

## REVERSED-PHASE CHROMATOGRAPHY OF ALKALINE EARTHS ON PAPER TREATED WITH DI-*n*-BUTYL PHOSPHATE

N. CVJETIĆANIN

*Hot Laboratory Department, Boris Kidrič Institute of Nuclear Sciences, Beograd (Yugoslavia)*

(Received July 27th, 1967)

Chromatographic paper or cellulose powder treated with dialkyl esters of phosphoric acid which act as liquid cation exchangers have proved to be very efficient for the separation of various metal ions, especially lanthanides<sup>1-3</sup>.

Investigations of the behaviour of rare earths have shown that a striking similarity exists between the results obtained by chromatography and those obtained by solvent extraction, if the same organophosphate is used in both methods<sup>3-5</sup>. The results of our preceding work, obtained on paper treated with di-*n*-butyl phosphate (HDBP)<sup>6</sup> also support this analogy.

The present work investigates the behaviour of beryllium magnesium, calcium, strontium and barium in reversed-phase partition chromatography, using paper impregnated with HDBP and hydrochloric acid as the eluent. The results obtained are interpreted in terms of a simple partition equilibrium in close analogy to the distribution of species in solvent extraction. At the same time the feasibility of mutual separation of alkaline earths as well as their separation from other elements is demonstrated.

### EXPERIMENTAL

#### *Materials and reagents*

The chromatographic paper was treated with a carbon tetrachloride solution of HDBP which was supplied by Albright Wilson Co., Oldbury (England). The purity of HDBP with respect to the content of H<sub>2</sub>MBP and H<sub>3</sub>PO<sub>4</sub> was checked chromatographically<sup>7</sup>. An 0.05 *M* solution of alkaline earths in the form of chlorides was used. The behaviour of aluminium and caesium was also investigated and for these purposes an 0.01 *M* solution of aluminium and caesium chloride was used, respectively.

All experiments were performed on Whatman No. 1 paper strips, 2 × 35 cm, in a glass cylinder 14 cm diam. × 40 cm, by ascending chromatography.

#### *Preparation of the paper and chromatographic procedure*

The chromatographic paper was treated in the same way as described previously<sup>6</sup>. The solution of HDBP in CCl<sub>4</sub> was equilibrated with 2 *M* HCl for 20 min. The paper sheets were carefully washed with 2 *M* HCl and rinsed with distilled water before treatment with HDBP. After drying, the paper was dipped in a solution of HDBP in CCl<sub>4</sub> for 1 min and dried in a stream of warm air.

An aliquot of  $\sim 0.005$  ml of the solution of the elements to be investigated was spotted on the paper at the starting position. These spots did not contain more than  $5 \cdot 10^{-7}$  equivalents of each ion.

After development the ions were detected with a suitable sensitive reagent.  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  spots were made visible in U.V. light after spraying the strips with a 0.5 % alcoholic solution of 8-hydroxyquinoline and exposing them to ammonia vapours.  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  were identified with a fresh 0.1 % solution of sodium rhodizionate<sup>8</sup> or a 0.5 % solution of sodium alizarinsulphonate<sup>9</sup>.  $\text{Al}^{3+}$  was detected with a 0.01 % solution of morin<sup>10</sup> and  $^{137}\text{Cs}$  by measuring its radioactivity along the paper strip with a G.M. counter.

When the dependence of the  $R_F$  values on the amount of HDBP impregnated in the paper was studied, the paper strips were treated with various solutions of HDBP, mostly in the concentration range 0.01–0.2  $M$ .

Chromatograms were developed with hydrochloric acid solutions from  $1 \cdot 10^{-3}$  up to 10  $M$ . The development took from 4 to 8 h, depending on the amount of HDBP impregnated and on the HCl concentration of the mobile phase. Usually the solvent front was allowed to run up to 25 cm. Two or three chromatograms were run simultaneously for each element and for each concentration of HCl and HDBP. The use of very low concentrations of hydrochloric acid in the mobile phase caused a small shift of HDBP concentration in the stationary phase. This effect is probably due to dissociation and a slight dissolution of HDBP in the mobile phase<sup>11</sup>, which influenced the  $R_F$  value of the ions. A previous equilibration of the aqueous acid solution with the organic phase apparently does not prevent this effect. However it was completely eliminated by shifting the starting position approximately 2 cm above the line at which HDBP starts to be washed out. Actually, by this technique a saturation of the mobile phase with HDBP is achieved before the mobile phase reaches the starting point. The line was clearly visible under U.V. light after spraying the developed paper strips (on which ions were not spotted) with an alcoholic solution of 8-hydroxyquinoline. As a consequence of this modification the development of the paper strips treated with low amounts of HDBP at a HCl concentration below  $10^{-2}$   $M$ , took 10–12 h. The reproducibility of the  $R_F$  values of the ions under these conditions was  $\pm 3$  %.

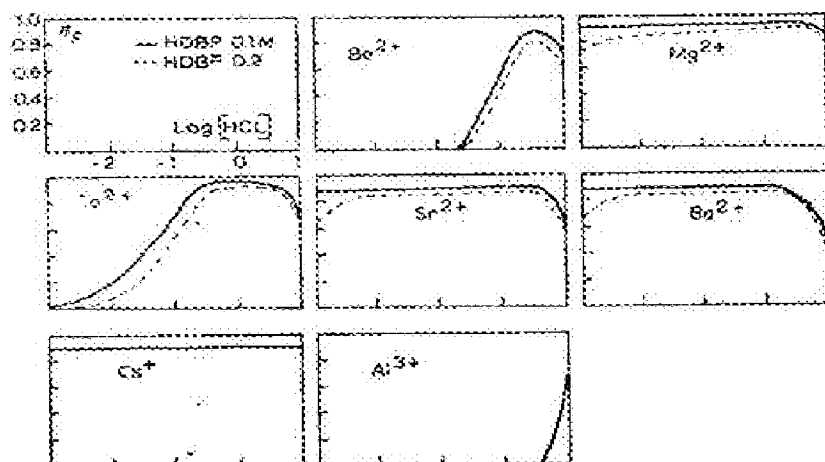


Fig. 1.  $R_F$  values of alkaline earths, aluminium and caesium vs.  $\log [\text{HCl}]$ . Paper treated with HDBP.

TABLE I

$R_F$  VALUES FOR ALKALINE EARTHS, ALUMINIUM AND CAESIUM, AS A FUNCTION OF HCl CONCENTRATION  
The paper is impregnated with HDBP.

HDBP		Cations HCl (M)									
(M)		0.001	0.005	0.01	0.03	0.04	0.05	0.075	0.1	0.14	0.19
0.2	Be <sup>2+</sup>								0.0		
	Mg <sup>2+</sup>	0.72	0.83			0.83			0.85		
	Ca <sup>2+</sup>	0.0		0.10	0.18	0.26	0.34	0.45	0.54	0.65	0.74
	Sr <sup>2+</sup>	0.66	0.85				0.83		0.84		
	Ba <sup>2+</sup>	0.68	0.86				0.84		0.85		
0.1	Be <sup>2+</sup>	0.0	0.0	0.0			0.0		0.0		
	Mg <sup>2+</sup>	0.92	0.93	0.93			0.94		0.94		
	Ca <sup>2+</sup>	0.0	0.10	0.20	0.33	0.45	0.50	0.62	0.69	0.81	0.88
	Sr <sup>2+</sup>	0.86	0.88	0.92			0.92		0.91		
	Ba <sup>2+</sup>	0.88	0.90	0.90			0.89		0.88		
	Cs <sup>+</sup>	0.90	0.90	0.90			0.91		0.91		
	Al <sup>3+</sup>										
0.075	Be <sup>2+</sup>								0.0		
	Ca <sup>2+</sup>				0.42	0.50	0.62	0.66	0.77		0.89
0.05	Be <sup>2+</sup>									0.08	
	Ca <sup>2+</sup>				0.48	0.59	0.67	0.72	0.80	0.90	
0.025	Be <sup>2+</sup>									0.11	
0.01	Be <sup>2+</sup>									0.15	

## RESULTS AND DISCUSSION

The dependence of the  $R_F$  values of the ions on the HCl concentration of the mobile phase for papers treated with 0.1 and 0.2 M HDBP is shown in Fig. 1. The numerical values are given in Table I.

From the data presented it can be seen that the  $R_F$  values of Ca<sup>2+</sup> and Be<sup>2+</sup> increase with increasing molarities of HCl. The  $R_F$  values for Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> are very high, which might imply that these elements do not show affinity to the organic extractant over a wide range of HCl concentration. A decrease in the  $R_F$  values at very high HCl concentrations was observed for all alkaline earth elements, and especially in the case of Sr<sup>2+</sup> and Ba<sup>2+</sup>. This effect was also found when the paper was impregnated with other organo-phosphorus compounds<sup>12-14</sup>. It might be due to a dehydration process which appears at high hydrochloric acid concentration. In the whole range of HCl concentration investigated, the  $R_F$  for Cs<sup>+</sup> is about 0.90, while the shape of the curve obtained for aluminium is similar to those found for trivalent rare earths<sup>6</sup>.

Based on the results shown in Table I and Fig. 1, the dependence of the  $R_F$  values of Be<sup>2+</sup> and Ca<sup>2+</sup> on the HCl and HDBP concentrations was investigated in more detail.

It is known that the behaviour of ions in reversed-phase partition chromatography can be correlated to a liquid-liquid partition by means of the following expression<sup>3,15</sup>:

0.40	0.50	0.75	1	1.5	2	2.5	3	4	6	8	10
0.10	0.15		0.41	0.57	0.69	0.71	0.78	0.82	0.74	0.66	0.62
	0.90		0.90		0.90			0.90	0.88	0.86	0.82
0.90			0.92		0.92			0.90	0.88	0.72	0.68
	0.88		0.88		0.88			0.87	0.77	0.65	0.60
	0.86		0.87		0.86			0.78	0.66	0.54	0.30
0.19	0.28		0.56		0.77	0.85	0.88	0.84	0.85	0.79	0.76
	0.95		0.94		0.96			0.95	0.89	0.90	0.88
	0.95		0.96		0.96			0.91	0.89	0.81	0.71
	0.92		0.92		0.93			0.89	0.86	0.68	0.63
	0.90		0.90		0.88			0.80	0.72	0.60	0.46
	0.92		0.91		0.92			0.92	0.90	0.88	0.89
	0.0		0.0		0.0			0.0	0.20	0.41	0.65
0.24	0.33	0.53	0.61	0.79	0.82	0.89					
0.29	0.41	0.58	0.67	0.83	0.87						
0.41	0.55	0.69	0.76	0.87							
0.46	0.68	0.76	0.84	0.90							

$$\log E_u^0 = \log (1/R_F - 1) + \log k \quad (1)$$

Here,  $E_u^0$  is the liquid-liquid distribution coefficient, while  $k$  is a constant parameter which depends on the experimental conditions. The relation between  $\log (1/R_F - 1)$  and  $\log [H^+]$  for both ions is shown in Figs. 2 and 3. These results were obtained using papers impregnated with different HDBP solutions (0.01–0.2 M). The slope of the straight line for  $Be^{2+}$  is  $-1.8$ , close to the theoretical value of  $-2$ , as obtained by liquid-liquid extraction<sup>16,17</sup>. However, for  $Ca^{2+}$  the slope is only  $-1.5$ .

The dependence of  $\log (1/R_F - 1)$  for  $Be^{2+}$  and  $Ca^{2+}$  on the amount of HDBP fixed on the paper was investigated at a constant concentration of HCl in the mobile phase. The amount of HDBP on paper expressed in mg/cm<sup>2</sup> was determined by weighing the paper strips before and after impregnation and drying. The mobile phase for  $Be^{2+}$  was 0.5 M HCl and for  $Ca^{2+}$  0.05 M HCl. The slopes of the lines obtained was 1.5 in both cases (Fig. 4).

It is known that HDBP tends to form dimeric molecules in nonpolar solvents. In carbon tetrachloride the dimerization constant of HDBP is very large ( $\log K_2 = 6.49$ ), so that even at very low concentrations of HDBP the monomeric form (HA) can be neglected. Hence, the whole amount of HDBP in the organic phase is practically in the form of the dimer ( $H_2A_2$ )<sup>11,18</sup>.

In the present case it was also assumed that di-*n*-butyl phosphate is dimerized and the concentrations were recalculated in millimoles of  $H_2(DBP)_2$  (see Fig. 4).

Taking into account that for both lines in Fig. 4 a slope of 1.5 was obtained, the following equilibrium is proposed:



In the above reaction the hydration of species is neglected. The equilibrium constant of this reaction equals:

$$K_e = \frac{[MA_2HA]_{org}[H^+]^2}{[M^{2+}][H_2A_2]_{org}^{3/2}} \times f(\gamma) \quad (3)$$

where  $f(\gamma)$  is an activity coefficient ratio. As a first approximation it is assumed that in the range of HCl concentrations used  $f(\gamma)$  is constant.

The extraction coefficient equals:

$$E_a^0 = \frac{[MA_2HA]_{org}}{[M^{2+}]}$$

Taking into account eqn. (1), it can be written:

$$\log (1/R_F - 1) = 1.5 \log [H_2A_2] - 2 \log [H^+] + \text{const.} \quad (4)$$

Here the term "const." includes  $K_e$ ,  $f(\gamma)$  and  $k$  from eqns. (1) and (3).

From eqn. (4) it is obvious that a plot of  $\log (1/R_F - 1)$  vs.  $\log [H^+]$  at constant concentration of  $H_2A_2$  should give a straight line of slope  $-2$ . As mentioned earlier, for  $Be^{2+}$  the slope was  $-1.8$  which is close to the theoretical value of  $-2$ , but for  $Ca^{2+}$  the slope was only  $-1.5$ . This deviation from the value of  $-2$  might be due to a partial complexing of the metal ion with chloride ion at higher HCl concentration:

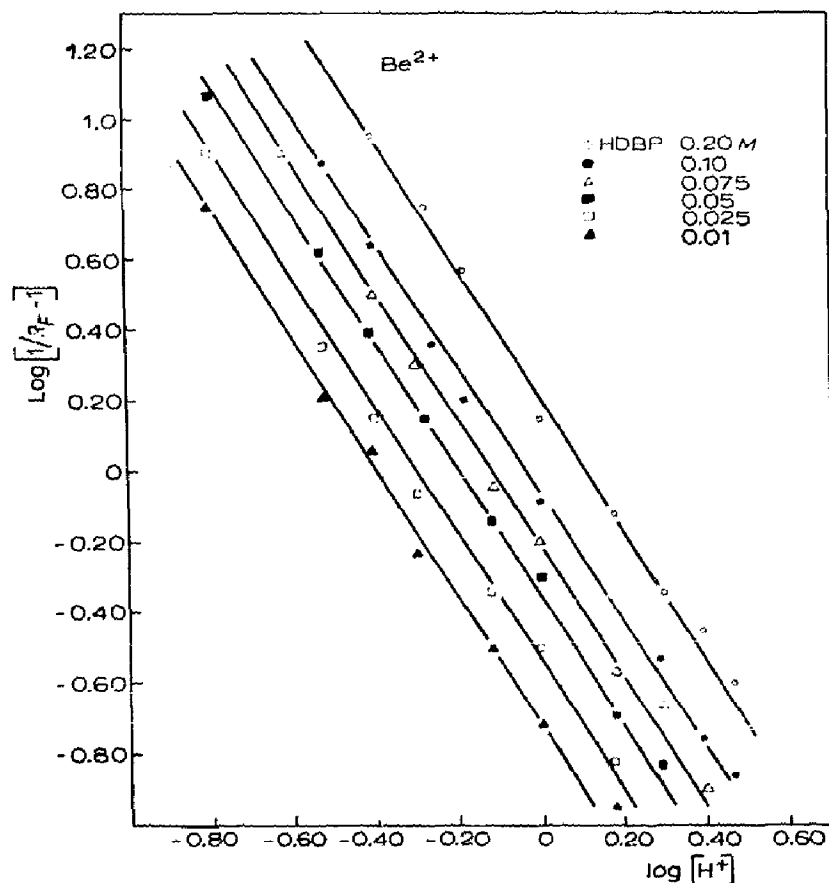


Fig. 2. Plot of  $\log (1/R_F - 1)$  vs.  $\log [H^+]$  for beryllium. The slope of the straight lines is  $-1.8$ .

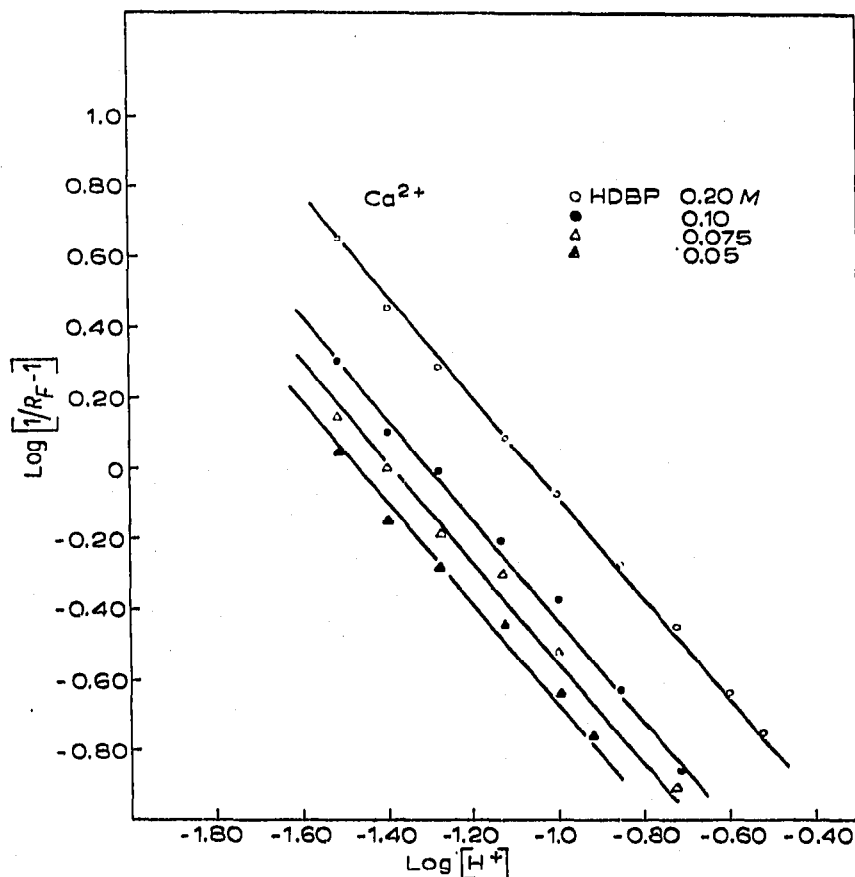
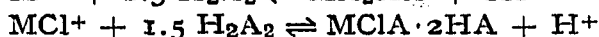
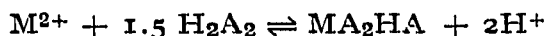


Fig. 3. Plot of  $\log (1/R_F - 1)$  vs.  $\log [H^+]$  for calcium. The slope of the straight lines is  $-1.5$ .



If both equilibria take place, a slope between  $-2$  and  $-1$  can be obtained in the plot of  $\log (1/R_F - 1)$  vs.  $\log [H^+]$ . Such intermediate values of slopes were also obtained for alkaline earths on paper treated with di(2-ethylhexyl) phosphate from chloride media<sup>19</sup>.

Taking into account the amount of HDBP fixed on the paper it was also possible to recalculate the data for rare earths which were reported earlier<sup>6</sup>. The plots of  $\log (1/R_F - 1)$  vs.  $\log [H_2A_2]$  for  $La^{3+}$  and  $Ce^{3+}$  (Fig. 5) are now straight lines whose slope is  $1.5$ . Hence, for the rare earths the following reaction seems to be valid:



The above equation agrees with the data obtained by liquid-liquid extraction in the range of low concentration of HDBP<sup>20, 21</sup>.

#### The apparent equilibrium constant

If the constant term of eqn. (4) is expressed as  $\log K_h = \log K_e - f(\gamma) - \log k$ , the following expression is obtained:

$$\log (1/R_F - 1) = \log \frac{[H_2A_2]^{3/2}}{[H^+]^2} + \log K_h$$

This is a straight line in a log-log plot, and by extrapolating to  $\log ([H_2A_2]^{3/2}/$

$[H^+]^3 = 0$  the apparent constant  $K_h$  can be obtained. Such a plot for  $Be^{2+}$  is shown in Fig. 6. By means of the least square method  $\log K_h = 4.62 \pm 0.09$  was obtained for  $Be^{2+}$ .

As mentioned before, the distribution of calcium between the two phases cannot be explained by a simple equilibrium, and therefore no attempts were made to calculate the apparent constant  $K_h$ .

In the case of  $La^{3+}$  and  $Ce^{3+}$  (see ref. 6), the  $K_h$  values were determined by means of the expression:

$$\log (1/R_F - 1) = \log \frac{[H_2A_2]^{3/2}}{[H^+]^3} + \log K_h$$

derived from eqn. (5). For  $La^{3+}$   $\log K_h = 3.63 \pm 0.08$  and for  $Ce^{3+}$   $\log K_h = 3.87 \pm 0.09$  was obtained (see Fig. 7).

Since  $\log K_h = \log (K_e/k \cdot f(\gamma))$  and  $k$  is the volume ratio between the mobile and the stationary phase, it was of considerable interest to determine the value of  $k$  by means of eqn. (1). For that purpose it is sufficient to determine the extraction coefficient  $E_a^0$  for one cation. The liquid-liquid distribution measurements were performed by using the radioactive isotope cerium-144 ( $Ce^{3+}$ ) and the same HDBP and HCl concentration in the organic and aqueous phases as in the chromatographic investigation. The mean value from a large number of determinations is  $\log k = -2.04$ . Using this value and defining an apparent equilibrium constant  $\log K = \log K_e -$

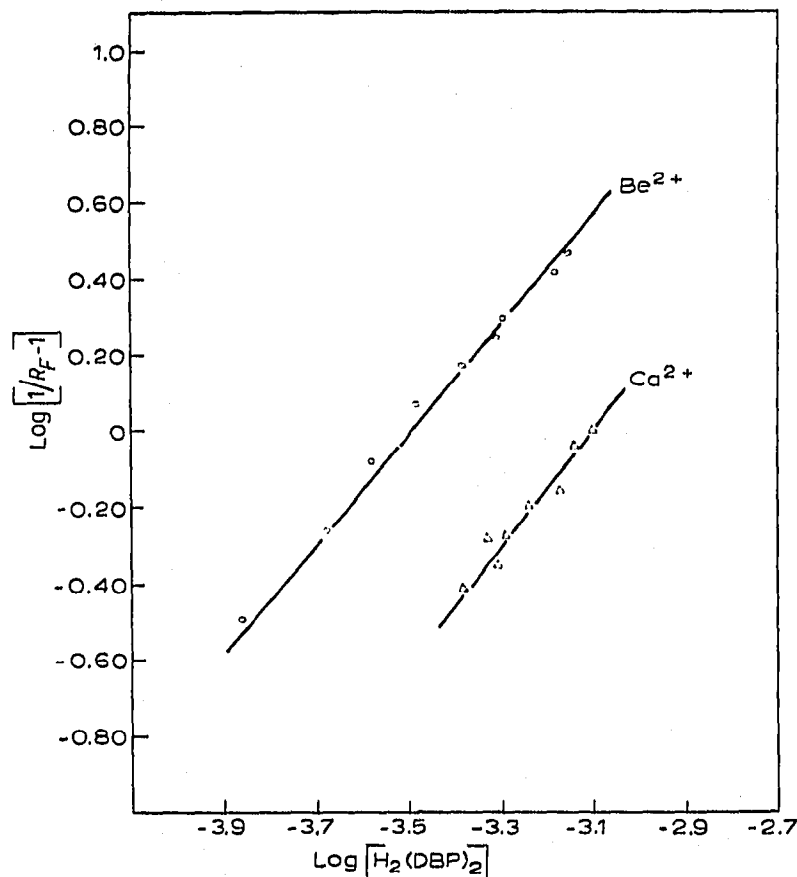


Fig. 4. Plot of  $\log (1/R_F - 1)$  vs.  $\log [H_2(DBP)_2]$  for  $Be^{2+}$  and  $Ca^{2+}$  with 0.5 and 0.05 M HCl, respectively.

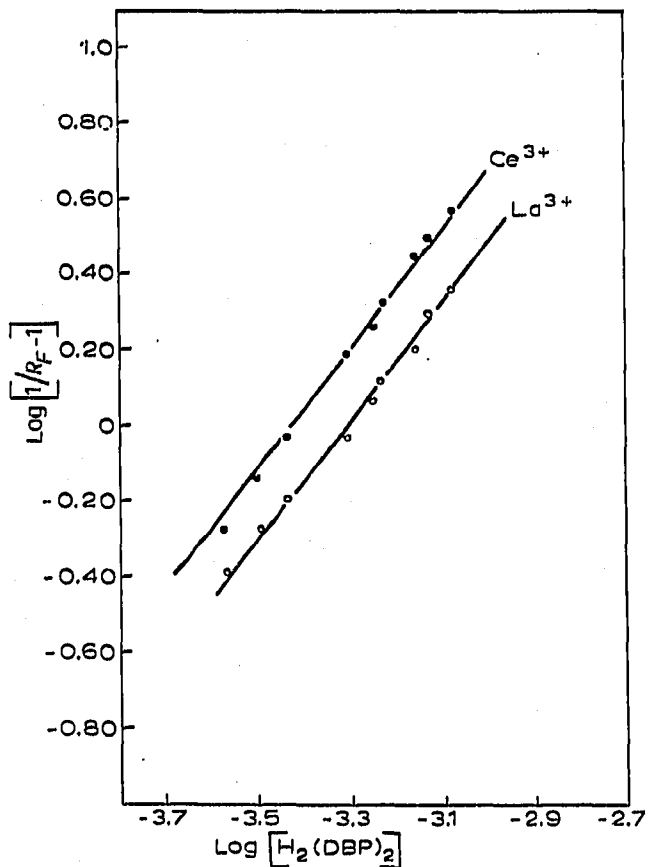


Fig. 5. Dependence of  $\log (1/R_F - 1)$  on  $\log [H_2(DBP)_2]$  for  $La^{3+}$  and  $Ce^{3+}$  with 0.35 M HCl. The slope of the straight lines is 1.5.

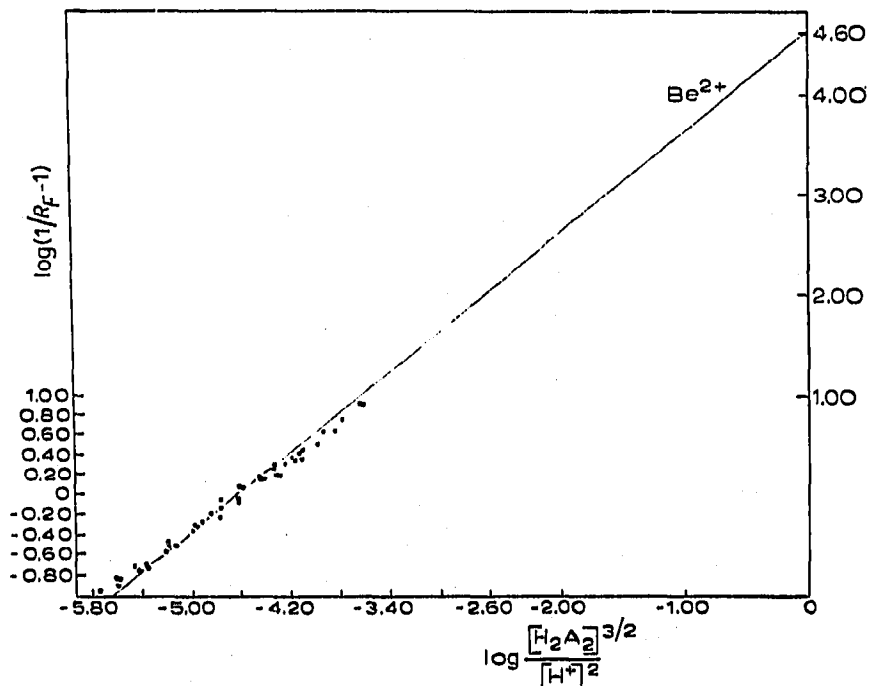


Fig. 6. Plot of  $\log (1/R_F - 1)$  vs.  $\log ([H_2A_2]^{3/2}/[H^+]^2)$  for  $Be^{2+}$ . The value of  $\log K_h$  is obtained by extrapolation.



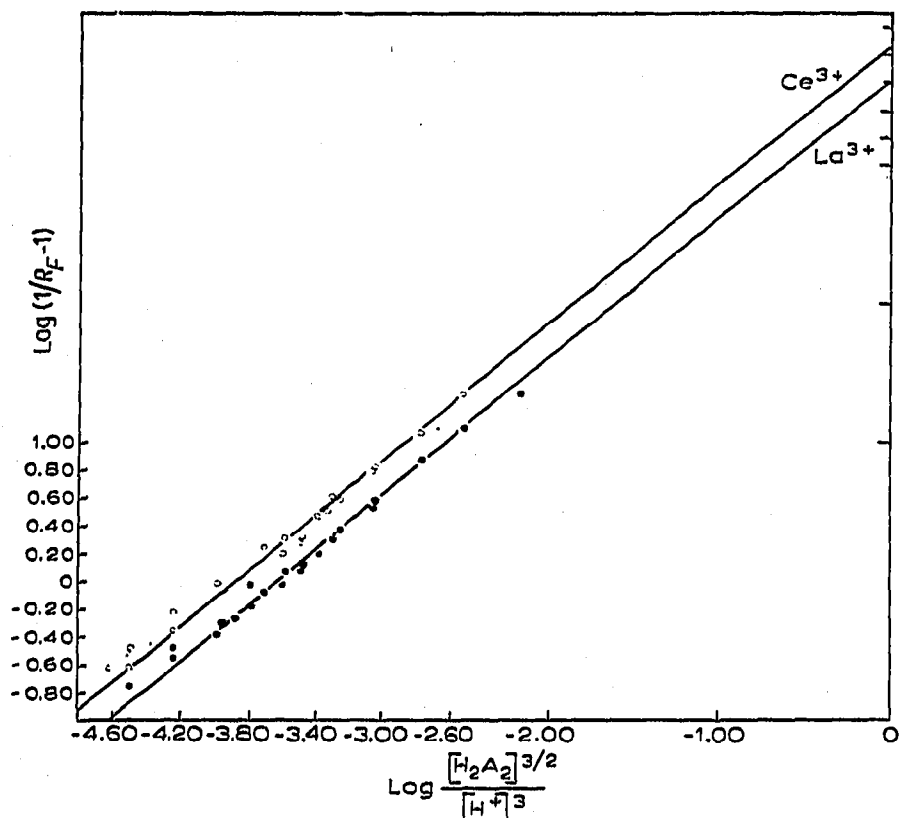


Fig. 7. Plot of  $\log (1/R_F - 1)$  vs.  $\log ([H_2A_2]^{3/2}/[H^+]^3)$  for  $La^{3+}$  and  $Ce^{3+}$ .

$\log f(\gamma)$ , the following values for  $\log K$  were obtained:  $Be^{2+}$  2.58;  $La^{3+}$  1.59 and  $Ce^{3+}$  1.83. These numerical values are fairly close to the values obtained in liquid-liquid distribution experiments<sup>16, 17</sup>.

#### Applications in analytical separations

The experimental results obtained in the present and earlier<sup>6</sup> work indicate that separation of alkaline earths and their separation from rare earths, aluminium and caesium can be carried out with a selected concentration of hydrochloric acid and HDBP. The separations which are feasible are listed in Table II.

TABLE II

CHROMATOGRAPHIC SEPARATIONS ON PAPER TREATED WITH HDBP  
Eluent: HCl, temperature  $23 \pm 1^\circ$ .

Element	HDBP (M)	HCl (M)	Solvent front (cm)	$R_F$
Be-Ca-Mg	0.1	0.04	19.0	Be = 0.0; Ca = 0.42; Mg = 0.88
Be-Ca-Sr	0.2	0.05	20.5	Be = 0.0; Ca = 0.32; Sr = 0.83
Al-Ca-Cs	0.1	0.1	21.7	Al = 0.0; Ca = 0.68; Cs = 0.90
Ba-La	0.1	0.3	20.5	La = 0.23; Ba = 0.92
<sup>90</sup> Sr- <sup>90</sup> Y	0.1	1	22.0	Y = 0.0; Sr = 0.90
Al-Be-Mg	0.1	1	23.5	Al = 0.0; Be = 0.58; Mg = 0.95
Ba-Sr-Mg	0.2	6	21.6	Ba = 0.65; Sr = 0.77; Mg = 0.88
Ba-Ca-Mg	0.1	9	22.0	Ba = 0.59; Ca = 0.71; Mg = 0.90
Sr-Ca-Mg	0.1	10	22.5	Sr = 0.61; Ca = 0.72; Mg = 0.87

## ACKNOWLEDGEMENTS

Thanks are due to Prof. M. Šušić and to Dr. I. GAL for their interest in this work and helpful discussion.

## SUMMARY

The chromatographic behaviour of beryllium, magnesium, calcium, strontium and barium was investigated on Whatman No. 1 paper impregnated with di-*n*-butyl phosphate (HDBP) as the stationary phase. Elution was performed with hydrochloric acid in a concentration range  $1 \cdot 10^{-3}$ – $10$  M.

The chromatographic data obtained for  $\text{Be}^{2+}$  and  $\text{Ca}^{2+}$  were interpreted by means of plots of  $\log (1/R_F - 1)$  vs.  $\log [\text{H}^+]$ , or *versus* the amount of HDBP fixed on the paper. From these plots apparent stability constants for the formation of metal complexes were determined using a simple correlation between the liquid-liquid extraction coefficient and the  $(1/R_F - 1)$  function in reversed-phase partition chromatography.

By a convenient choice of the concentration of hydrochloric acid in the mobile phase and that of HDBP in the stationary phase, separation of alkaline earths and their separation from other cations can be achieved.

## REFERENCES

- 1 E. CERRAI, C. TESTA AND C. TRIULZI, *Energia Nucl. (Milan)*, 9 (1962) 193.
- 2 E. CERRAI, C. TESTA AND C. TRIULZI, *Energia Nucl. (Milan)*, 9 (1962) 377.
- 3 E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
- 4 D. F. PEPARD, G. W. MASON, J. L. MAIER AND W. J. DRISCOLL, *J. Inorg. Nucl. Chem.*, 4 (1957) 334.
- 5 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 24 (1966) 383.
- 6 N. CVJETIĆANIN, *Bull. Boris Kidrič Inst. Nucl. Sci. (Beograd)*, 15 (1964) 201.
- 7 N. CVJETIĆANIN AND J. ČVORIĆ, *Bull. Boris Kidrič Inst. Nucl. Sci. (Beograd)*, 13 (1962) 35.
- 8 E. BLASIUS, *Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1958, p. 253.
- 9 F. J. WELCHER, *Organic Analytical Reagents*, Vol. IV, Van Nostrand, New York, 1948, p. 433.
- 10 F. FEIGL, *Spot Tests, Inorganic Applications*, Elsevier, Amsterdam, 1954, p. 175.
- 11 D. DYRSSEN, *Acta Chem. Scand.*, 11 (1957) 1771.
- 12 E. CERRAI AND C. TESTA, *J. Chromatog.*, 7 (1962) 112.
- 13 N. CVJETIĆANIN, J. ČVORIĆ AND I. OBRENOVIĆ-PALIGORIĆ, *Bull. Boris Kidrič Inst. Nucl. Sci. (Beograd)*, 14 (1963) 83.
- 14 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 18 (1965) 124.
- 15 R. CONSDEN, A. H. GORDON AND A. J. P. MARTIN, *Biochem. J.*, 38 (1944) 224.
- 16 C. J. HARDY, B. F. GREENFIELD AND D. SCARGILL, *J. Chem. Soc.*, (1961) 174.
- 17 C. F. BAES, JR., *J. Inorg. Nucl. Chem.*, 24 (1962) 707.
- 18 D. DYRSSEN AND F. KRAŠOVEC, *Acta Chem. Scand.*, 13 (1959) 561.
- 19 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 15 (1964) 236.
- 20 A. P. SAMODELOV, *Radiokhimiya*, 6 (1964) 286.
- 21 Z. A. SHEKA AND E. E. KRIS, *Zh. Neorgan. Khim.*, 7 (1962) 658.