of the grains of the supporting materials used by various authors. It also seems that the height of the plate may depend on the extracting agent itself because it is lower, on the average, for columns where tributyl phosphate (TBP) is used as extractant than for columns with HDEHP.

With respect to the separation factor for adjacent rare earths, HDEHP is vastly superior to TBP. However, PEPPARD, MASON AND HUCHER⁵ have shown that 2-ethylhexyl phenylphosphonic acid (HEHØP) is an even more selective extracting agent for rare earths than HDEHP (the mean separation factor is 2.8, as compared with 2.5 for HDEHP). Provided that the height of the plate for columns with HEHØP supported on silicone-treated kieselguhr is not too great, HEHØP should be an excellent extracting agent for reversed phase partition chromatography of rare earths.

The possible applications of HEHØP in reversed phase partition chromatography of rare earths are discussed and the results are presented in this paper. A comparison with other systems has also been made.

EXPERIMENTAL

Silicone-treated kieselguhr "Hyflo Supercel" was used as the solid support for HEHØP. The column material was prepared as in the case of HDEHP¹ by mixing the appropriate amounts of kieselguhr and HEHØP with hexane, and evaporating the solvent at room temperature. The columns used in the course of this work were about 3 mm in diameter and the length of the bed was 9 cm. Such columns contained about 0.36 g of kieselguhr. The amount of HEHØP varied between 5 and 14 % relative to the weight of kieselguhr. The columns containing HEHØP as the extractant were perfectly stable and could be used for many runs.

The HEHØP used was kindly synthesised for us in the Department of Organic Chemistry at the Institute of Technology, Łódź. Its purity, as determined by titration, was 98 %. Most of the radio-isotopes used were prepared by irradiation of appropriate targets in the Polish reactor "EWA". Some radio-isotopes were obtained from the Radiochemical Centre, Amersham. The amount of the rare earth carriers was always below 0.001 mg. It was observed, in accordance with the results obtained for HDEHP, that the greater the amount of carrier the greater the influence on the shape and position of the elution peaks.

Most elutions were carried out at room temperature using acids pre-equilibrated with HEHØP. The flow rate was about $1 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$. The volume of the sample introduced into the column was about 0.04 ml. The free volume of the column was determined using ^{137}Cs .

RESULTS AND DISCUSSION

The effect of various factors on the height of the plate

To determine the height of the plate the number of plates was calculated from the equation given by GLUECKAUF⁶

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

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.

No systematic study was performed on the effect of the grain size on the height of the plate. After some preliminary experiments a specific fraction of kieselguhr which settled within about 20 min in a 20 cm high beaker was selected. Using this fraction columns could be prepared which had a plate height of about 0.22 mm.

The height of the plate is affected by the amount of HEHØP retained on the kieselguhr in a similar way to that observed in the case of HDEHP¹. This is illustrated by the data quoted in Table I. The height of the plate was calculated from the position and width of the europium peak. Elution was carried out with hydrochloric acid (0.95 M).

The influence of flow rate and temperature on the height of the plate is also shown in Table I. This seems to be even more pronounced than in the case of HDEHP.

Separation factors

Reversed phase partition chromatography allows the very exact determination of the separation factors from the positions of peak maxima. The results obtained for HEHØP are shown in Table II. The mean geometric separation factor calculated from these results is 2.50 for HCl as the eluting agent. Our data for HCl as the eluting agent show also that the mean separation factor for the rare earths from La to Gd is equal to 2.20 and is much lower than that for the rare earths from Gd to Lu, which in turn is equal to 2.85. The value of the mean separation factor for the rare earths from Gd to Lu is 3.02, when HNO_3 is used as the eluting acid.

The comparison of separation factors for the different groups of rare earths determined by the elution method is based on the assumption that separation factors

TABLE I

THE EFFECT OF FLOW RATE, TEMPERATURE AND AMOUNT OF HEHØP ON THE HEIGHT OF THE PLATE

<i>Flow rate</i> (<i>ml · cm⁻² · min⁻¹</i>)	<i>Temperature</i> (°C)	<i>mg of</i> <i>HEHØP per</i> <i>100 mg</i> <i>kieselguhr</i>	<i>Height of the</i> <i>plate</i> (<i>mm</i>)
0.25	20	14	0.11
0.50	20	14	0.16
1.0	20	14	0.22
1.0	20	14	0.22
1.0	25	14	0.19
1.0	30	14	0.16
1.0	20	9	0.20
1.0	20	14	0.22
1.0	20	18	0.25
1.0	20	30	0.45

are independent of the concentration of acid, because it is impossible to elute all the rare earths with one concentration of the acid. It has been verified in the course of this work that, at least up to 2 M HCl, the separation factors are independent of the concentration of acid, so that the values of separation factors for all the light rare earths are directly comparable. The same is true for the group of heavy rare earths since they were all eluted with HCl of constant concentration, using different amounts of HEHØP retained on the columns. But comparison of the mean separation factors for the two groups of rare earths includes some arbitrariness caused by the different concentrations of the eluting acid.

There are considerable deviations in the separation factors for different pairs of adjacent rare earths from the mean value. It is interesting to note that the sequence of positive and negative deviations from the mean value of the separation factor is very similar in the two groups of rare earths (La-Gd and Gd-Lu).

Examples of separations

In the course of this work, conditions for the separation of all rare earths in groups of several have been established. Fig. 1-4 show examples of such separations including all those pairs of the adjacent rare earths which have low values for the separation factors. As follows from Table II there are six such pairs: Ce-Pr, Pr-Nd, Eu-Gd, Tb-Dy, Dy-Ho and Yb-Lu. In spite of the low values of the separation factors all these separations are excellent. In the case of the heavy rare earths a smaller amount of HEHØP was used (9 % and 4.7 % relative to the amount of kieselguhr) to decrease the concentration of acid necessary for elution.

Comparison with other systems

Rare earths can be separated by the method of reversed phase partition chromatography using TBP, HDEHP and HEHØP as extractants. From the point of view of separation factors the system in which HEHØP is used as the extractant is the best, although the difference between HEHØP and HDEHP under the conditions

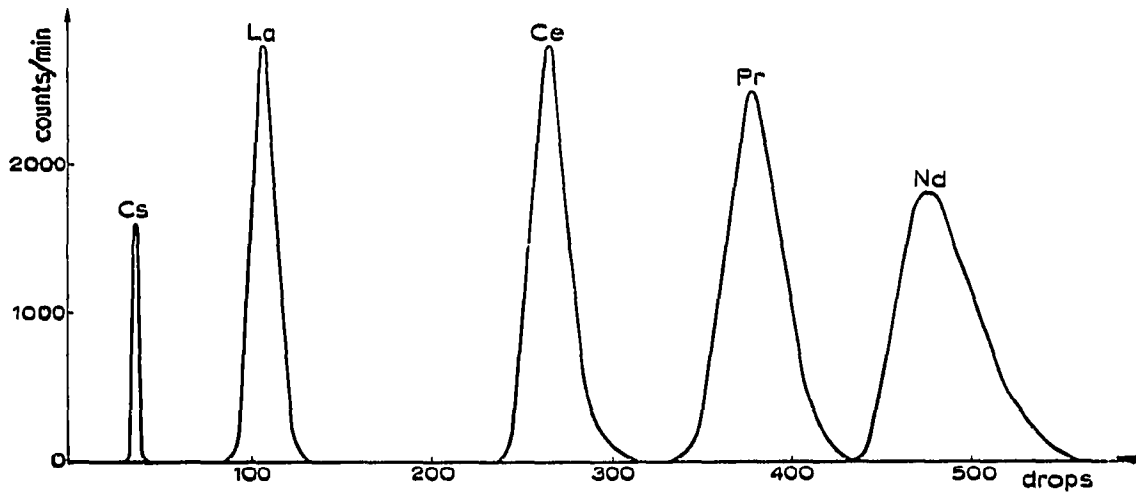


Fig. 1. Separation of La-Ce-Pr-Nd with 0.42 M HCl at 20°. Amount of HEHØP: 14% (relative to the weight of kieselguhr).

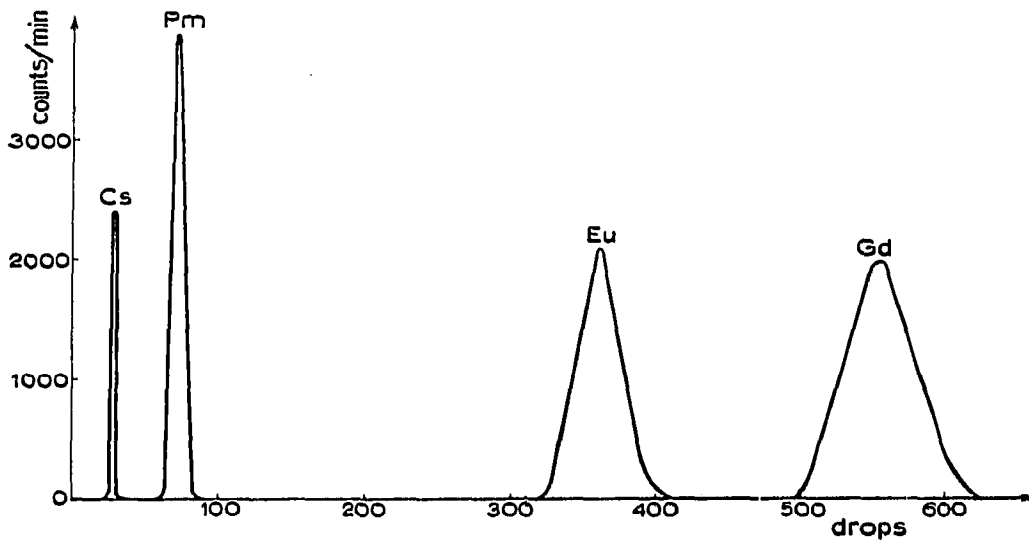


Fig. 2. Separation of Pm-Eu-Gd with 0.95 M HCl at 29°. Amount of HEHØP: 14%.

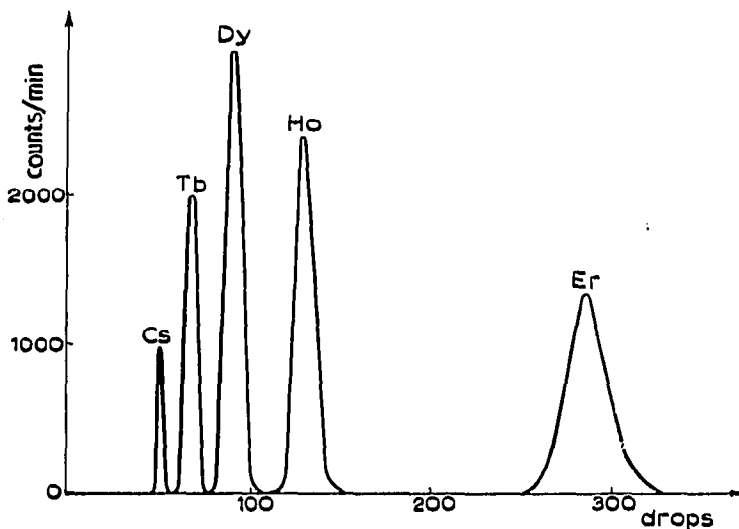


Fig. 3. Separation of Tb-Dy-Ho-Er with 7.4 M HNO₃ at 20°. Amount of HEHØP: 9%.

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
<i>Elution with HCl</i>														
Separation factor	3.3	1.5	1.3	2.8	3.6	2.3	1.6	5.4	2.1	1.9	2.9	3.8	3.2	3.0
Molarity of acid	0.42	0.42	0.42	0.66	0.66	0.95	0.95	1.94	6.58	6.58	6.58	6.58	6.58	6.58
	0.57	0.57	0.57	0.95	0.95	1.94	1.94	7.06	7.06	7.06	7.06	7.06	7.06	7.06
<i>Elution with HNO₃</i>														
Separation factor							1.8	5.9	2.3	2.0	3.0	4.0	3.4	2.1
Molarity of acid							2.06	2.06	7.39	7.39	7.39	7.39	7.39	7.39

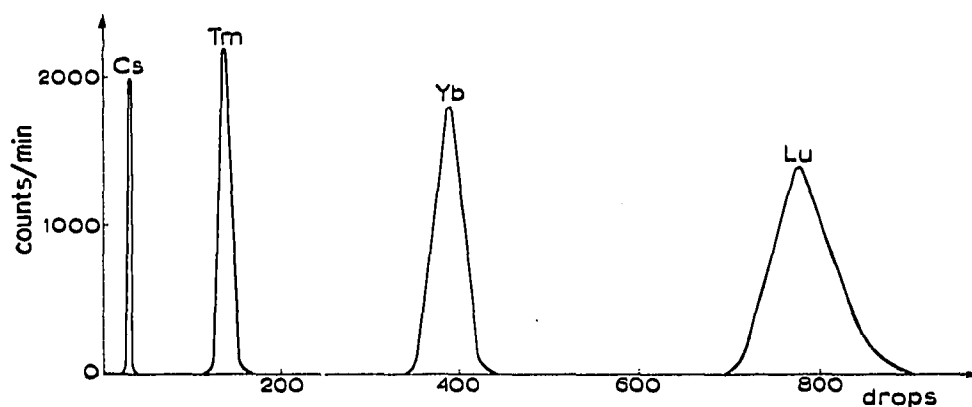


Fig. 4. Separation of Tm-Yb-Lu with 7.4 M HNO₃ at 20°. Amount of HEHØP: 4.7%.

used is rather small. Both systems show higher separation factors for the rare earths from Gd to Lu than from La to Gd (the values for HDEHP are: 2.05 and 2.81¹; elution carried out with HCl). Because of the separation factor, HNO₃ is a better eluting agent for the group of heavy rare earths than HCl. In the system with HDEHP as the extractant, HCl cannot be used at all for the elution of the heavy rare earths, because of the broadening of the elution peaks. This effect was not observed in the case of HEHØP as the extractant. HCl, in turn, is a better eluting agent for light rare earths in the HDEHP system. HEHØP is a stronger extracting agent than HDEHP, so that more concentrated acid must be used for the elution, or a smaller amount of HEHØP must be placed on the column. In the latter case the capacity of the column is decreased. As far as the separation factors are concerned the system with TBP as extractant is less favourable for the separation of heavy rare earths than the two systems with acidic extractants. The mean separation factor in the system TBP-HNO₃ for the rare earths from Gd to Lu is 1.5 and that for light rare earths is about 1.9. It should also be noted that for the separation of the light rare earths in the system TBP-HNO₃, highly concentrated acid must be used as an eluant, which is very inconvenient in some applications. Besides, at such high concentrations of HNO₃ columns are unstable and can only be used for few experiments.

As regards the second factor determining the separating ability of a system, TBP seems to be somewhat more favourable than the two acidic extractants. The height of the plate for columns with TBP as the stationary phase can be as low as 0.15–0.14 mm, whereas for columns containing HDEHP or HEHØP it is generally not less than 0.22 mm. Since for columns containing tri-*n*-octylphosphine oxide (TOPO) the height of the plate is also very low, it seems that neutral extracting agents are better in this respect than acidic extractants. The system with TBP also seems to be less sensitive to the amount of carrier.

Nevertheless the higher separation factors and the lower concentrations of acid needed for elution together with a sufficiently low value of the plate height make the acidic extractants, and especially HEHØP, the best extractants for the separation of trace amounts of rare earths by reversed phase partition chromatography.

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SUMMARY

Reversed phase partition chromatography with 2-ethylhexyl phenylphosphonic acid retained on kieselguhr as the stationary phase was applied to the separation of rare earths. A comparison with other extracting agents used in partition chromatography has been made.

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