CHROMATOGRAPHIC SEPARATION OF RARE EARTHS BY MEANS OF PAPER TREATED WITH THE LIQUID CATION EXCHANGER DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID

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Many interesting chemical separations have been performed by means of cellulose treated with tri-*n*-octylamine (TNOA) or with tri-*n*-octylphosphine oxide (TOPO), as reported in previous papers[1-5]. In cellulose treated with TNOA the selectivity for the various elements arises from the anion exchange property of TNOA. Therefore, elements that differ as regards the strength of the anionic complexes that they form are retained to a different extent by the treated cellulose. Elements that do not form anionic complexes in a given medium are not retained at all. Tri-*n*-octylphosphine oxide is a neutral extractant which does not act through ion exchange, but generally by combination with a neutral compound of the extractable element. As in the case of TNOA, the selectivity of TOPO in solvent extraction phenomena, is practically maintained in chromatographic separations by TOPO treated cellulose.

A considerable contribution to solvent extraction[6-10], particularly for uranium recovery[11-13], has been made by using an acidic phosphoric compound, di-(2-ethylhexyl) orthophosphoric acid (HDEHP). In general, HDEHP acts as a cation exchanger since the hydrogen atom can be replaced by a cationic equivalent.

PEPPARD *et al.*[7,9] reported that HDEHP is very effective for the separation of rare earths from each other by liquid–liquid extraction, the percent extraction of each element of the family gradually increasing with the atomic number of the element. The possibility of counter-current liquid–liquid contact for rare earth separation was also suggested.

It was our aim, in the present work, to show that chromatographic separation of rare earths can be achieved on paper treated with HDEHP. The relationships between the R_F values and the concentration of the eluting agent or of the solution used for pretreatment, and the influence of the operating temperature were also investigated.

Besides the rare earths, some elements that are interesting in the nuclear field, such as yttrium, scandium, thorium, uranium, zirconium, iron and aluminium, were also considered.
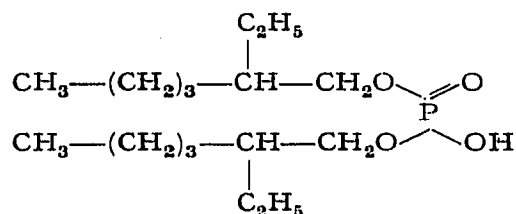
To increase the separating properties of some papers, experiments were also carried out with paper strips of which one end had been treated with HDEHP (cation exchanger) and the other with TNOA (anion exchanger).

EXPERIMENTAL

Reagents and equipment

Di-(2-ethylhexyl) orthophosphoric acid (HDEHP), the chemical formula of which is

given below, is a liquid with a molecular weight of 322.42 and $\rho = 0.97$. The product used was a Virginia-Carolina Chemical Co. (Richmond, U.S.A.) product supplied by Soc. Eigenmann and Veronelli (Milan).

$$CH_3—(CH_2)_3—\underset{\underset{C_2H_5}{|}}{CH}—CH_2O\diagdown_{P}\diagup^{\diagup O}_{\diagdown OH}$$
$$CH_3—(CH_2)_3—\underset{\overset{|}{C_2H_5}}{CH}—CH_2O\diagup$$

A 0.1 M solution of HDEHP in cyclohexane was used.

Tri-n-octyl-amine was supplied by Fluka (Buchs SG, Switzerland). A solution in benzene was used for the papers treated with two exchangers.

The rare earths (metals and oxides) were supplied by Fluka and Light's (London, England). The required amount of product was dissolved in the minimum volume of conc. HCl and then carefully dried. Afterwards, 0.1 M HCl was added to obtain solutions containing 2.5 mg of each element per ml.

For comparative chromatographic studies, the following rare earths, which are reported together with their atomic number, were used: La(57), Ce(58), Pr(59), Sm(62), Eu(63), Gd(64), Dy(66), Er(68) and Yb(70). For single chromatograms also the other members of the rare earth series were used, except Pm(61).
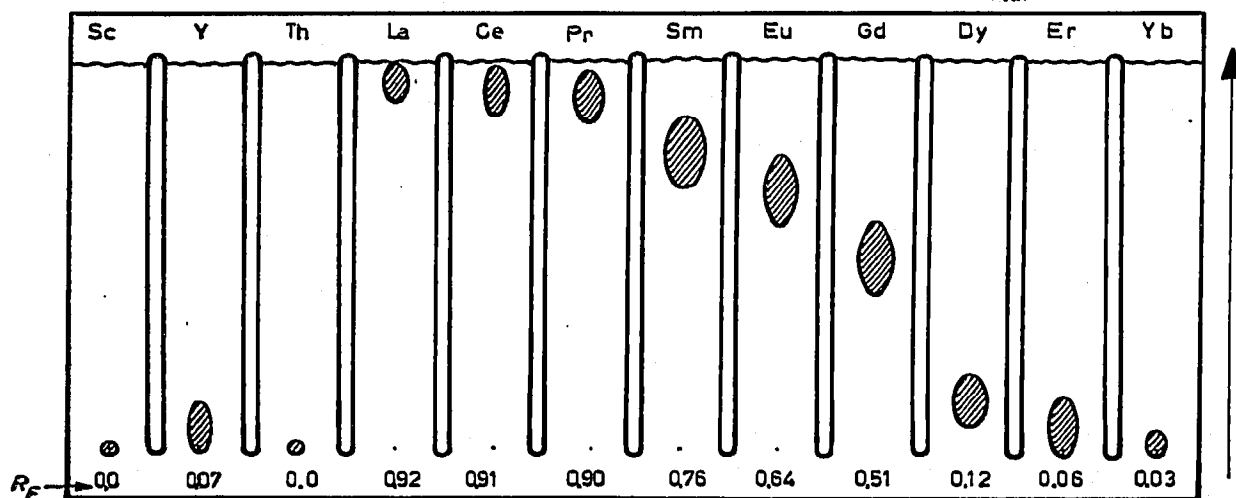

Fig. 1. Example of ascending chromatogram on type CRL/1 paper with nine rare earths and three additional elements. Paper treated with 0.1 M HDEHP, elution with 1 M HCl.

The spots were developed with a 1 % solution of 8-hydroxyquinoline dissolved in a 50/50 (vol.) water–ethanol solution. The spots became clearly visible on exposure of the strips to ammonia vapours.

The chromatographic paper used was Whatman No. 1, in sheets for single experiments, and of the type CRL/1 (Fig. 1) for multiple experiments.

The experimental chromatographic assembly used in the present work has already been described in a previous paper[4].

Experiments at controlled temperatures were carried out in a refrigerated cell for values below room temperature, and in a laboratory oven for those above room temperature.

Treatment of the paper and chromatographic procedure

The 0.1 M HDEHP–cyclohexane solution was shaken for 10 min with twice the volume of 1 M HCl. The organic phase was then percolated through cotton lint to remove any traces of the inorganic solution. The equilibrated HDEHP solution was transferred to a glass container where the paper sheets were immersed for about 30 sec. The papers were then allowed to drip, and finally dried with a current of warm air. The spots were deposited, as indicated in Fig. 1, by using 0.01 to 0.02 ml of solution (25 to 50 μg of the element). Each sheet of the CRL/1 type, was folded to form a cylinder and placed for ascending elution in a closed atmosphere inside the device described elsewhere[4]. A period of 20 to 40 min, depending on the molarity of the eluting acid, was required for the front to move 9 cm.

For normal chromatographic separations (Fig. 7a) strips of 2 × 20 cm were used. Sheets treated with two exchangers (Fig. 7b) were obtained by first soaking one end of the strip in a 0.1 M TNOA solution up to the required level; after drying, the other end of the strip was dipped into a 0.1 M HDEHP solution, until the liquid reached the level of the previously treated portion.

Conventional chromatographic separations were also carried out by ascending elution in a closed atmosphere, using suitable cylindrical columns.

TABLE I

R_F VALUES FOR NINE RARE EARTHS AND SEVEN ADDITIONAL ELEMENTS AS FUNCTIONS OF THE MOLARITY OF THE HCl USED AS ELUENT

Operating temperatures 25 ± 1°. Paper treated with 0.1 M HDEHP

| | R_F | | | | | | | | | |
| | HCl molarity | | | | | | | | | |
	0.1	*0.2*	*0.3*	*0.5*	*1*	*2*	*4*	*6*	*8*	*10*
La (57)	0.11	0.41	0.70	0.92	0.92	0.96	0.93	0.92	0.92	—
Ce (58)	0.08	0.22	0.55	0.82	0.91	0.93	0.91	0.90	0.91	—
Pr (59)	0.04	0.17	0.47	0.81	0.90	0.91	c.90	0.89	0.90	—
Sm (62)	0.0	0.04	0.09	0.35	0.76	0.85	0.88	0.88	0.89	—
Eu (63)	0.0	0.02	0.06	0.21	0.64	0.83	0.87	0.87	0.85	—
Gd (64)	0.0	0.0	0.04	0.14	0.51	0.82	0.84	0.85	0.85	—
Dy (66)	0.0	0.0	0.0	0.03	0.12	0.24	0.72	0.81	0.80	—
Er (68)	0.0	0.0	0.0	0.0	0.06	0.18	0.45	0.76	0.78	—
Yb (70)	0.0	0.0	0.0	0.0	0.03	0.08	0.32	0.43	0.59	—
Y (39)	0.0	0.0	0.0	0.02	0.07	0.22	0.60	0.81	0.81	—
Sc (21)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	—
Th (90)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	—
U (92)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.03
Zr (40)	0.0	—	—	—	0.0	—	—	—	—	0.0
Fe (26)	0.0	—	—	—	0.0	—	—	—	—	0.46
Al (13)	0.10	—	—	—	0.96	—	—	—	—	0.96

R_F values as functions of the molarity of the acid eluent

The spots of the twelve elements, namely Sc, Th, Y and nine of the rare earths, were arranged as shown in Fig. 1. Experiments were carried out with the following HCl molarities: 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, 3.0, 4.0, 6.0 and 8.0.
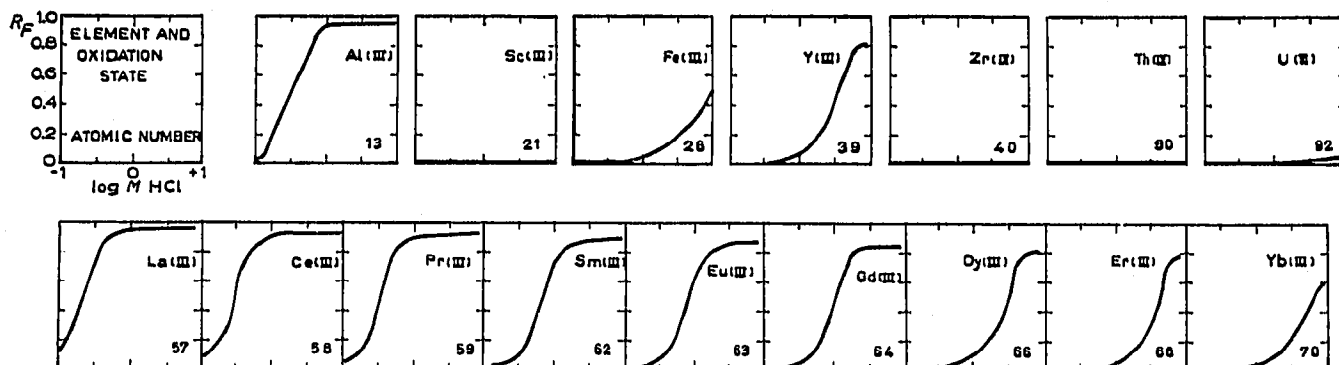

Fig. 2. R_F values of nine rare earths and seven additional elements plotted *vs.* log M HCl. Paper treated with 0.1 M HDEHP.

The results, collected in Table I and plotted in Fig. 2, show that:

(i) For a given molarity of HCl used as eluent the retention of the rare earths increases with the atomic number: for example at 0.5 M HCl, La (57) has an R_F of 0.86, whereas Er (68) and Yb (70) have R_F values = 0.

(ii) For a given element the R_F value increases with the HCl molarity: for example for Ce the R_F = 0.08 with 0.1 M HCl and 0.91 with 1 M HCl.

Table I and Fig. 2 show the results for the nine rare earths, for Y, Sc and Th, and for the four additional elements Zr, U, Al and Fe. The behaviour of yttrium is intermediate between that of Dy (66) and that of Er (68), which is in agreement with the values of their ionic radii. Zirconium and uranium give R_F = 0 at all molarities of HCl, whilst the behaviour of aluminium is similar to that of lanthanum and, finally, iron is intermediate.

Previous work[1,2,4] has shown that, by comparing extraction behaviour with chromatographic data for a given element, the higher the extraction coefficient E_a^o the lower the R_F value, provided that the extractant and the inorganic medium are the same.

In the case of chromatography with papers treated with organic extractants the two quantities E_a^o and R_F can be related as follows: the basic assumption is that the velocity dx/dt of the spot along the strip is related to the velocity dl/dt of the solvent front by the simple equation:

$$\frac{dx}{dt} = \frac{dl}{dt}(1 - \alpha)$$

where $0 \leqslant \alpha \leqslant 1$, and α is such that αQ is the amount of substance retained by the organic phase (stationary phase) at equilibrium.

By integrating over the whole run of the spot and solvent, one obtains:

$$x = l(1 - \alpha), \text{ and also } R_F = \frac{x}{l} = 1 - \alpha, \tag{1}$$

and finally:

$$\alpha = 1 - R_F$$

On the other hand, the extraction coefficient E_a^o (ratio of the concentrations in the two phases at equilibrium) is defined by:

$$E_a^o = \frac{\alpha \cdot \dfrac{Q}{v}}{(1 - \alpha)\dfrac{Q}{v'}} = \frac{\alpha v'}{(1 - \alpha) v} \tag{2}$$

where v and v' are the volumes of organic and inorganic phases respectively that enter into the partition process.

Combination of eqns. (1) and (2), gives:

$$E_a^o = \frac{v'}{v}\left(\frac{1}{R_F} - 1\right) \tag{3}$$

If we regard v'/v as the ratio of the cross sectional area occupied by the mobile phase (A_L) and the stationary phase (A_S), since the height of the volumes involved is the same for both phases, eqn. (3) is identical to

$$E_a^o = \frac{A_L}{A_S}\left(\frac{1}{R_F} - 1\right)$$

which is the equation developed by MARTIN AND SYNGE[14] from different assumptions.

The extraction of rare earths from chloride systems with HDEHP has been studied by PEPPARD et al.[7]. Their experiments showed that a linear relationship holds between log E_a^o and the atomic number of the various elements of the rare earth group, and also between log E_a^o and log M HCl.

From eqn. (3) we can obtain:

$$\log E_a^o = \log\left(\frac{1}{R_F} - 1\right) + \log k \tag{4}$$

where the ratio v'/v is considered as a constant k in each chromatogram. According to the results obtained by PEPPARD et al. reported above, it is to be expected that the right hand side of eqn. (4) is a linear function of the atomic number Z. In fact, by plotting (Fig. 3) the experimental results obtained for the nine elements considered, a family of parallel straight lines is obtained. These straight lines have different intercepts with the ordinate axis which depend on the molarity of the HCl. The results reported in Fig. 3 have been evaluated on the basis of the most reliable experimental data, that is not considering R_F values too close to zero and to unity.

A family of straight lines is also obtained by plotting log $(1/R_F - 1)$ versus log M HCl (Fig. 4). The straight lines are approximately parallel.

The effect of HCl molarity depends on the hydrogen ion concentration and not on the concentration of chloride. In fact, on eluting with 0.5 M LiCl the spots do not
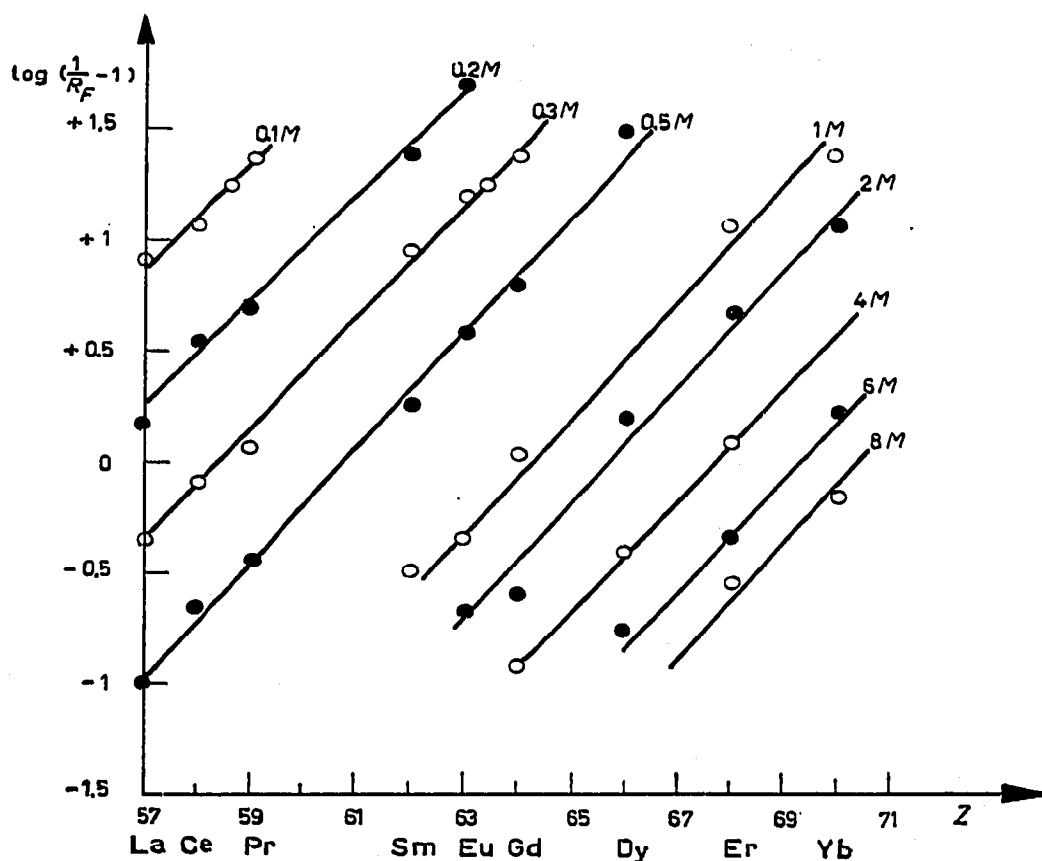
Fig. 3. Plot of log $(1/R_F - 1)$ *vs.* atomic number Z for nine rare earths. Paper treated with o.1 M HDEHP, elution with HCl. The molarities of the eluent are indicated.
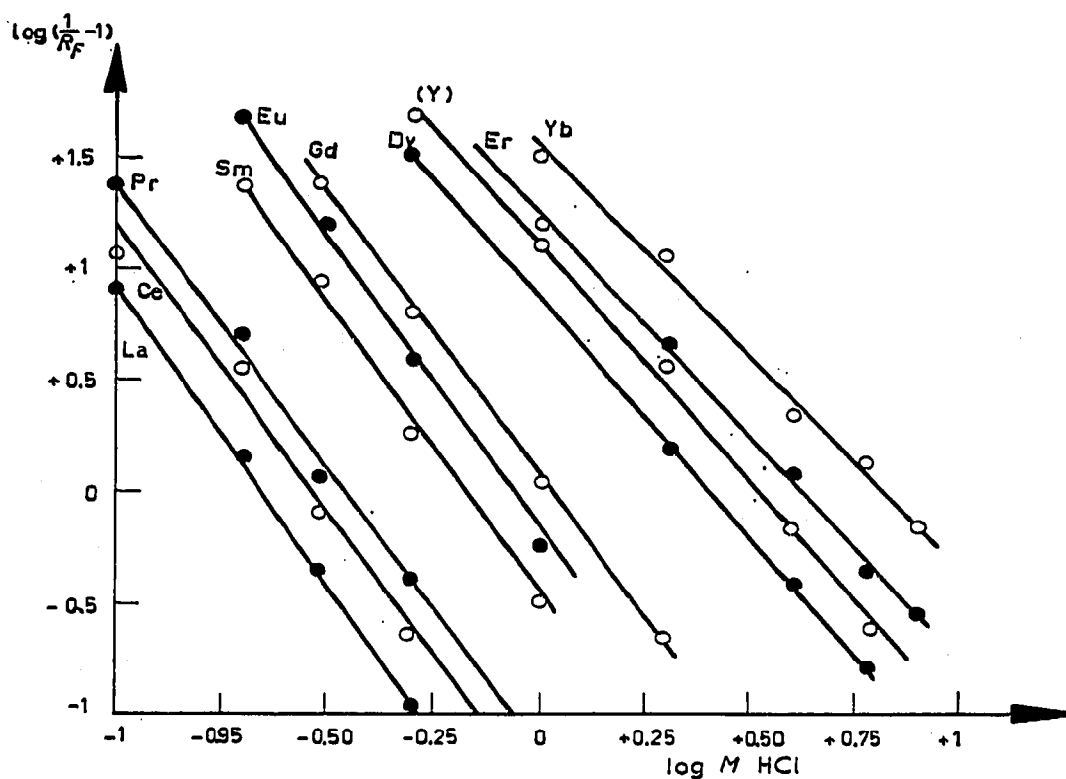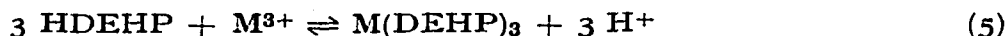

Fig. 4. Plot of log $(1/R_F - 1)$ *vs.* log M HCl for nine rare earths and yttrium. Paper treated with o.1 M HDEHP.

move from the starting point, whereas 0.5 M HNO_3, 0.5 M $HClO_4$ and 0.5 N H_2SO_4 give practically the same results as those obtained with 0.5 M HCl.

From the following equilibrium, also reported by PEPPARD et al.[14]

$$3 \text{ HDEHP} + M^{3+} \rightleftharpoons M(DEHP)_3 + 3 H^+ \tag{5}$$

it follows that

$$Ke = \frac{[M(DEHP)_3] [H^+]^3}{[M^{3+}] [HDEHP]^3} ,$$

but since

$$E_a^\circ = \frac{[M(DEHP)_3]}{[M^{3+}]}$$

then

$$\log Ke = \log E_a^\circ + 3 \log [H^+] - 3 \log [HDEHP] \tag{6}$$

and finally, from eqn. (4) it follows that

$$\log \left(\frac{1}{R_F} - 1 \right) = - 3 \log [H^+] + \text{const.}$$

In our case, the slope of the straight lines in Fig. 4 is not equal to —3, but —2.7 for light rare earths, and has gradually decreasing values for the heavier ones. This discrepancy is probably due to the difference between the molarity of the HCl solution and the hydrogen ion concentration, because of incomplete dissociation of concentrated hydrochloric acid, and, in addition, to other factors such as the elution rate, which becomes gradually lower as the HCl molarity increases, and retention on cellulose of dehydrated cations with small ionic radius[15].

R_F values as functions of the concentration of the solution used for treatment of the paper

As a general rule, the R_F value, for the same element and under the same elution conditions, decreases appreciably as the concentration of the treatment solution increases[2,4]. This is also true in the case of rare earths with HDEHP-treated paper and is in accordance with the extraction behaviour reported by PEPPARD et al.[7], who found that the extraction of rare earths increases with the concentration of the HDEHP used as extractant.

The effect of the concentration of HDEHP was checked for three of the rare earths (Sm, Gd, Dy) by using paper strips treated with four different solutions of

TABLE II

EFFECT ON THE R_F VALUE OF THE MOLARITY OF HDEHP
USED FOR TREATMENT OF THE PAPER

Eluent 0.5 M HCl. Operating temperature 25 ± 1°

	R_F			
	HDEHP molarity			
	0.01	*0.025*	*0.05*	*0.10*
Sm (62)	0.83	0.59	0.54	0.41
Gd (64)	0.65	0.29	0.22	0.14
Dy (66)	0.18	0.06	0.04	0.02

extractant, with the following molarities o.o1 M, 0.025 M, 0.05 M and 0.1 M. The experimental results are given in Table II and are plotted in Fig. 5. As can be seen in the figure, the plot of log $(1/R_F - 1)$ versus log M(HDEHP) is linear, which could be anticipated from the linearity found by PEPPARD et al.[7] for log E_a^0 versus log M (HDEHP). The slope, however, which according to eqn. (6), log [H$^+$] and log Ke
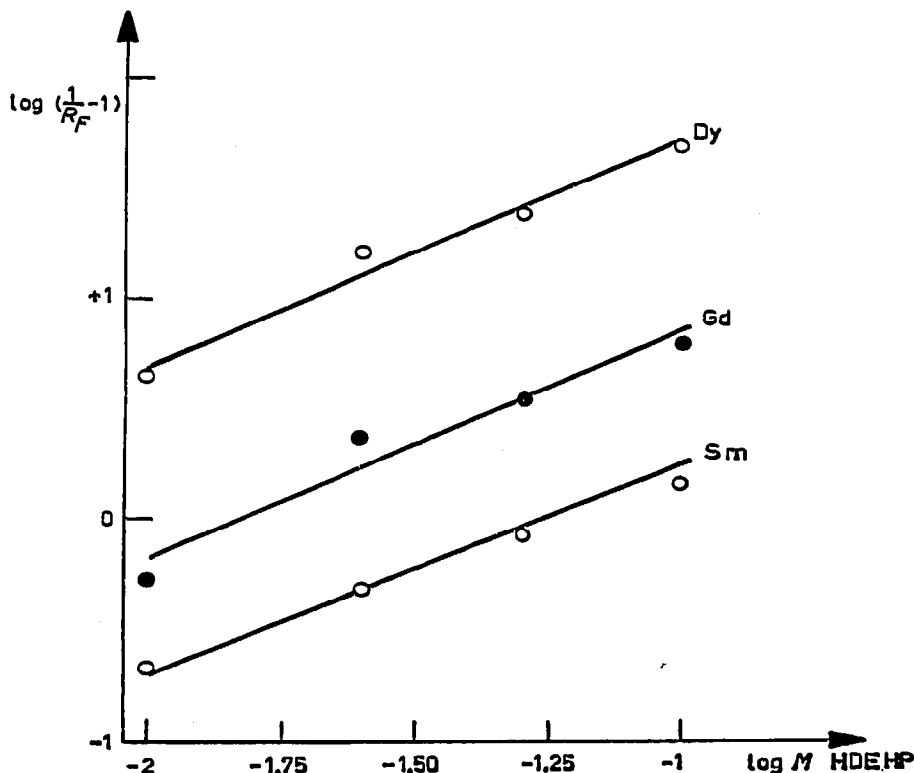
Fig. 5. Plot of log $(1/R_F - 1)$ vs. log M HDEHP used for treatment of papers. Elution with 0.5 M HCl.

being constant, should be $+ 3$, is in this case much lower than 3. This can be caused by HDEHP behaving differently when in the form of a liquid solution than when fixed on cellulose.

In conclusion, it can be said that the concentration of HDEHP in the solution used for the treatment of paper has an appreciable influence on the R_F value.

TABLE III

EFFECT OF ELUTION TEMPERATURE ON THE R_F VALUE

Eluent 0.5 M HCl; paper treated with o.1 M HDEHP

	R_F			
	Temperature °C			
	5	28	50	70
Pr (59)	0.81	0.88	0.93	0.95
Sm (62)	0.42	0.47	0.57	0.72
Gd (64)	0.17	0.22	0.27	0.34

The effect of temperature on the R_F value

Table III shows the experimental results obtained by eluting gadolinium, samarium and praseodymium with 0.5 M HCl at different temperatures. By plotting log $(1/R_F — 1)$ *versus* log T (°K) a straight line is obtained for each element (Fig. 6). The slope gradually increases going from the heavy elements to the lighter ones. Since
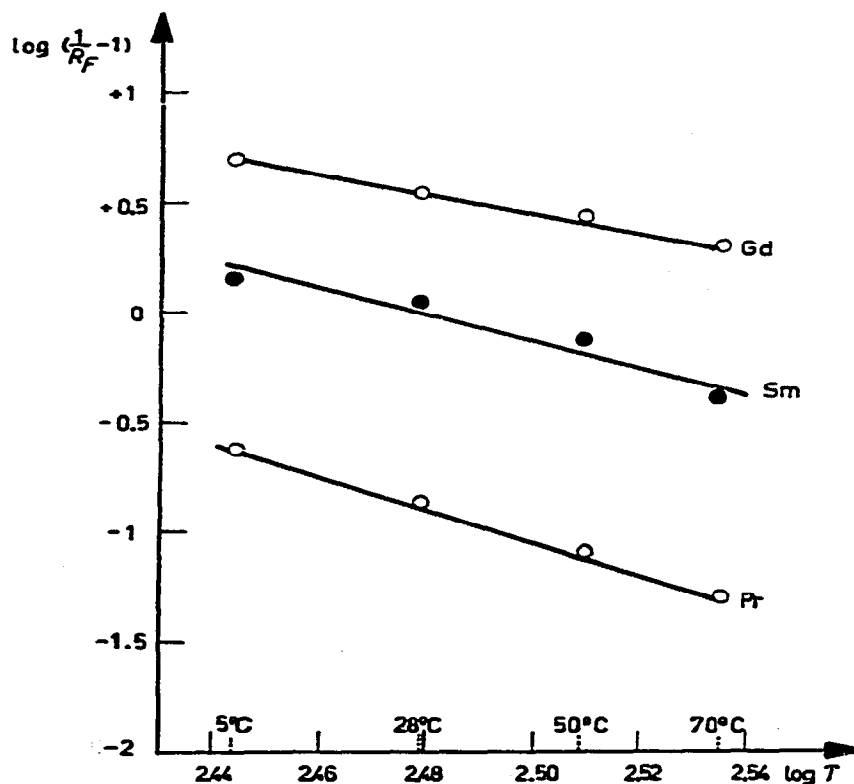

Fig. 6. Plot of log $(1/R_F — 1)$ *vs.* log T (absolute temperature, °K). Paper treated with 0.1 M HDEHP, eluent 0.5 M HCl.

the quantity log $(1/R_F — 1)$ is related to log $K'e$, where $K'e$ is the dissociation constant for the reaction

$$M(DEHP)_3 \rightleftharpoons M^{3+} + 3(DEHP)^-$$

the effect of temperature on R_F depends mainly on the variation of $K'e$ with T. Furthermore, the slight difference presented in the slopes of the straight lines given in Fig. 6, can mean that at each temperature the heavier rare earths form more stable compounds (lower $K'e$, *i.e.* dissociation equilibrium relatively more displaced to the left) than the lighter ones.

Application of paper treated with 0.1 M HDEHP to the separation of rare earths

Separations of two, three or four rare earth elements have been carried out by selecting suitable conditions on the basis of the experiments described before. The behaviour of the elements that had been examined before was in agreement with previous results, and the behaviour of additional rare earths was in agreement with the predictions that were made by averaging results obtained with contiguous elements.

Ascending chromatography was used for the separations, the conditions and results of which are reported in Table IV. It can be noted that the R_F values obtained in this case with 2 × 20 cm strips are in good agreement with those obtained before with paper sheets type CRL/1. Besides HCl, HNO_3 was used as the eluent in some cases.

As an example, the diagram of the chromatogram for La–Pr–Sm–Dy is given in Fig. 7a.

TABLE IV

ASCENDING CHROMATOGRAMS OBTAINED WITH 2 × 20 cm STRIPS TREATED WITH 0.1 M HDEHP

Operating temperature 25 ± 1°

Separations	Run cm	Eluent	R_F			
Ce–La*	15.7	0.1 M HNO_3	Ce = 0.11;	La = 0.40		
Eu–Ce–La	17.2	0.2 M HCl	Eu = 0.0;	Ce = 0.22;	La = 0.42	
Ho–Nd–La	12.7	0.3 M HCl	Ho = 0.0;	Nd = 0.26;	La = 0.69	
Sm–Nd–La	13.0	0.3 M HCl	Sm = 0.06;	Nd = 0.30;	La = 0.69	
Tb–Nd–Ce	15.4	0.3 M HCl	Tb = 0.0;	Nd = 0.27;	Ce = 0.57	
Yb–Sm–Pr–La	14.5	0.3 M HNO_3	Yb = 0.0;	Sm = 0.14;	Pr = 0.37;	La = 0.62
Dy–Sm–Pr–La	15.0	0.4 M HCl	Dy = 0.03;	Sm = 0.31;	Pr = 0.69;	La = 0.88
Dy–Eu–Pr	14.5	0.5 M HCl	Dy = 0.03;	Eu = 0.21;	Pr = 0.75	
Er–Gd–Sm–Pr	17.0	0.5 M HNO_3	Er = 0.02;	Gd = 0.18;	Sm = 0.36;	Pr = 0.70
Y–Gd–Ce	15.0	1 M HCl	Y = 0.04;	Gd = 0.58;	Ce = 0.93	
Lu–Tb–Eu–Nd	15.7	1 M HCl	Lu = 0.03;	Tb = 0.27;	Eu = 0.77;	Nd = 0.93
Tm–Tb–Nd	16.4	1 M HCl	Tm = 0.03;	Tb = 0.27;	Nd = 0.94	
Tm–Ho–Tb	17.0	2 M HCl	Tm = 0.10;	Ho = 0.41;	Tb = 0.72	
Yb–Y–La	14.4	4 M HCl	Yb = 0.13;	Y = 0.52;	La = 0.87	
Lu–Ho–Pr	11.0	4 M HCl	Lu = 0.13;	Ho = 0.61;	Pr = 0.88	
Yb–Er–La	14.7	6 M HCl	Yb = 0.45;	Er = 0.77;	La = 0.92	
Sc–Lu–Tm	15.7	8 M HCl	Sc = 0.0;	Lu = 0.33;	Tm = 0.80	

* Paper treated with 0.025 M HDEHP.

Application of paper treated with 0.1 M TNOA and 0.1 M HDEHP

The behaviour of strips simultaneously treated with TNOA and HDEHP was also investigated.

Owing to the different properties of TNOA and HDEHP, papers treated in this way can fix chemical elements both in the anionic form and in the cationic form. For instance, by eluting with HCl a paper strip, a short length of which had been treated with TNOA and the remainder with HDEHP, the separation of zirconium, iron and uranium (which form anionic chloride complexes) from thorium, scandium, yttrium and rare earths (which do not form anionic chloride complexes) can easily be carried out. In fact, zirconium, iron and uranium are retained in the first, TNOA-treated, part of the strip, whilst the others are retained in the second, HDEHP-treated, part. In Fig. 7b an example is given of the separation of U–Sc–Yb–Y–La. In Table V results are reported on chromatographic separations in which iron, uranium and zirconium are retained as chloride complexes or thorium is retained as nitrate complex[2]. If the solvent is run over the HDEHP-treated portion before the TNOA-treated portion, the change in the R_F values is obvious. For instance, in the separation of Al–Zr–Th with 4 M HCl, the R_F of zirconium passes from 0 in the former case to 0.11 in the latter case, while for thorium the R_F alters from 0.16 to 0.

TABLE V

ASCENDING CHROMATOGRAMS OBTAINED WITH STRIPS PART OF WHICH HAD BEEN TREATED WITH 0.1 M TNOA AND THE REMAINDER WITH 0.1 M HDEHP

Separations	Total run cm	TNOA portion cm	Eluent	R_F
Fe–Zr–Gd–Pr	16.0	4.0	1 M HCl	Fe = 0.11; Zr = 0.25; Gd = 0.80; Pr = 0.96
U–Y–Gd–La	14.7	2.2	1 M HCl	U = 0.10; Y = 0.20; Gd = 0.73; La = 0.94
U–Th–Yb–Gd	17.0	3.7	4 M HCl	U = 0.0; Th = 0.21; Yb = 0.43; Gd = 0.93
U–Sc–Yb–Y–La	15.7	2.8	4 M HCl	U = 0.0; Sc = 0.18; Yb = 0.31; Y = 0.69 La = 0.9
Th–U–Yb–La	15.6	7.8	6 M HNO$_3$	Th = 0.07; U = 0.48; Yb = 0.62; La = 0.95
Zn–Th–Al	12.7	2.0	4 M HCl	Zn = 0.0; Th = 0.16; Al = 0.83
Th–Zn–Al*	14.7	13.0	4 M HCl	Th = 0.0; Zn = 0.11; Al = 0.96

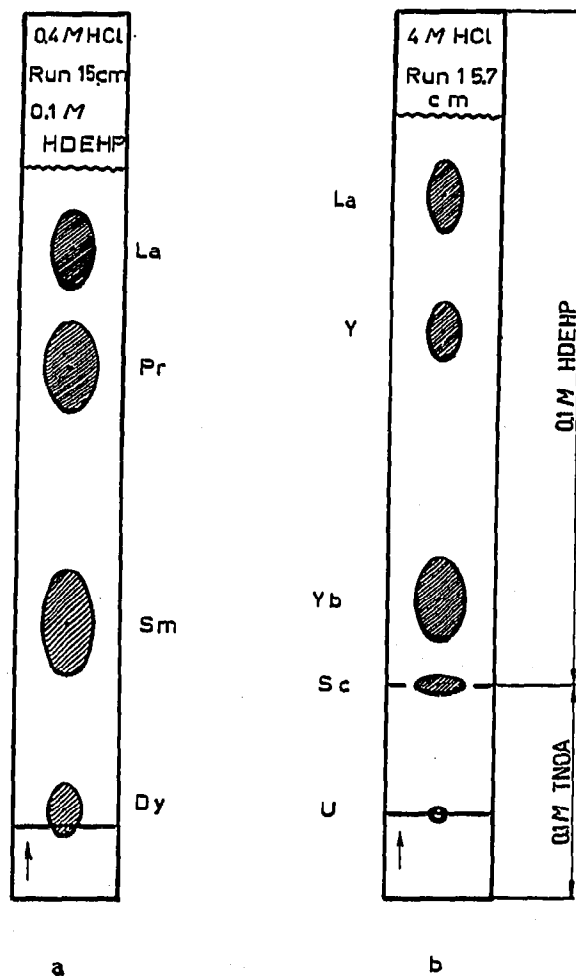* The lower part of the strip was treated with 0.1 M HDEHP, the upper part with 0.1 M TNOA.

Fig. 7. (a) Diagram of the separation of Dy–Sm–Pr–La on paper treated with 0.1 M HDEHP. Eluent 0.4 M HCl. (b) Diagram of the separation of U–Sc–Yb–Y–La on paper part of which had been treated with 0.1 M TNOA and the remainder with 0.1 M HDEHP. Eluent 4 M HCl.

CONCLUSIONS

From the experimental results reported in this paper it can be concluded that there is great similarity between the extraction properties of HDEHP and the chromatographic behaviour of paper treated with HDEHP.

The R_F value of each element can be influenced by:

The rare earth elements show a gradually varying dissimilarity, which makes it possible to separate such elements from each other.

Since the mechanism based on a cationic substitution is the predominant phenomenon in treated paper selectivity, the type of acid used as the eluent is not significant, provided that such acid is of sufficient strength to make an appreciable hydrogen ion concentration available.

The R_F value of each element can be influenced by:

(i)   the molarity of the acid used as eluent;
(ii) the concentration of the solution used for treatment of the paper;
(iii) the operating temperature.

A further increase of the separating potentiality of paper can be obtained by using a paper strip that has an anionic exchange capacity in a portion of its surface and a cationic exchange capacity in the remaining portion. This can be obtained by treating the two parts of the paper with TNOA and HDEHP respectively.

Appreciable amounts of rare earths can be separated by means of column beds consisting of cellulose powder treated with HDEHP. Preliminary experiments have given encouraging results. Moreover, an HDEHP-treated cellulose powder bed can be preceded by an additional layer consisting of cellulose powder treated with TNOA[3] or TOPO[5]; in this way a very versatile tool for a great number of chemical separations is obtained. The experimental results on this will be published in a further paper.

ACKNOWLEDGEMENT

SUMMARY

The chromatographic behaviour of rare earths on paper treated with di-(2-ethylhexyl) phosphoric acid (HDEHP) has been investigated. The quantity $\log (1/R_F - 1)$ has been related to: (i) the atomic number of the element, (ii) the molarity of the acid used as eluent, (iii) the molarity of the solution with which the paper is treated, and (iv) the operating temperatures.

Under the same conditions, the R_F values increase as the atomic number decreases; furthermore, for a given element, R_F increases with the molarity of the eluting acid (HCl), with the operating temperature and, finally, it decreases with the concentration of HDEHP on the paper.

Some examples are given of the chromatographic separation of rare earths from each other and from Y, Sc, Th, U, Fe, Al, Zr.

In addition to paper treated with HDEHP alone, strips have been investigated on which tri-n-octylamine (TNOA) had been fixed on a small part of the surface, and HDEHP on the remaining surface.

The possibility of separating large amounts of rare earths by means of columns filled with HDEHP-treated cellulose powder or with mixed beds is anticipated.

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