

# REVERSED-PHASE CHROMATOGRAPHY OF Al, Ga, In, Tl AND THE TRANSITION METALS OF THE IRON GROUP ON PAPER TREATED WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID IN CHLORIDE MEDIUM

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## INTRODUCTION

In a previous paper<sup>1</sup> the possibility of a good separation of Al, Ga, In and Tl was demonstrated by means of reversed-phase paper chromatography. Such a separation was based on the use of paper treated with solutions of di-(2-ethylhexyl) orthophosphoric acid (HDEHP) and elution with hydrochloric acid.

Similar chromatographic techniques have already been applied to the separation of rare earths<sup>2</sup>, alkali metals and alkaline earths<sup>3,4</sup>.

All the chromatographic investigations performed so far have shown that valuable information can be obtained on the extraction behaviour of the elements with respect to the extractant used: in this case HDEHP. Therefore it appeared that some hypotheses could be made on the chemical interaction between the various components of the system, namely the metallic ion, the extractant molecule and the aqueous solution of the anion.

To continue this investigation and to get a more detailed picture of the various phenomena, a systematic study carried out with the elements aluminium, gallium, indium, thallium, iron, cobalt, and nickel is described below. Criteria for evaluation of results were almost the same as in previous publications<sup>3,4</sup>; some special consideration was given to aluminium, and occasionally to iron, because of their peculiar behaviour toward HDEHP.

As a consequence of the systematic study some theoretical conclusions were obtained and, at the same time, interesting separations of such elements from one another and from additional ones, such as barium, calcium, titanium, strontium, manganese, yttrium, zirconium and uranium, were carried out.

## EXPERIMENTAL

### *Reagents and equipment*

Di-(2-ethylhexyl) orthophosphoric acid (HDEHP) was a Virginia-Carolina Chemical Co. (Richmond, U.S.A.) product supplied by Soc. Eigenmann and Veronelli (Milan).

Reagents were all analytical grade: 0.1 *N* stock solutions of each element were prepared and then diluted to 0.005 *N* to obtain solutions for spotting. The Al, Ga, In

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and Tl stock solutions were obtained as described in a previous paper<sup>1</sup>. The stock solutions of Fe, Co and Ni were obtained by dissolving the respective chlorides (RP grade, Carlo Erba, Milan) and kept slightly acidic to avoid hydrolysis.

Chromatographic paper Whatman No. 1 (CRL/1 type) was treated with cyclohexane solutions of HDEHP which had been previously equilibrated with 2.5 M HCl, in the usual manner<sup>2</sup>.

The equipment used in this work has already been described<sup>3</sup>. Spots of about 0.05 ml each were applied to the paper according to the standard procedure. After development with HCl, iron and cobalt were detected on the paper by spraying with a saturated aqueous solutions of KCNS, and nickel with a 5% (w/v) dimethylglyoxime solution in ethanol. Aluminium and indium were detected with a 0.1% alcoholic morin solution, and gallium and thallium with a similar quercetin solution<sup>1</sup>.

Experiments were generally performed with HDEHP as supplied, but some of them were also carried out with HDEHP purified by a method derived from that described by STEWART AND CRANDALL<sup>5</sup>. Elution of various cations on paper treated with this purified HDEHP gave the same  $R_F$  values as those on paper treated with unpurified HDEHP.

## RESULTS AND DISCUSSION

### General

In Table I, experimental  $R_F$  values for the metal ions are collected as functions of the molarity of hydrochloric acid used as eluent, the papers being treated with five concentrations of HDEHP solution in cyclohexane, *viz.* 0.010 M, 0.025 M, 0.050 M, 0.075 M, and 0.0100 M. In this table values in parentheses refer to tailing spots.

In Fig. 1  $R_F$  values are plotted against the logarithm of the hydrochloric acid concentration. The experiments were carried out over a range of acidity for HCl from 10 M to  $1 \cdot 10^{-4}$  M, but the lowest concentrations were neglected in drawing Fig. 1 since the relative results showed no interesting features. A decrease of  $R_F$  value for some of the elements can be seen from Fig. 1, *e.g.* gallium, when very concentrated hydrochloric acid is used as the eluent; this behaviour, reported also in the literature on liquid-liquid extraction and ion-exchange experiments, is very similar to that of the alkaline earths with both hydrochloric and acetic acid<sup>3,4</sup>. It deserves special consideration and will be discussed in a future paper. Our present discussion will deal essentially with the behaviour of cations in the ranges of concentration of eluent in which their  $R_F$  values increase with increasing acidity.

When the HCl concentration was between 5.5 and 6.5 M, gallium showed two spots, one of which was with the front of the eluent, and the other corresponding to the value reported in Table II and in the figure; this phenomenon will also be discussed in the future.

As already mentioned<sup>2</sup>, the  $R_F$  values for a given metallic ion on paper treated with a liquid extractant and eluted with an aqueous solution can be related to the extraction coefficient  $E_a^\circ$  of the same ion in the analogous liquid-liquid system through the relationship:

$$\log \left( \frac{1}{R_F} - 1 \right) = \log E_a^\circ + \log k \quad (1)$$

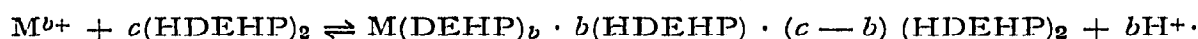
TABLE I

$R_F$  VALUES FOR ALUMINIUM, GALLIUM, INDIUM, THALLIUM AND THE TRANSITION METALS OF THE IRON GROUP, AS FUNCTIONS OF THE MOLARITY OF THE HCl ELUENT

Paper treated with HDEHP. Operating temperature  $23 \pm 1^\circ$ .

HDEHP molarity	Cations	$R_F$									
		HCl molarity									
		10	9	7	6	3	1	0.5	0.3	0.2	0.1
0.010	Al <sup>3+</sup>	0.88	0.91	(0.83)	(0.66)	(0.47)	0.00	0.00	0.00	0.00	—
	Ga <sup>3+</sup>	0.46	0.47	0.56	0.63	0.90	0.94	0.83	0.75	0.54	0.22
	In <sup>3+</sup>	0.86	0.86	0.84	—	—	0.65	0.25	0.03	0.00	—
	Tl <sup>3+</sup>	0.71	0.73	—	0.79	0.78	0.82	—	0.80	—	0.82
	Fe <sup>3+</sup>	0.28	0.43	0.69	0.79	0.63	0.00	0.00	0.00	0.00	—
	Co <sup>2+</sup>	0.86	—	0.88	0.88	0.89	0.91	—	0.92	0.92	0.91
	Ni <sup>2+</sup>	0.85	—	0.88	0.89	0.90	0.92	—	—	0.93	0.92
0.025	Al <sup>3+</sup>	0.90	(0.86)	0.87	(0.80)	(0.40)	0.00	—	—	—	0.00
	Ga <sup>3+</sup>	0.16	0.20	0.29	0.51	0.90	0.89	0.81	0.62	0.38	0.15
	In <sup>3+</sup>	0.88	0.89	0.86	0.84	0.82	0.61	0.18	0.00	0.00	0.00
	Tl <sup>3+</sup>	0.38	0.44	0.57	0.66	0.75	0.80	0.80	—	0.82	0.82
	Fe <sup>3+</sup>	0.02	0.08	0.40	0.75	0.40	0.00	—	0.00	0.00	—
	Co <sup>2+</sup>	0.78	0.79	0.86	0.86	0.93	0.93	—	0.92	0.93	0.93
	Ni <sup>2+</sup>	0.82	0.84	0.86	0.86	0.93	0.93	—	0.92	—	0.94
0.050	Al <sup>3+</sup>	0.90	(0.85)	(0.73)	(0.74)	(0.32)	0.00	0.00	0.00	—	0.00
	Ga <sup>3+</sup>	0.10	0.12	0.20	0.26	0.90	0.91	0.73	0.52	—	0.08
	In <sup>3+</sup>	0.88	0.85	0.84	0.85	0.82	0.54	0.10	0.00	—	0.00
	Tl <sup>3+</sup>	0.22	0.30	0.50	0.57	0.77	0.81	—	0.80	—	—
	Fe <sup>3+</sup>	0.00	0.05	0.40	0.72	0.32	0.00	0.00	—	—	0.00
	Co <sup>2+</sup>	0.86	0.81	0.87	0.85	0.90	0.88	0.90	0.89	—	0.90
	Ni <sup>2+</sup>	0.85	0.81	0.87	0.86	0.87	0.90	0.92	0.91	—	0.91
0.075	Al <sup>3+</sup>	0.90	0.84	(0.78)	0.64	(0.20)	0.00	0.00	0.00	—	0.00
	Ga <sup>3+</sup>	0.00	0.06	0.12	0.26	0.86	0.86	0.65	0.33	0.19	0.05
	In <sup>3+</sup>	0.83	0.86	0.84	0.83	0.82	0.46	0.07	0.00	0.00	0.00
	Tl <sup>3+</sup>	0.09	0.16	0.39	0.47	0.70	0.74	0.76	0.76	0.75	0.76
	Fe <sup>3+</sup>	0.00	0.04	0.41	0.70	0.19	0.00	0.00	0.00	0.00	0.00
	Co <sup>2+</sup>	0.77	0.78	0.87	0.85	0.88	0.90	0.89	0.89	0.90	0.89
	Ni <sup>2+</sup>	0.81	0.82	0.87	0.86	0.88	0.90	—	—	0.90	—
0.100	Al <sup>3+</sup>	0.86	0.84	(0.62)	(0.54)	0.09	0.00	0.00	0.00	0.00	0.00
	Ga <sup>3+</sup>	0.00	0.00	0.02	0.22	—	0.90	0.58	0.32	0.18	0.00
	In <sup>3+</sup>	0.87	0.90	0.85	0.86	0.80	0.35	0.04	0.00	0.00	0.00
	Tl <sup>3+</sup>	0.10	0.12	0.35	0.53	—	0.80	0.77	—	0.77	0.81
	Fe <sup>3+</sup>	0.00	0.04	0.40	0.75	0.16	0.00	0.00	0.00	0.00	0.00
	Co <sup>2+</sup>	0.84	0.79	0.86	0.90	0.88	0.94	0.94	0.94	0.95	0.94
	Ni <sup>2+</sup>	0.85	0.82	0.88	0.90	0.88	0.94	0.95	0.95	0.94	0.95

where  $k$  is a constant which depends on the experimental conditions. Further, the extraction coefficient  $E_a^\circ$  may be related to the activities of the chemical species involved in the reaction postulated as the extraction mechanism through an equilibrium constant. As already pointed out<sup>4</sup>, the equilibrium generally accepted as representing the extraction mechanism with HDEHP may be written as:



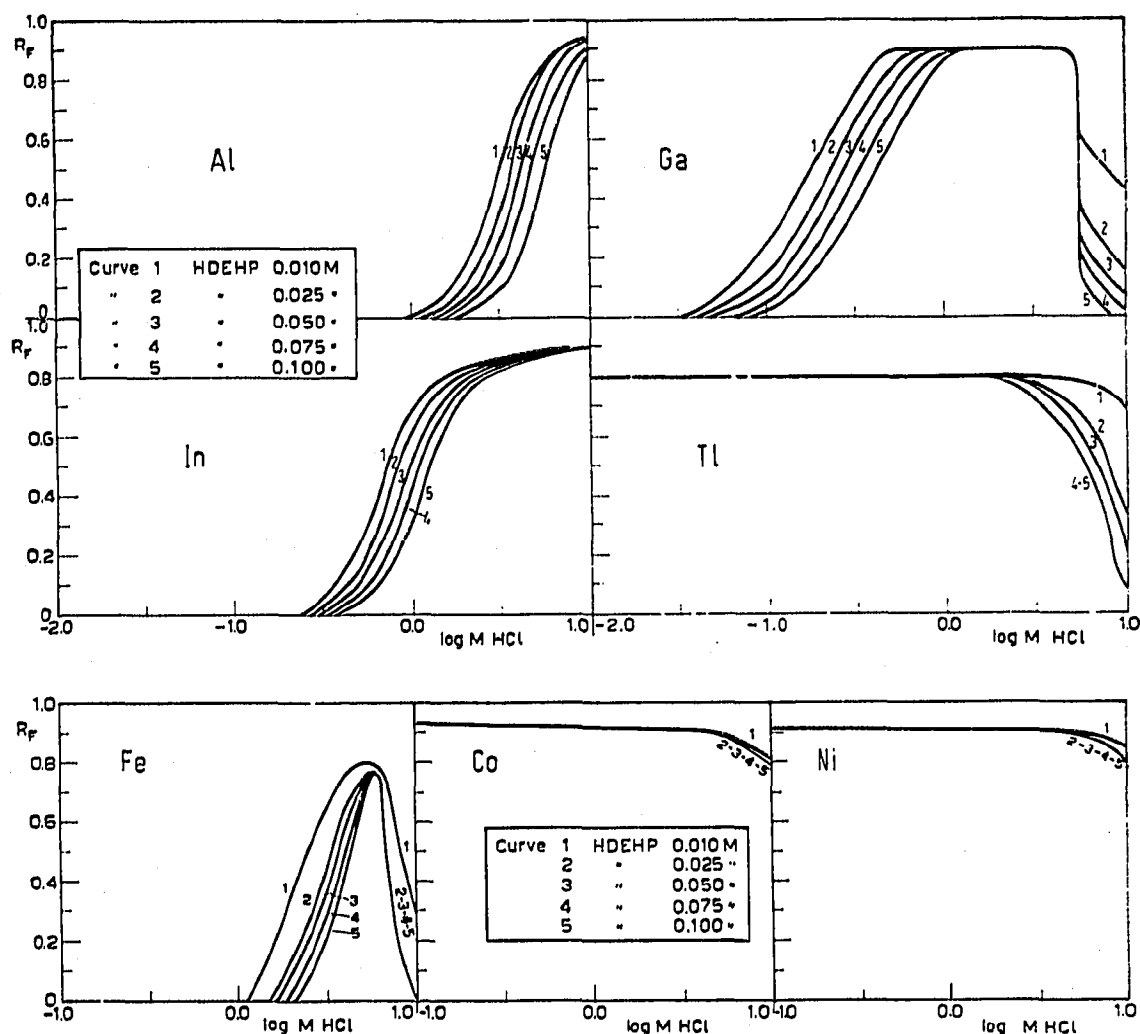


Fig. 1.  $R_F$  values of aluminium, gallium, indium, thallium and the transition metals of the iron group plotted vs.  $\log M$  HCl. Paper treated with HDEHP.

From the equilibrium constant  $K$  of that reaction and from Eqn. (1), the following relationship may be obtained:

$$\log \left( \frac{1}{R_F} - 1 \right) = c \log [\text{HDEHP}]_{\text{eff}} - b \log a_{\text{H}^+} + \text{const.} \quad (2)$$

where  $[\text{HDEHP}]_{\text{eff}}$  is the effective HDEHP concentration on the paper<sup>3,4</sup>,  $a_{\text{H}^+}$  is the activity of the hydrogen ion and "const." stands for  $\log K + \log k$ . In Eqn. 2 the activity  $a_{\text{H}^+}$  can be used for the hydrogen ion concentration since solutions of concentrated hydrochloric acid are involved. The hydrogen ion activities were calculated from the  $\text{H}^+$  molarities by taking as activity coefficients the mean activity coefficients for hydrochloric acid (at the corresponding molalities) as reported by ROBINSON AND STOKES<sup>6</sup>.

For a given element, plots of  $\log (1/R_F - 1)$  against either  $\log [\text{HDEHP}]_{\text{eff}}$  or  $\log a_{\text{H}^+}$  yield the values of the coefficients  $c$  and  $b$  respectively, which appear in Eqn. 2, thus giving information on the extraction mechanism.

TABLE II

$R_F$  VALUES FOR GALLIUM, INDIUM AND IRON ELUTED WITH HCl, AS FUNCTIONS OF THE HDEHP CONCENTRATION IN THE SOLUTION USED TO TREAT THE PAPER

Operating temperature  $23 \pm 1^\circ$ .

HCl molarity	Cation	$R_F$							
		HDEHP molarity							
		0.010	0.015	0.030	0.040	0.050	0.060	0.080	0.100
0.2 M	Ga <sup>3+</sup>	0.55	0.42	0.34	0.28	0.25	0.21	0.19	0.13
0.5 M	In <sup>3+</sup>	0.26	0.24	0.18	0.15	0.14	0.09	0.10	0.09
2.3 M	Fe <sup>3+</sup>	0.34	0.25	0.18	0.12	0.11	0.09	—	—

To obtain additional data on the role of HDEHP in this mechanism, simultaneous elutions were carried out with paper treated with HDEHP at eight different concentrations. The experimental  $R_F$  values for gallium, indium and iron are collected in Table II.

#### Aluminium, gallium, indium and thallium

Figs. 2, 3 and 4 show the plots of  $\log (1/R_F - 1)$  against the logarithm of the hydrogen ion activity in the eluting solution, for Al, Ga and In, respectively.

The plots of  $\log (1/R_F - 1)$  against  $\log k [\text{HDEHP}]_{\text{eff}}^{3,4}$  for these elements are shown in Fig. 5. The developing solutions were 4 M HCl for Al, 0.2 M for Ga and 0.5 M for In. For such plots the  $R_F$  values derived from Fig. 1 and Table II were used.

No data are reported for aluminium in Table II because this element generally gives rise to the formation of tailed spots. It is known from the literature<sup>7</sup> that in a liquid-liquid system aluminium is very slowly extracted by HDEHP and equilibrium

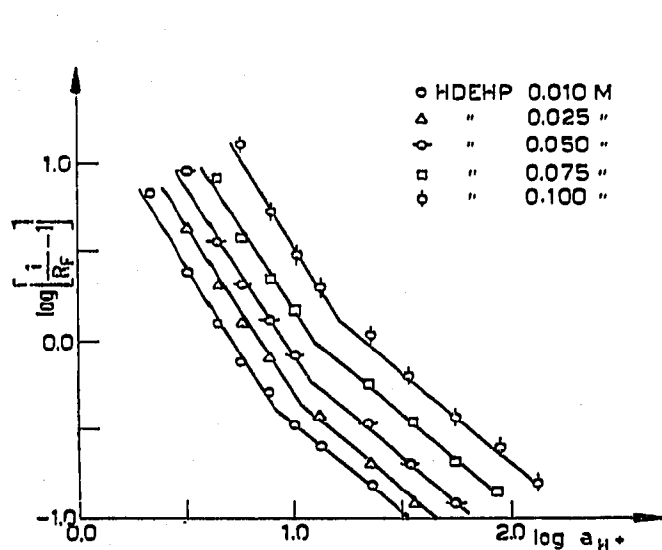


Fig. 2. Plot of  $\log (1/R_F - 1)$  vs.  $\log a_{\text{H}^+}$  for aluminium. Paper treated with HDEHP at various concentrations. Slopes  $-2$  and  $-1$ .

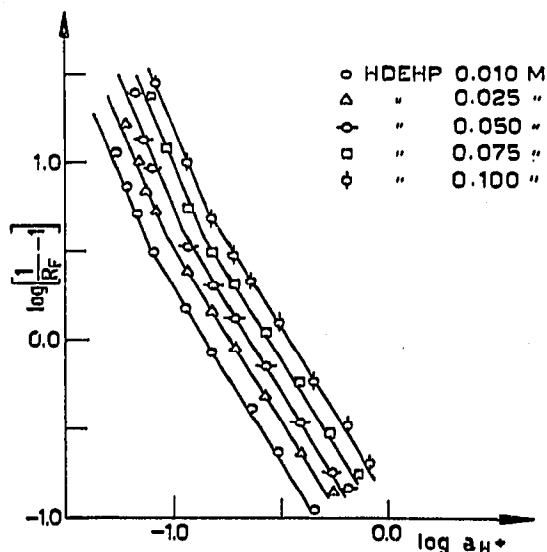


Fig. 3. Plot of  $\log (1/R_F - 1)$  vs.  $\log a_{\text{H}^+}$  for gallium. Paper treated with HDEHP at various concentrations. Slopes  $-3$  and  $-2$ .

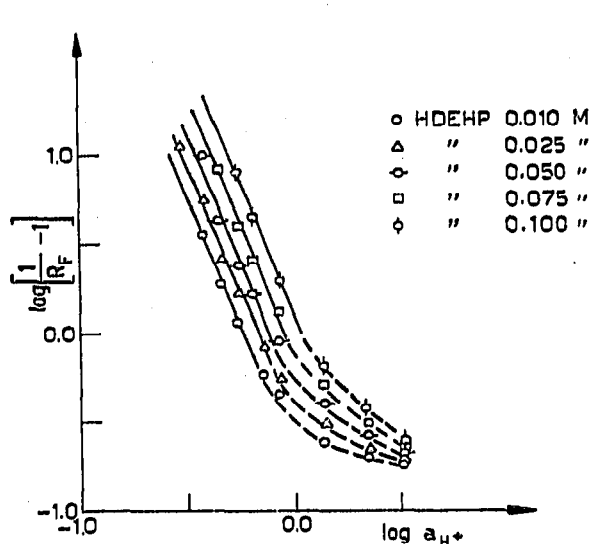


Fig. 4. Plot of  $\log (1/R_F - 1)$  vs.  $\log a_{H^+}$  for indium. Paper treated with HDEHP at various concentrations. Slopes  $-3$  and  $-3$ .

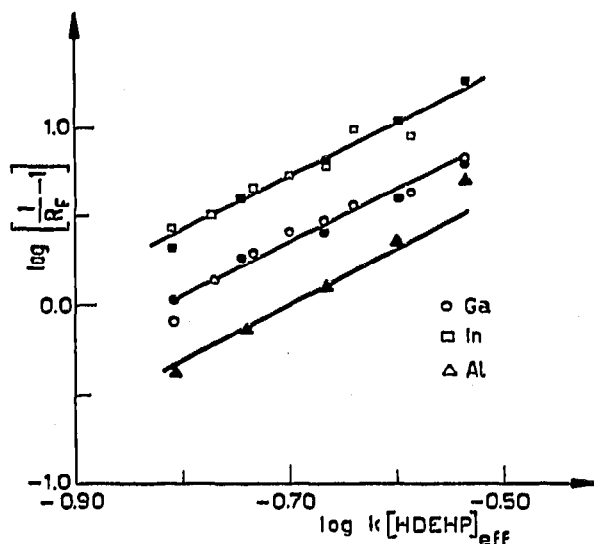


Fig. 5. Plot of  $\log (1/R_F - 1)$  vs.  $\log k[HDEHP]_{eff}$  for gallium, indium and aluminium eluted with  $0.2 M$  HCl,  $0.5 M$  HCl and  $4 M$  HCl, respectively. Data from Table II (open symbols) and data from plots of Figs. 2 to 4 (closed symbols). Slope  $+3$ .

is only reached after a long contact time. This is responsible for irregular spots in reversed-phase chromatography with HCl up to  $7 M$ ; only after a very large number of experiments was it possible to obtain reliable mean  $R_F$  values for use in the curves reported in Fig. 1. For that reason results obtained for aluminium with simultaneous elutions of papers treated with various HDEHP concentrations were not reliable.

No plots were made for thallium, since, as can be seen in Fig. 1, the  $R_F$  values do not show any increase with the HCl concentration within the range investigated.

From the slopes of curves in Fig. 2 the value of 2 was calculated for coefficient  $b$  for aluminium up to a concentration of  $4 M$  HCl ( $\log a_{H^+} = -0.9$ ) which changes to 1 above that concentration. Gallium in Fig. 3 has a slope of  $-3$  just up to about  $0.1 M$  HCl ( $\log a_{H^+} = -1.10$ ), which becomes  $-2$  above that value. Similar behaviour is shown by indium (Fig. 4), which changes slope from  $-3$  to  $-2$  at about  $1 M$  HCl.

From the considerations referred to above, such values which are derived from chromatographic data should agree with those from liquid-liquid extraction. Although few data are available in the literature on the extraction behaviour of these elements by HDEHP, a significant comparison can be made. KIMURA<sup>8</sup> reports a  $b$  value of 3 for liquid-liquid extraction of aluminium, gallium and indium by 50% HDEHP-toluene from HCl solutions up to  $1 M$ . In addition a nearly constant value of  $E_a^\circ$  with the acidity was found for  $Tl^{3+}$ . Except for aluminium these results are consistent with those derived from chromatography, as reported above.

A further comparison can be made with respect to coefficient  $c$ , which correlates  $\log E_a^\circ$ , or  $\log (1/R_F - 1)$ , with  $\log [HDEHP]$ . From the slope of the plots in Fig. 5 a value of 3 is obtained for aluminium, gallium and indium. Such a value agrees with that obtained by KIMURA<sup>9</sup> for indium, whilst a slope of 2 is reported for gallium by the same author. This result is probably due to the high HDEHP concentration used

for extraction. Data for aluminium and thallium are not reported. In HDEHP extraction of aluminium from sulphate solutions BLAKE *et al.*<sup>7</sup> have found  $b = 3$  and  $c = 3$ .

It will be seen from the results given above that the value of coefficient  $b$  is often lower than 3, which is the ionic charge of the metallic species supposedly involved in the chemical reaction. Such a reduction of the value  $b$  can be explained by assuming that the adduct with the extractant is not formed by the bare cation. As already discussed in the case of the alkali metals and alkaline earths<sup>3,4</sup>, the cation is likely to pass into the organic phase surrounded by a number of molecules of the anionic species which is present in the aqueous phase. This tendency is generally greater the higher the concentration of the anion, thus coefficient  $b$  differs from 3 when this concentration increases. Bonding of anions to the cation is very probable in the case of the three elements considered here, because they are known to form chloride complexes with various degrees of complexation in the range of the HCl concentration used in our experiments. If the chloride complex reaches the structure of an anion, as in the case of  $Tl^{3+}$ , which forms  $TlCl_4^-$ , even when the HCl concentration is lower than  $0.1 M^{10}$ , the extraction by HDEHP, which under such conditions is mainly a cation exchanger, becomes very poor. Therefore the  $R_F$  values of that element would be consistently high even with dilute HCl. Actually a higher retention than was expected from these considerations was found, since an  $R_F = 0.80$  instead of 1.00 resulted. But experiments performed with untreated paper showed that such an  $R_F$  value is solely due to the effect of the cellulose.

In addition to considering the behaviour of thallium, it can be concluded that aluminium, gallium and indium are retained by HDEHP on paper through a mechanism which involves the bare ion when the chloride concentration is low. At higher  $Cl^-$  concentrations the ionic species retained should be a complex of the cation with one chloride ion. In all cases, three dimeric molecules of HDEHP bind the cation, probably by means of a mechanism similar to that already suggested for the alkaline earths<sup>4,11</sup>.

#### *Iron, cobalt and nickel*

As expected from literature data on liquid-liquid extraction<sup>8</sup>, nickel and cobalt ran with the front and therefore no study on the retention mechanism was possible.

In Figs. 6 and 7  $\log (1/R_F - 1)$  for iron is plotted against  $\log a_{H^+}$  and  $\log k [HDEHP]_{eff}$ , respectively.

Iron, like aluminium, has a long equilibration time in liquid-liquid extraction with HDEHP<sup>7</sup>. Therefore iron, although to a less extent than with aluminium, had some tailing of the spots which affected the reproducibility of results. It was thought that because of this long equilibration time in extraction, the  $R_F$  values for iron would be affected by the elution speed. Thus, experiments were carried out with ascending chromatography by putting the drops to be eluted at different heights above the surface of the eluent solution, and developing until the front line reached the same distance from the point at which the spot had been applied. Chromatograms were obtained having the same front run and a longer elution time the farther the respective start line was from the liquid surface.

Results showed that among the seven elements considered in this work, only the  $R_F$  values of iron, and perhaps also of aluminium, are slightly dependent on

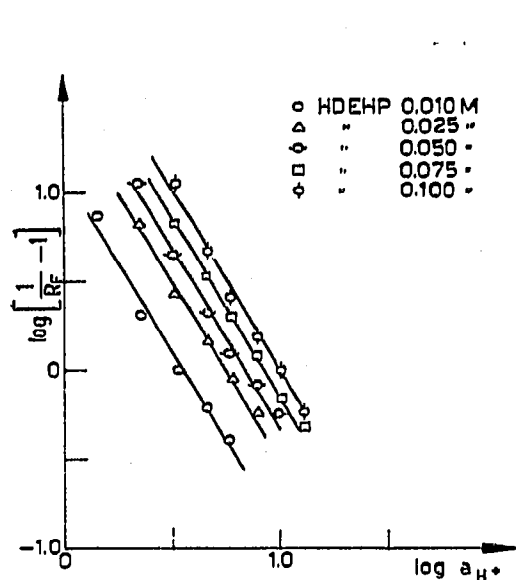


Fig. 6. Plot of  $\log (1/R_F - 1)$  vs.  $\log a_{H^+}$  for iron. Paper treated with HDEHP at various concentrations. Slope  $-2$ .

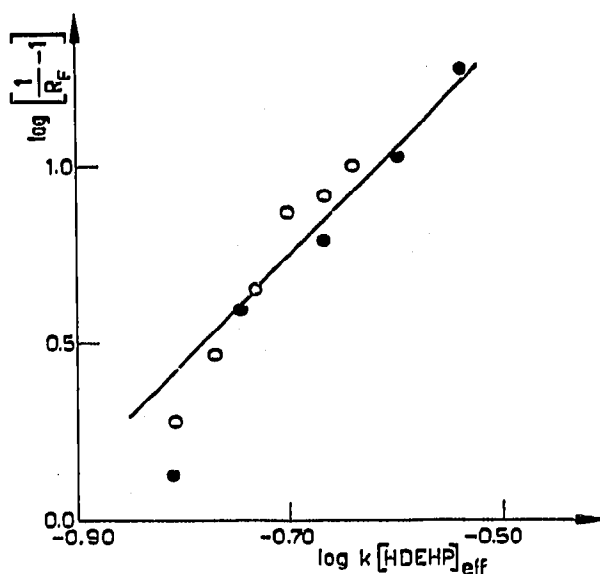


Fig. 7. Plot of  $\log (1/R_F - 1)$  vs.  $\log k[\text{HDEHP}]_{\text{eff}}$  for iron. Data from Table II (open symbols) and data from plots of Fig. 6 (closed symbols). Slope  $+3$ .

elution time. Although these results show that equilibrium is not actually reached during development, we considered that the plots in Figs. 5 and 6 were in fact useful in revealing information on the extraction mechanism. In comparison, data reported by KIMURA<sup>8</sup> on the extraction of iron by HDEHP from chloride solutions show that although the extraction coefficients are lower the shorter the shaking time, their behaviour toward acid concentration is similar with any fixed shaking time.

From Figs. 6 and 7 the values of the reaction coefficients  $b$  and  $c$  appear to be 2 and 3, respectively. The value of 3 for coefficient  $c$  agrees with results reported by BAES AND BAKER<sup>12</sup> for liquid-liquid extraction of iron with HDEHP from perchlorate solutions. Extraction of iron by HDEHP from chloride solutions is reported by KIMURA<sup>8,9</sup> to give  $b = 3$  and  $c = 2$ , which is not in agreement with chromatographic data. This disagreement may be explained by assuming that the chromatography was carried out using higher HCl concentrations than were used in extraction experiments. A value of  $b$  lower than 3 should therefore result from the formation of chloride complexes such as was discussed for aluminium, gallium and indium. It should be noted that iron has a considerable tendency to form chloride complexes, and in the range of acidity considered might retain one chloride ion in the molecule of the adduct which extracts into the organic phase.

From Fig. 1 it can be seen that some elements show an increase of  $R_F$  with HCl molarity followed by an appreciable decrease when the HCl concentration becomes high. Although extensive discussion is deferred to a further publication, some observations are made here. The fact that the adsorption of those elements increases is not attributable to a cation exchange mechanism through the DEHP<sup>-</sup> radical, since such elements are supposed to be in the form of anionic chloride complexes, but rather to a sort of bonding with the oxygen atom of the P=O groups of the extractant. This bonding occurs normally with tributyl phosphate. Such a mechanism, which



takes place when the ion begins to dehydrate because of the very low activity of water in the solution, is responsible not only for the rapid decrease of  $R_F$  values of  $\text{Ga}^{3+}$  and  $\text{Fe}^{3+}$ , but is also responsible for the slow decrease of  $R_F$  in the case of  $\text{In}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and of the alkaline earths.

Studies are being carried out to decide whether the peculiar decrease of  $R_F$  values of thallium is due to the same cause or to another one, as for example reduction of the ion from the trivalent state to the univalent one, which is complexed by chloride to a minor extent.

#### *Application to chromatographic separations*

From the experimental results described above, it appears that many interesting separations are feasible for aluminium, gallium, indium, thallium and the transition metals of the iron group. In addition some other ions, which were investigated in previous publications<sup>3,4</sup>, can be considered. The complete separation of Al-Ga-In and Tl has already been published<sup>1</sup>. Other separations obtained are listed in Table III,

TABLE III

ASCENDING CHROMATOGRAMS OBTAINED WITH  $3 \times 40$  CM PAPER STRIPS TREATED WITH HDEHP  
Operating temperature  $23 \pm 1^\circ$ .

No.	Separation of	Run (cm)	HDEHP molarity	Eluent	$R_F$
1	Be-Fe-Al-Sr	28.3	0.100	7.5 M HCl	Be = 0.00; Fe = 0.12; Al = 0.48; Sr = 0.8
2	Ti-Ga-Fe-Tl-U-Ba-Ca-Ni	29.2	0.050	8 M HCl	Ti = 0.00; Ga = 0.03; Fe = 0.10; Tl = 0.16; U = 0.34; Ba = 0.56; Ca = 0.76; Ni = 0.96
3	Zr-Fe-Y-In-Ni	33.1	0.025	2 M HCl	Zr = 0.00; Fe = 0.04; Y = 0.37; In = 0.8; Ni = 0.96
4	Ti-Fe-Tl-U-Ba-Sr	29.5	0.100	8 M HCl	Ti = 0.00; Fe = 0.09; Tl = 0.16; U = 0.2; Ba = 0.56; Sr = 0.64
5*	Ga-Fe-Ba-Mn	29.5	0.100	7 M HCl	Ga = 0.10; Fe = 0.41; Ba = 0.68; Mn = 0.9
6*	Y-Ga	31.5	0.100	1.5 M HCl	Y = 0.08; Ga = 0.92
7*	Ga-Y	29.8	0.100	7 M HCl	Ga = 0.05; Y = 0.84

\* Operating temperature  $28^\circ$ .

together with the concentration of HDEHP in cyclohexane used to treat the paper and the hydrochloric acid concentration of the eluent. The length of the run to the solvent front of each chromatogram is also given. Strips  $40 \times 3$  cm of Whatman No. 1 paper were used and were cut perpendicular to the machine direction. Paper was treated with HDEHP in the same way as CRL/1 sheets used in fundamental work. Diagrams of the separations quoted in Table III are reported in Fig. 8.

#### SUMMARY

Reversed-phase chromatography of aluminium, gallium, indium, thallium and the transition metals of the iron group on paper treated with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) has been investigated, using hydrochloric acid as eluent in a range of concentrations from  $10 M$  to  $1 \cdot 10^{-4} M$ . The quantity  $(1/R_F - 1)$

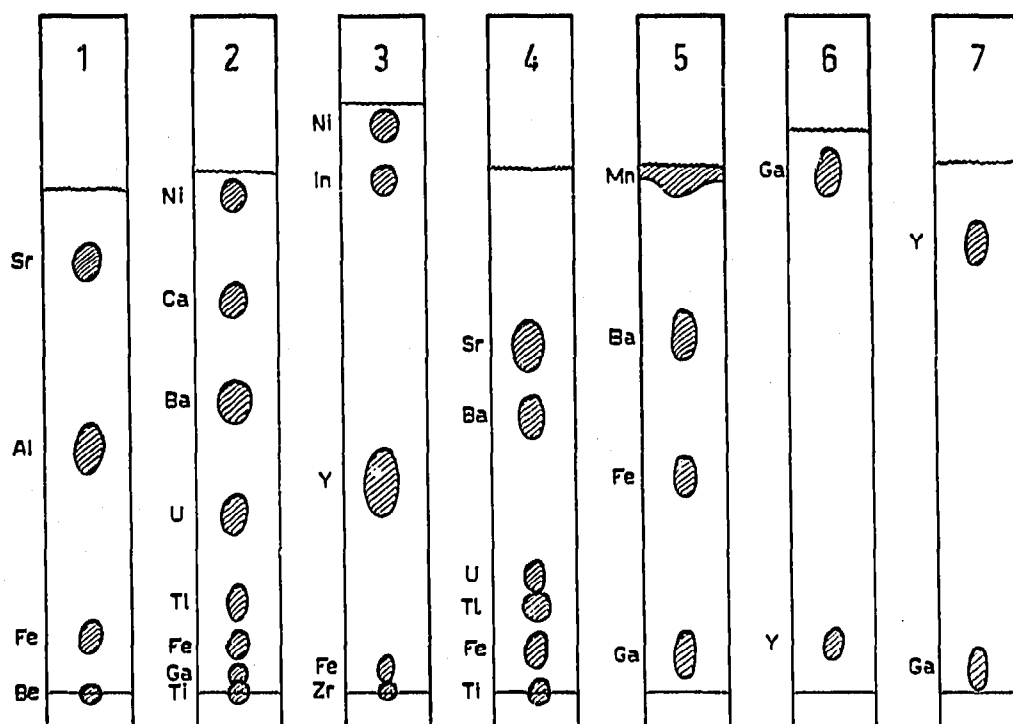


Fig. 8. Diagrams of the separations quoted in Table III.

has been related to the hydrogen ion activity in the mobile phase and to the effective HDEHP concentration on the paper.

The chromatographic behaviour has been correlated with that in liquid-liquid extraction systems. Chromatographic separations of the above elements from each other and from additional cations such as barium, calcium, titanium, strontium manganese, yttrium, zirconium and uranium were performed.

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