CHROMATOGRAPHIC TECHNIQUES USING LIQUID ANION EXCHANGERS[*]

III. SYSTEMATIC THIN-LAYER CHROMATOGRAPHY OF THE ELEMENTS IN HCl SYSTEMS

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INTRODUCTION

In a previous publication[2] on the behaviour of supports treated with liquid anion-exchangers in chromatography, it was pointed out that it would be necessary to gather information on the behaviour of ions in HCl systems for more elements. The present paper deals with the systematic investigation of this subject, as carried out by us, making use of the rapid method of thin-layer chromatography. In addition, a number of qualitative separations are reported in order to show the excellent possibilities for the use of the liquid anion-exchanger·HCl system.

In order to obtain a considerable amount of information, three liquid anion-exchangers of widely divergent adsorption strength were selected. From our previous results[2], it was evident that Primene JM-T was the most suitable as a weakly adsorbing amine; Amberlite LA-1 (though it had no superiority over Amberlite LA-2) was chosen as a moderately adsorbing compound; and thirdly, Alamine 336 was selected from the strongly adsorbing class. In the latter class, a rather large number of anion-exchangers were well suited to the purpose, but Alamine was the most suitable, when practically important aspects such as price, purity, elution speed and quality of the thin layers were considered.

As regards the method used for the experimental work, they were by and large the same as those described previously but some standardizations were introduced that are outlined below.

MATERIALS AND METHODS

For the preparation of the thin layers silica gel Type DO (Fluka), impregnated with one of the three amines mentioned below, was used. Details concerning equilibration of the amines, application of the impregnated silica gel to the microscope slides, and ascending chromatography in Hellendahl staining jars may be found in ref. 2; the standardization of the procedure is described under *Apparatus*. In the

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[*] For the preceding parts of this series, see refs. 1 and 2.
[**] This paper forms part of the work done by U.A.Th. B. for his Ph. D. Thesis.
[***] Abbreviations: TOPO = tri-*n*-octylphosphine oxide; TBP = tri-*n*-butyl phosphate.

case of the strongly reducing ions Fe(II) and Sn(II), dry ice was added to the jars in order to create a CO_2 atmosphere.

The selected amines were: Alamine 336 (General Mills, Kankakee, Ill.), a tertiary straight-chain alkyl amine with an average mol. wt. of 392; Amberlite LA-1 (Rohm and Haas, Philadelphia, Pa.), an unsaturated secondary amine with an average mol. wt. of 372; Primene JM-T (Rohm and Haas, Philadelphia, Pa.), a primary amine with an average mol. wt. of 311.

All ions* were applied using solutions containing 2–12 μg ion/μl, which were acidified as far as necessary to prevent hydrolysis. In the case of cations, the chloride salts were used, except with Pb, Ag and Tl(I), where the nitrates were selected. Anions were present either as the free acid or as an alkali salt. Investigations with iodide showed this to make no significant differences.

Detection

The ions were identified using conventional reagents as far as possible. However, some procedures commonly used for the detection of ions on chromatograms fail when applied to amine-treated supports. Therefore, it seems useful to record briefly the identification reactions employed. Colours are given only for the less common reactions.

H_2S. After treatment with NH_3 vapour the chromatoplates are exposed to H_2S gas. These and all other procedures involving gases were carried out in Hellendahl staining jars. The chromatoplates are placed upside down on a piece of glass tubing to avoid contact with the reagent solution.

Hg(I), Hg(II), Pb, Bi, Sb(III), Sb(V), Au, Pt, Pd, SeO_3^{2-}, and TeO_3^{2-} are detected.

8-Hydroxyquinoline. Spraying of the chromatoplates with a 1 % soln. in ethanol is followed by NH_3 treatment. For some ions the development of the colour proceeds slowly (V(IV), VO_3^-); most ions must be visualized in ultraviolet light.

Be, Mg, Ca, Al, Fe(II), Fe(III), Mn, Zn, Cd, Ga, In, V(IV), VO_3^-, WO_4^{2-} and U are detected.

Dithizone. The ions are detected by spraying them with a fresh 1 % soln. in acetone. (A soln. in chloroform gives much less satisfactory results.) Except for Sb, treatment with NH_3 sometimes gives better results.

Hg(I), Hg(II), Pb, Bi, Zn, Cd, Ag, Sn(II), Sn(IV), Sb(III), and Sb(V) are detected; As(III) and As(V) sometimes show up as a light spot on the green background.

Dithiooxamide. After NH_3 treatment, the chromatoplates are sprayed with or dipped into a satd. soln. of the reagent in acetone.

Ni, Co, Cu and Ru can be detected. For Ru the treatment is extended by leaving the chromatoplates in HCl fumes for 2 min and heating to 150°, when blue stains develop (*cf.* ref. 3, p. 142).

Quinalizarin. The spots are visualized by treating the chromatoplates with NH_3 and subsequently leaving them for 1 min in a 1 % quinalizarin soln. in diethyl ether. Exposure to the vapour of glacial acetic acid may enhance the contrast.

Mg, Al, Sc, Y, rare earths, GeO_3^{2-}, Ga, In, Ti, Zr, Hf, Th, and U are detected.

Reduction via heating. Some ions are reduced to the elemental form by carefully

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* A complete list of the ions studied and their valencies can be read from Figs. 5 or 6. Valencies are given in the text only where necessary.

heating the chromatoplates in a colourless bunsen flame or better a small electric oven at 300°[*].

Au, Pt, SeO_3^{2-}, and TeO_3^{2-} can be detected by this method.

Sodium rhodizonate. After heating the chromatoplates for 2–4 min at 300° in order to remove the amine, they are cooled down and dipped into a 0.2 % collodion soln. in acetone (reinforcement of the thin layer). Subsequently, the chromatoplates are left for 1 min in a freshly prepared satd. soln. of the reagent in water which will detect Sr, Ba and Pb. The colour of Pb is enhanced by dipping into a buffer solution, pH 2.8 (*cf.* ref. 2 and ref. 3, p. 73).

Ammonium molybdate and tolidine. After treatment with collodion, the chromatoplates are dipped into hot (80°) 10 % ammonium molybdate–nitric acid, s.g. 1.2 (1:1, v/v). Drying is carried out at 100° after removal of adhering liquid on the back and edges of the plates and is continued till nitric acid fumes have disappeared. At this stage, yellow spots may already be visible.

The cooled plates are dipped into a 1 % tolidine soln. in diethyl ether. PO_4^{3-} and As(V) now show up as blue stains on a nearly white background. For As(III) the same procedure applies after oxidation to As(V) via treatment with NH_3, bromine vapour (from bromine water) and again NH_3. However, detection of As(III) fails for HCl normalities above 6 N, especially in the presence of amines.

Diphenylcarbazide. $Cr_2O_7^{2-}$ and ReO_4^- are visualized as violet stains by spraying with a 1 % reagent soln. in ethanol, in the case of ReO_4^- followed by treatment with HCl fumes[4]. Identification of $Cr_2O_7^{2-}$ only succeeds up to approx. 7 N HCl.

Tannic acid. When identifying Ti and NbO_3^-, the chromatoplates are first treated with collodion. Ti develops a yellow stain when dipped into a 2 % tannic acid soln. containing 5 % sodium acetate. For NbO_3^- the tannic acid soln. is used without the addition of sodium acetate[5], and after heating to 200° a yellow-brown colour results.

Potassium iodide. Tl(III) is detected by spraying with a 5 % soln. of KI in water, and Tl(I) by dipping into the same soln. after treatment with collodion (Tl(III) spots disappear on collodion treatment and/or dipping). After heating for some min at 300°, a white to violet fluorescence shows up when observing the chromatoplates in short-wave ultraviolet light (254 nm) (*cf.* ref. 6).

Leucomalachite green. Dipping into a 1 % soln. in diethyl ether is used to detect Ir (*cf.* ref. 7) and Mn. The latter ion must first be oxidized with KIO_4 under ammoniacal conditions[2], after which brown stains are often already visible.

Fluorescein and chlorine. After NH_3 treatment the chromatoplates are dipped into a satd. soln. of fluorescein in diethyl ether and placed in a very dilute Cl_2 atmosphere. Br^- spots are detected by oxidation to Br_2, which converts the reagent to red-violet eosin; too much chlorine decolorizes the whole thin layer.

Diphenylcarbazone. Cr(III) is detected by dipping the chromatoplates thrice into a satd. soln. of diphenylcarbazone in diethyl ether, and carefully heating to approx. 250°. Violet spots develop (*cf.* ref. 8), that disappear on prolonged heating.

Phenylhydrazine. After treatment with NH_3 and collodion, the chromatoplates are dipped into a 10 % soln. of this reagent in diethyl ether, and heated at 150°.

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[*] An easily controllable oven consists of two concentric glass tubes, the inner one having an interanl diameter of approx. 28 mm. A heating coil is placed in the narrow space between them and connected to a variable transformer.

While excess reagent is evaporating, red spots develop when MoO_4^{2-} is present (*cf.* ref. 3, p. 117). (With an aged reagent soln., the colour is obtained at room temperature.)

Phenylthiourea. The chromatoplates are treated with NH_3 and subsequently dipped into a 1% soln. of the reagent in acetone–diethyl ether (1:1, v/v). After heating at 300°, brown stains develop when Rh is present (*cf.* ref. 9). The reaction is not sensitive.

General remark. Some ions are often directly visible. For instance Ir, I⁻ and Ru show up as yellow, yellow-brown and brown spots, respectively.

Apparatus

Following the application of the impregnated silica gel to the chromatoplates (*cf.* ref. 2), superfluous support material is wiped off in the apparatus drawn in Fig. 1. Two pieces of rubber (A) are mounted on a bottom plate in such a way that on pushing in the chromatoplates up to stop B, a 4-mm wide margin is made along the edges. Simultaneously, the back of the plate is cleaned by means of a piece of rubber (C) fixed on a spring. Subsequently, a groove is made in the thin layer by moving a vertically held needle along the edge of disc D, which is mounted at a distance of 38 mm from B.

The chromatoplates are now placed on a rack (Fig. 2) and an 8-mm thick ruler E is placed just in front of the slides (F), which are spotted[2] by moving a pointed paper strip (G), impregnated with the solution to be analysed, along the upper edge of the ruler. The distance between the applied spots (origin) and the front groove is now exactly 30 mm.

The elution is terminated when the eluate reaches the groove; after drying and identification, the R_F values are measured in the apparatus illustrated in Fig. 3. This consists of a metal plate in which there is a rectangular slot that takes the chromatoplate. Alongside, there is an engraved scale, H, 30 mm in length which has been graduated in hundredths. The plates are pushed up to stop K; the origin and the horizontal groove now correspond with 0 and 100, respectively. The hairline of a perspex rider L is adjusted on to the centre of the spot to be measured, the R_F of which can now be read from the scale.

For radial chromatography, the apparatus in Fig. 4 may be used. A U-shaped metal wire M twice as thick as the chromatoplate has been mounted on a bottom plate. Two discs shaped as shown in Fig. 4 have been soldered on to the wire. After a chromatoplate has been placed in the apparatus, a groove is drawn with a needle, going from N via O-P-Q to R. The radius of the half-circle measures approx. 10 mm. On the chromatoplate so prepared a spot may be applied in the aperture in the lower part of the groove (N-R).

RESULTS AND DISCUSSION

The results on the thin-layer chromatographic behaviour of approx. 55 ions in HCl systems are summarized in Figs. 5 and 6. The silica gel layers were impregnated with Amberlite LA-1, Alamine 336 or Primene JM-T, exemplifying the moderately, strongly and weakly adsorbing anion-exchangers, respectively. Data on the last-named amine are not recorded when R_F values of 1.0 were consistently obtained with the other two amines. Chromatography in the HCl system was also carried out on
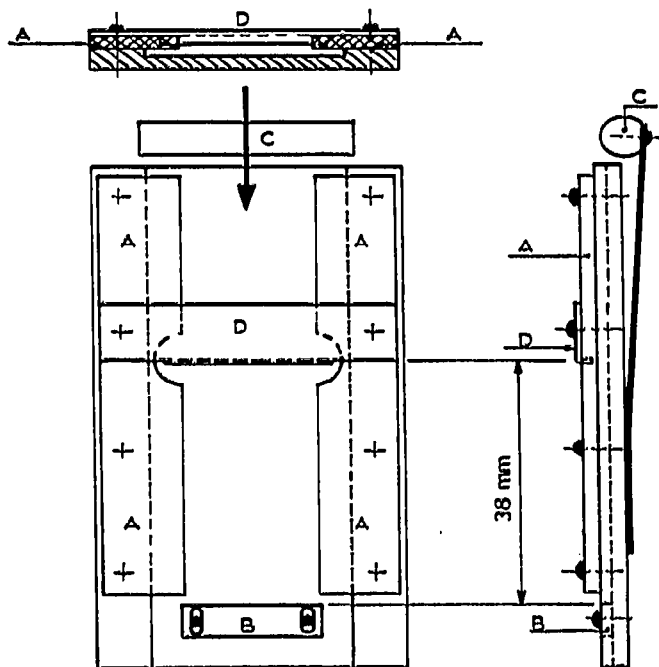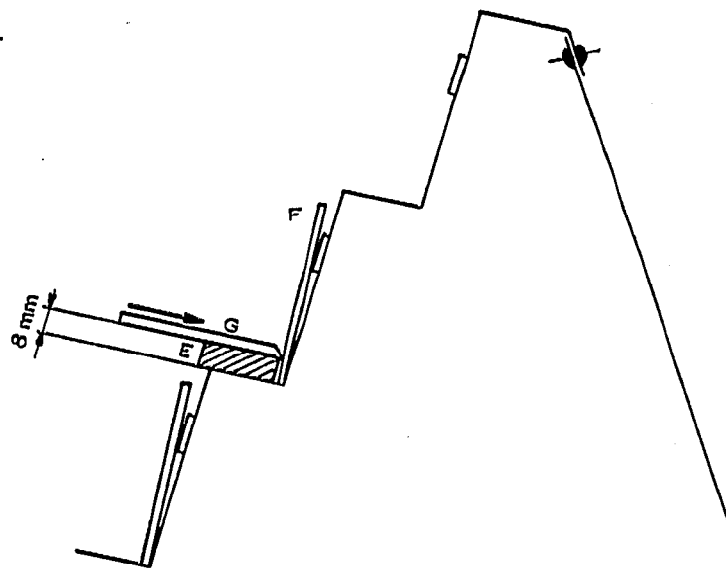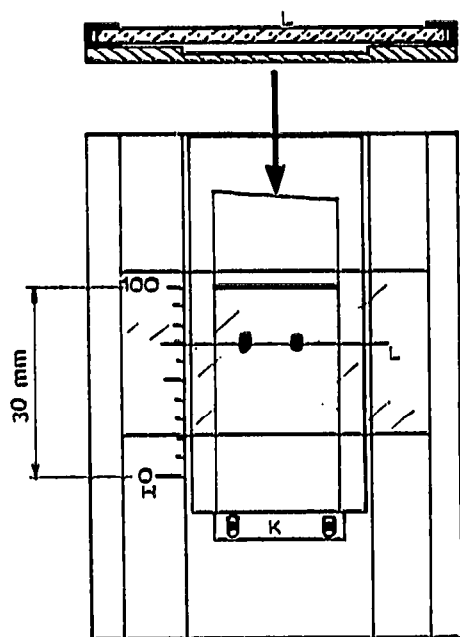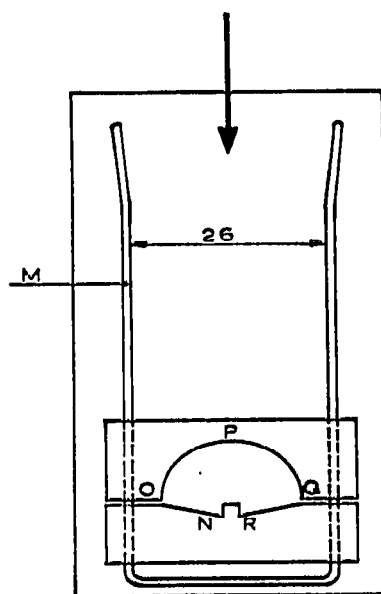
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 1–4. Apparatus used in thin-layer chromatography. For details, see text.

silica gel which had not been impregnated with anion-exchanger, in order to determine the effects of phenomena such as hydrolysis, precipitation and adsorption to the support. These results are included in Fig. 5.

When examining our results, comparisons have been made to literature data on *e.g.* paper impregnated with liquid anion-exchangers[10,11] or the neutral organo-phosphorus compounds TOPO and TBP[12-14], the solid resin-impregnated papers used by LEDERER and coworkers[15,16] and, briefly, the anion-exchange experiments of KRAUS AND NELSON[17]. This has shown that for a great majority of ions three rules apply: (a) the adsorption of an ion increases in the sequence Primene < Amberlite < Alamine; (b) TOPO-treated supports and Amberlite SB-2 paper may be classified among the strongly adsorbing compounds, while DE- and AE-cellulose papers and TBP belong to the weakly adsorbing class; (c) the R_F *vs.* concentration of HCl plots (R_F spectra) of an ion, obtained by using the various methods, are very similar. The exceptions pertain to ions such as Ti, Zr, Hf, MoO_4^{2-} and Rh, for which, in the main, the presence of anion-exchangers cannot be held responsible for the deviations (see below). The three conclusions confirm our previous statement[2], based on the behaviour of a limited number of ions.

Apart from these general conclusions, some critical remarks may be made with respect to the various literature data. Our results show a very close correspondence with those obtained when using the solid resin Amberlite SB-2 paper[15,16]. One rather remarkable phenomenon should, however, be mentioned: for a number of ions, notably some commonly encountered ones such as Fe(III), Cu and Co, the adsorptivity of the Amberlite SB-2 paper falls back to the level of the liquid anion-exchangers Amberlites LA-1 and LA-2.

With papers impregnated with liquid anion-exchangers, our data resemble those of CERRAI AND GHERSINI[10] more than those of SASTRI *et al.*[11]. A more interesting point we noted in the study of the latter authors was that their results on the "adsorption strength"[2] of the liquid anion-exchangers in HCl systems must be regarded with some caution. In general, they found that Aliquat > trilaurylamine > dilaurylamine (though the differences are small), but the primary amine hexadecylamine is certainly not always found in last place, as suggested by the authors[11], but repeatedly ranks in first place. Apart from invalidating their general order of extraction, this fact yields an example of an amine, that cannot be placed as yet in our "adsorption sequence".

The remarkable correspondence of data obtained with supports impregnated with liquid anion-exchangers and with the neutral compound TOPO has previously been noted[2,14]. The more extensive comparison, now possible, shows this to hold for most ions (and also in the case of TBP), though not as strictly as with the exchangers discussed above. Leaving out Cr(III) (see ref. 18), one finds major deviations with Sc and Th, which give distinctly stronger adsorption in the case of TOPO, and the same occurs with Zr and Hf. However, for all these ions, the TOPO-treated-paper data are confirmed well by experiments on TOPO-impregnated silica gel[18], which suggests that adsorption to the support cannot explain the differences.

As regards the experiments in the absence of anion-exchangers, an agreeable overall correspondence with the paper-chromatographic data of LEDERER and co-workers[15,16] was noted, though their R_F values are generally somewhat lower than ours. Attention is drawn to the absence of adsorption to the support found for most

ions including Au, where this result is contrary to expectations[15]. The curves and streaks (cf. legends to Figs. 5 and 6) found for elements such as Ag, Sn, Sb and Hg(I) and probably NbO_3^- indicate the occurrence of hydrolysis and precipitation phenomena, at least in part of the HCl range.

Lastly, some importance may be attached to the strong adsorption of ions such as $FeCl_4^-$, $AuCl_4^-$ and $TlCl_4^-$ in contrast to anions such as ReO_4^- and I^-. This phenomenon, previously encountered both on anion-exchange columns[17] and with solid-resin-impregnated paper[15] may be due to adsorption in the network of the exchanger[15], though e.g. the strong acidity of the complex metal acids must also be borne in mind. Elucidation of these problems must await further research, in which generally the role of the support will be negligible (see above).
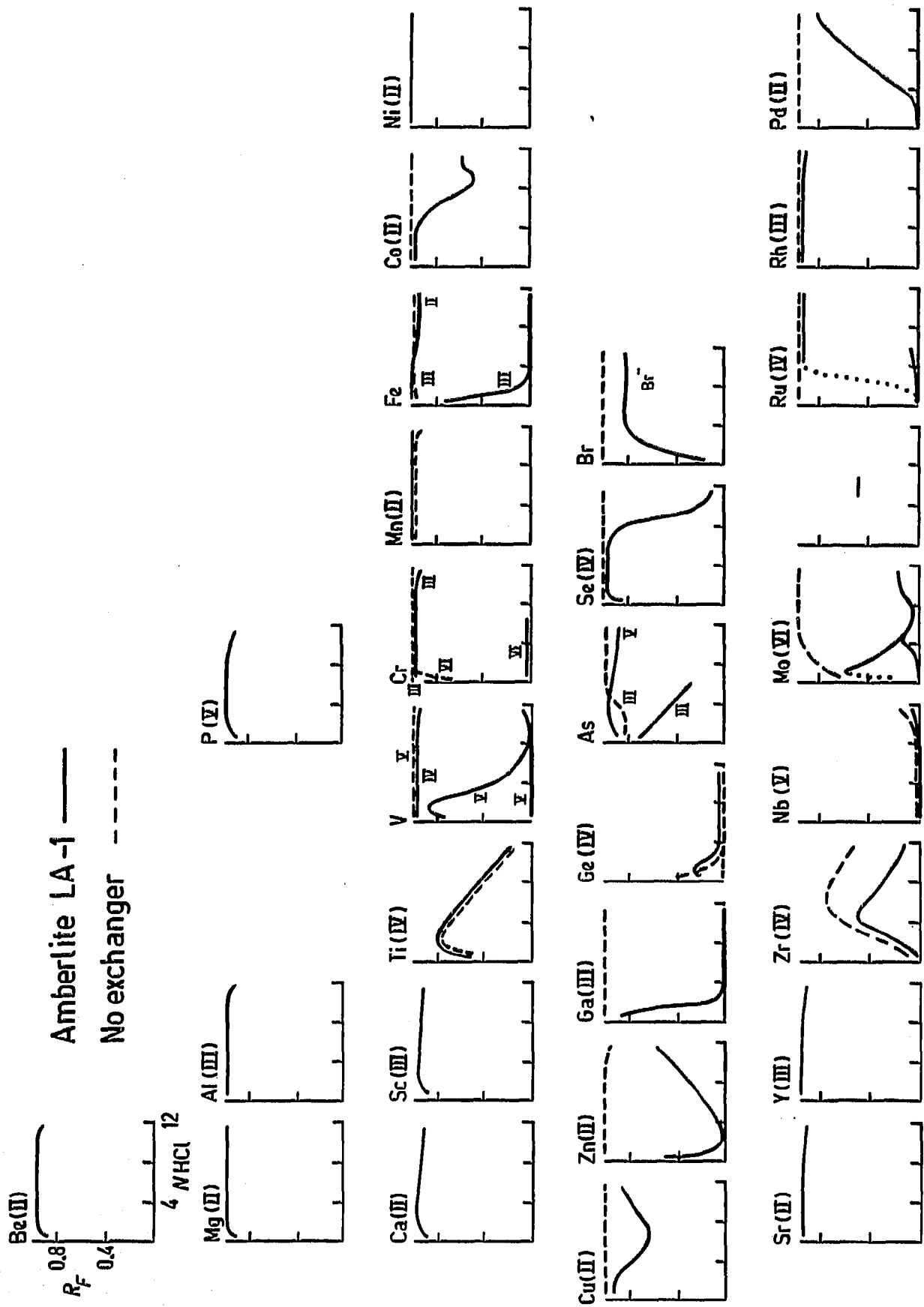
The somewhat exceptional behaviour of a number of ions, briefly mentioned above, will be more fully discussed now. (Several details of less importance are recorded in the legends to Figs. 5 and 6.)

With some ions, curves found in the presence and absence of liquid anion-exchangers show a marked resemblance. This phenomenon points to an insignificant role by the anion-exchanger and is most clearly shown by Ti, where the four curves recorded in Figs. 5 and 6 are in fact identical. Incidentally, the long streaking spots obtained with Ti are generally irrespective of whether the applied solution is 3, 6 or 9 N with respect to HCl. The R_F spectra indicate the position of the mass centers of the spots and these agree satisfactorily with the literature data, though most authors report a somewhat lower adsorption than found by us (see also below).

Anion-exchange is also negligible with Zr and Hf below approx. 7 N HCl, where these ions also yield closely corresponding R_F spectra, though these clearly diverge at high HCl concentrations. As regards Zr, when using a $ZrOCl_2$ solution in water, long streaking spots are obtained, especially for 0.1–2.0 N HCl, when the largest part of the Zr is found at or close to the solvent front. The R_F spectra so obtained resemble those recorded by SASTRI et al.[11], though these authors do not mention any streaking of the spots. This streaking is probably due to hydrolysis, followed by adsorption or precipitation on the support[10]: it is much less apparent when dissolving the $ZrOCl_2$ (or $HfOCl_2$) in 2 N HCl, when the curves shift to lower R_F values, especially with dilute HCl and—apart from a distinctly stronger adsorption— agree with those found by CERRAI AND GHERSINI[10].

Lastly, attention is drawn to Ba, where identical R_F spectra also point to the absence of an anion-exchange mechanism. Here, the element moves with the solvent front up to 6–7 N HCl, while for the remainder the major portion is found at the origin. This fact, coupled with the occurrence of weakly showing streaks with intermediate R_F values for 6–8 N HCl, clearly points to the slight solubility of $BaCl_2$, in more concentrated HCl solutions (approx. 1 mg Ba/ml in 8 N HCl), determining the form of the curves.

In several cases, part of the element remains at the origin and part moves with the solvent. When this phenomenon was encountered over a fairly large HCl concentration range, two curves have been drawn in Figs. 5 and 6. This especially applies to VO_3^- and GeO_3^{2-}, and occurs to a lesser extent with MoO_4^{2-}. In the latter case, the two curves mostly converge in the region of 2 to 6 N HCl, but it is remarkable that for VO_3^- in the case of Primene (where the upper curve consistently has R_F 1.0)

Amberlite LA-1 ——

No exchanger - - - -

R_F 0.8 0.4   4 N HCl 12

Be(II), Mg(II), Al(III), P(V), Sc(III), Ca(II), Ti(IV), V, Cr, Mn(II), Fe, Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Ge(IV), As, Se(IV), Br, Sr(II), Y(III), Zr(IV), Nb(V), Mo(VI), Ru(IV), Rh(III), Pd(II)
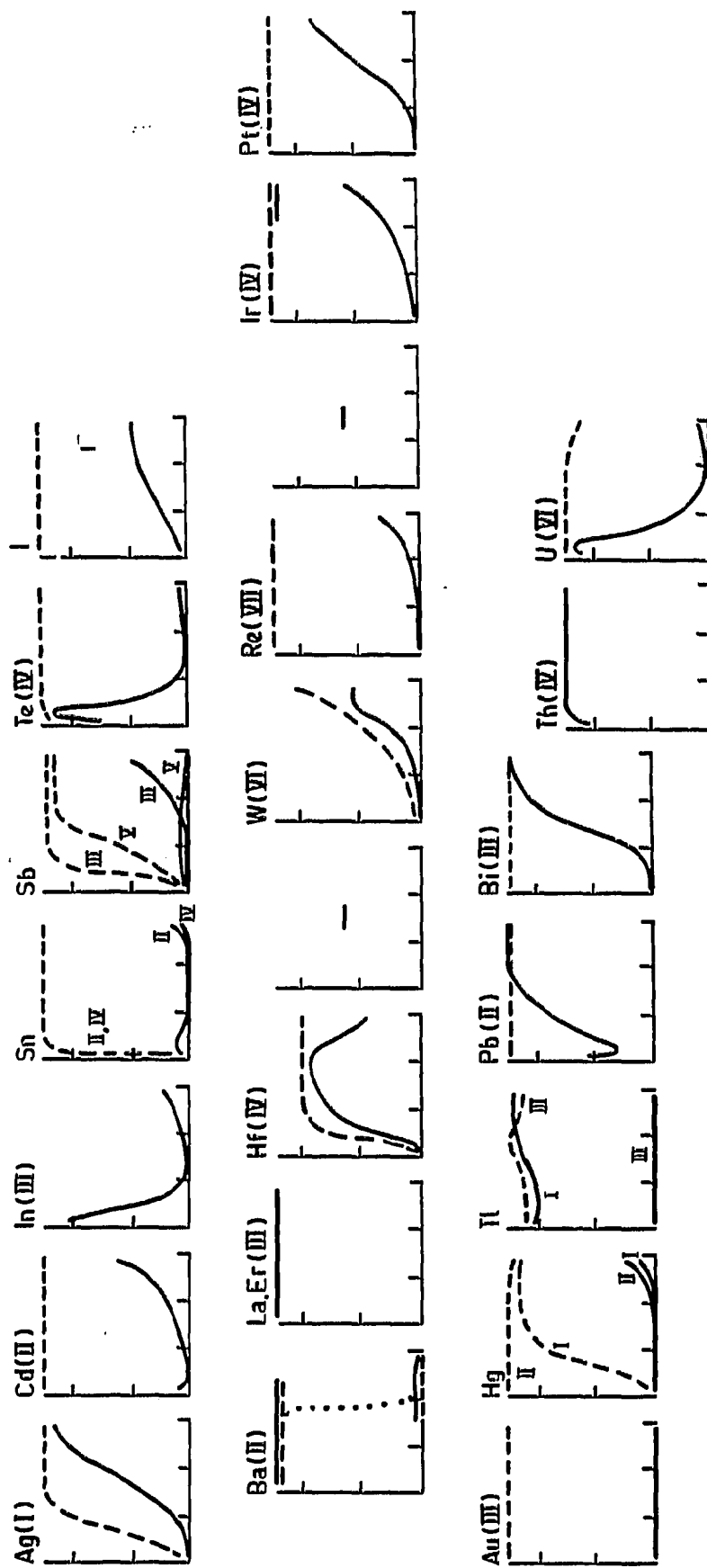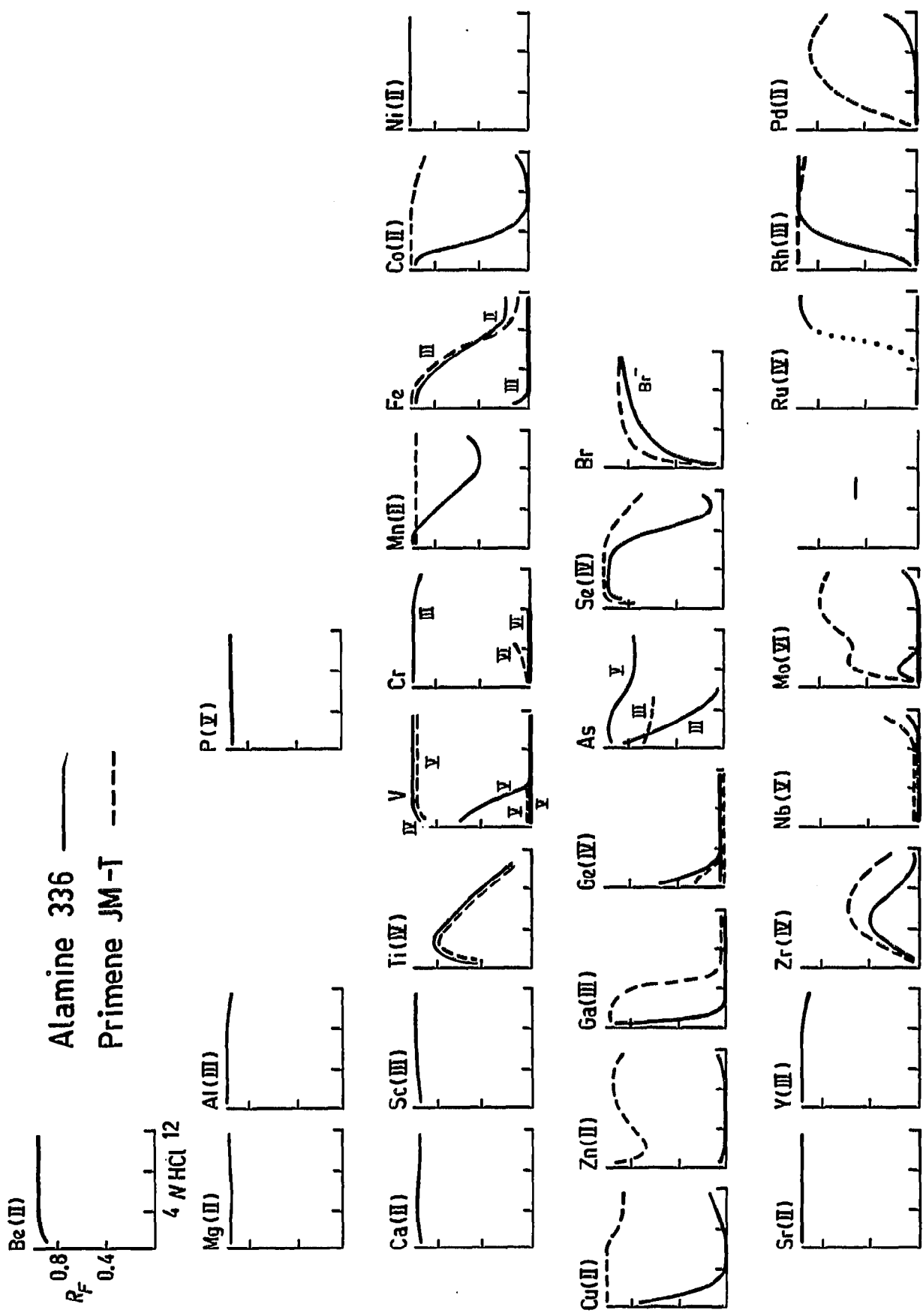
Fig. 5. R_F spectra in thin-layer chromatography for the HCl system, using silica gel impregnated with Amberlite LA-1 and untreated silica gel. Characteristics of the curves not mentioned in the text are as follows: With Amberlite LA-1 (———) steep parts of the curves often lead to elongated spots, e.g. with Fe(III) and Ga at 0.5–1.0 N HCl, with Ag at 4–7 N HCl, and with SeO$_3$$^{2-}$ and TeO$_3$$^{2-}$ at 0.1 N HCl. This phenomenon is not further defined. Al has long tailing spots (often R_F 0.3–1.0) with conc. HCl; Sr tends to tail at most HCl concentrations, especially high ones; WO$_4$$^{2-}$ has comets with 0.1–2.0 N HCl; Tl(I) has fairly long spots at most HCl concentrations; Pb has streaks with 0.1–2.0 N HCl. With silica gel only (– – –) the elongated spots at steep parts of the curves are not specifically mentioned. Sb(V) has streaks with an R_F 0.0–1.0 over the whole HCl range; Hg(I) has elongated spots above 2 N HCl; WO$_4$$^{2-}$ gives elongated spots with 0.1–4.0 N HCl.
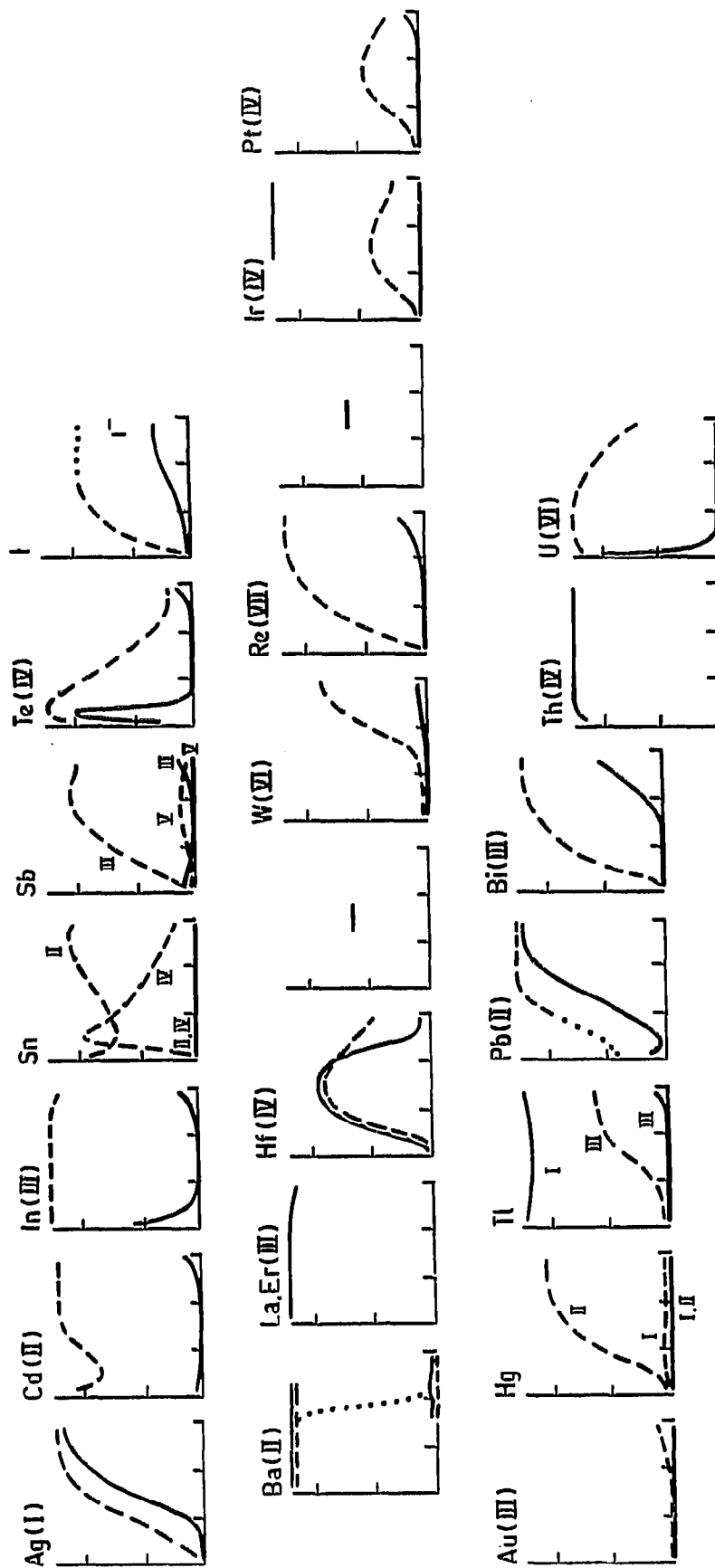
Alamine 336 ———
Primene JM-T ----

Fig. 6. R_F spectra in thin-layer chromatography using the Alamine 336·HCl and the Primene JM-T·HCl system. Apart from details given in the text, the following points may be observed. (Elongated spots at steep parts of the curves are not specified; cf. legend to Fig. 5.) With Alamine 336 (——) Al has elongated spots at 0.1 N and conc. HCl; Sr tends to tail at most HCl concentrations; WO_4^{2-} has small comets at low and weak tails at high HCl concentrations. With Primene JM-T (– – –). Ag tails excessively at 2–6 N HCl; Sb(V) has long comets, especially with 4–9 N HCl; WO_4^{2-} has comets with 0.1–2.0 N HCl; Pb has streaking spots below 6 N HCl, while part remains at the origin.

the curve at R_F 0.0 can still be found only up to 6 N HCl. A ready explanation of these phenomena is not available, particularly as the behaviour of these ions in the absence of liquid anion-exchanger is totally different (see Fig. 5).

With GeO_3^{2-}, streaks are generally observed between the two spots found at low HCl concentrations. As regards MoO_4^{2-}, it was noted that the spectra given by LEDERER AND OSSICINI[15] and SASTRI et al.[11] are recorded only down to approx. 1 N HCl. Bearing this in mind, one may conclude that the divergence between our results and those in the literature may well be less than is apparent at first sight from the curves (cf. ref. 16: MoO_4^{2-} curve in HBr).

Some of the platinum metals show interesting peculiarities:

(1) With Rh, our R_F spectra agree reasonably with those reported in the literature[11,15], but attention is called to the deviating sequence of the adsorption strength of the various exchange materials. Unlike that normally found, Amberlite SB-2 and AE-30 cellulose paper yield nearly identical R_F spectra, and clearly surpass Amberlite LA-1 in adsorption strength; the latter in its turn surprisingly only equals DE-20 cellulose paper. Furthermore, Aliquat and trilaurylamine, generally heading the list in SASTRI's experiments, consistently give high R_F values with Rh; in contrast to this it is found close to the origin with dilauryl- and hexadecylamine.

(2) In our experiments, the main portion of Ir (directly visible as a yellow spot) is always found at low R_F values, which agrees with literature data. However, a minor part of the ion, which therefore may have been overlooked by others, is often (see figures) found at the solvent front on detection with the sensitive reagent leuco-malachite green. These results were obtained with less than 24-hour-old solutions of Ir, dissolved in either 1 or 6 N HCl.

(3) In the case of Ru, we merely remark that Ru(IV), dissolved in 1 or 6 N HCl, yields very irreproducible R_F spectra in the presence of amine, especially with Primene. Using Amberlite and Alamine, at low HCl concentrations the main portion of the element is found close to the origin, while at higher HCl strengths it has R_F 1.0.

These details described for Rh, Ir and Ru may partly be due to phenomena such as hydrolysis and ageing of the solution[20]. A further discussion cannot, however, be made now, because the complicated solution chemistry of these elements would necessitate too extensive an investigation.

Finally, two aspects of mainly experimental importance are mentioned. For the chromatography of Tl(I), a saturated solution of TlCl has to be used in order to get satisfactory results, since the use of a $TlNO_3$ solution leads to severe streaking. Secondly, with a few ions oxidation–reduction phenomena are encountered. With Fe(II) and Sn(II), for instance, even under CO_2, a partial oxidation of the divalent ions is observed, especially with the latter ion. Here double spots are obtained; with Primene this occurs over the whole HCl range investigated and with Amberlite at high HCl concentrations, i.e. when the curves for Sn(II) and Sn(IV) diverge. The reverse effect is found with As(V), which shows partial reduction to As(III), while the same phenomenon is less apparent with Sb(V) (see legend to Fig. 6). As regards As(III), our curves agree with the one recorded by BAGLIANO et al.[16], but distinctly deviate from the data reported by some other authors[11,12], who always found $R_F \geqslant 0.7$. The lower R_F values found by us are not due to adsorption to the support, as shown by Fig. 5.

SEPARATIONS

In order to test the usefulness for analytical work of the thin-layer chromatographic R_F data recorded, a number of interesting qualitative separations were investigated.

Whenever possible, the mixtures were all applied as solutions of the chlorides; in all other cases, nitrates were used. The solutions generally contained from 2 to 12 μg/μl of each cation present in the mixture. The results obtained for the most interesting separations are schematically represented in Fig. 7; R_F values for the other separation procedures are recorded in the text.

R_F spectra may also be used as guides for selecting favourable conditions for quantitative (column) work*. Therefore, this kind of data has been included tentatively for some of the mixtures discussed below.

Ni–Co–Mn–Zn

The $(NH_4)_2S$ group of the classical H_2S system can easily be separated using Alamine and 3–5 N HCl as eluant. A successful separation is also possible when using a radial method. Results found with either of the two techniques and using 4.5 N HCl as eluant are shown in Fig. 7. With e.g. 3 N HCl, Mn and Co have higher R_F values, of approx. 0.9 and 0.65, respectively.

The radial method may be compared with that recently described by HASHMI et al.[21]: their elution time (2–3 min) is about equal, but our method is instrumentally simpler.

A separation of either Ni, Co or Mn (R_F 1.0 for each ion) from Zn (R_F 0.0) can best be accomplished on Amberlite or Alamine at approx. 2 N HCl.

Ni–Co–Cu–Mn–Fe(III)

This interesting separation, which has been repeatedly investigated on anion-exchange columns, may be carried out with Alamine and 3–4 N HCl. In the absence of Mn 2 N HCl is also satisfactory, while Amberlite may now be used in combination with approx. 8.5 N HCl (cf. ref. 22). The radial method yields very satisfactory results in the analysis of the 5-component mixture.

Ni can best be separated from Co or Cu using Alamine and approx. 6 N HCl, when the latter two elements both have R_F values of approx. 0.03.

Fe (R_F 0.0) can easily be separated from any of the other four elements on either Amberlite or Alamine with 2–4 N HCl.

Al–In–Ga

These 3 elements can be successfully separated using Amberlite combined with either 3 or 10 N HCl; with the latter normality the R_F values of the three ions hardly differ from those found at 3 N HCl (see Fig. 7).

A quick separation of Al—or for that matter, rare earths mixtures, Y, Sc, etc.—may be accomplished on Amberlite using approx. 5 N HCl, when both In and Ga have R_F 0.0.

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* Preliminary experiments with Adogen 464-impregnated Hyflo Supercel appear promising.
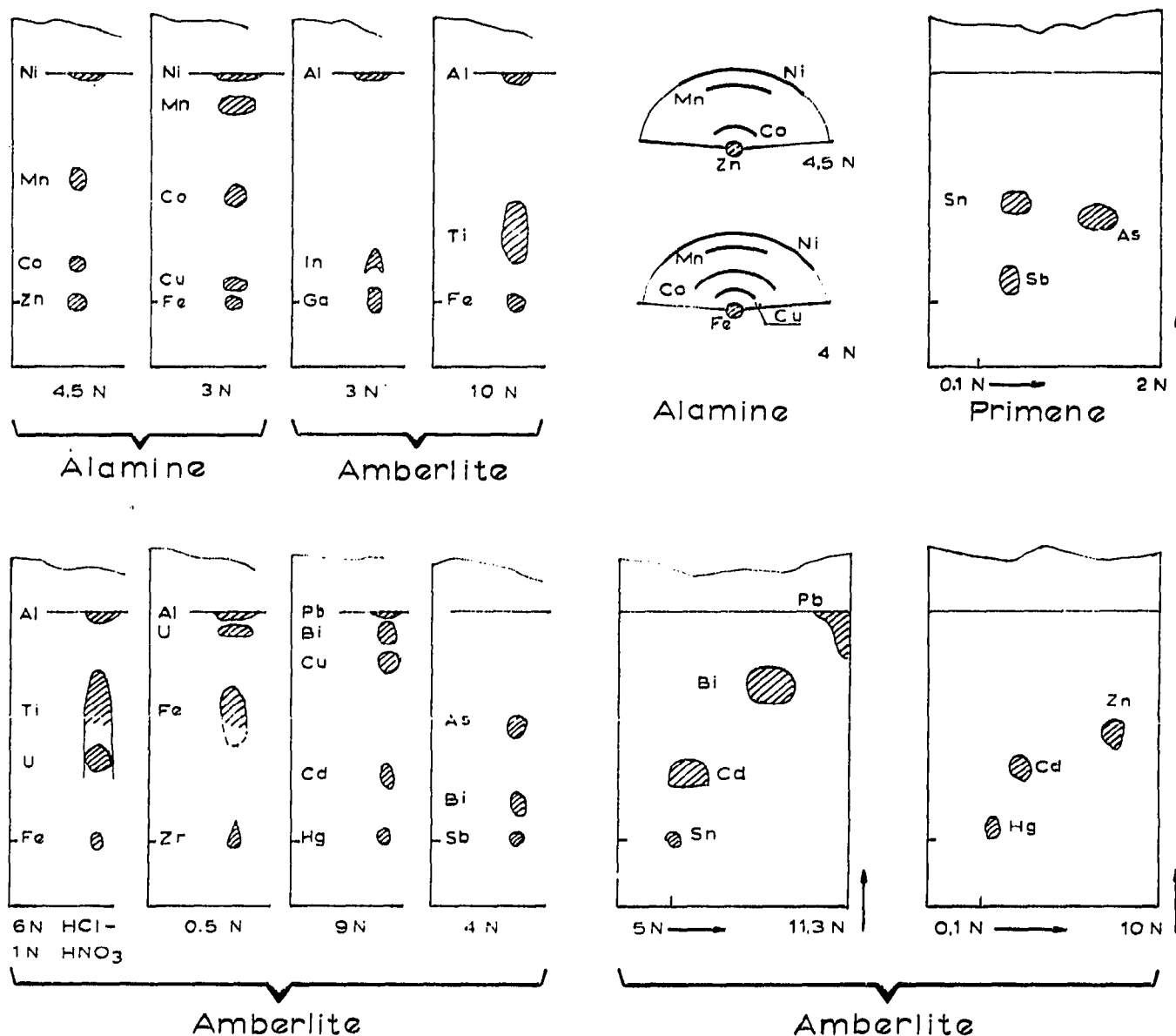
Fig. 7. Some examples of qualitative separations carried out with HCl of various normalities as eluant.

Al–Ti–U–Fe(III)

The complete separation of the NH_3 group, in classical analysis, is not easily accomplished. However, Al, Ti and Fe may be separated using Amberlite and 10 N HCl (R_F 1.0, 0.3–0.4 and 0.0, respectively), while 0.5 N HCl suffices to separate Al, U and Fe (see below). When all four elements are present, it is best to use 6 N HCl–1 N HNO_3 (1:1, v/v) as eluant. Though the spots of Ti and U now show some overlap, they are easily identified at not too extreme concentration ratios of both elements, especially as U shows up much better with 8-hydroxyquinoline than Ti.

Al–U–Fe(III)–Zr

These four elements are well separated using Amberlite and 0.5 N HCl, while

a somewhat less satisfactory separation may be accomplished using Alamine. It can be seen that Al may be replaced by other elements, such as the rare earths and Y or Sc.

Cu–Cd–Pb–Bi–Hg(II)

The complete separation of the H_2S-II group, in classical analysis, may be carried out on Amberlite-impregnated silica gel using approx. 9 N HCl as eluant. For detection either dithizone alone or H_2S gas and 8-hydroxyquinoline, suffice. This method compares favourably with that of CANIĆ et al.[23] who separated the same group on maize starch. Their technique took 2 h for a rather doubtful separation. The radial method of HASHMI et al.[21] takes less time, but Cd and Hg have nearly the same R_F values. Techniques like those of SEILER AND SEILER[24] all have the drawback of taking up to 2 h.

In the H_2S-II group, Cu can quickly be separated from Cd, Bi and Hg on Amberlite when using approx. 2 N HCl; various other separation procedures may easily be derived from Figs. 5 and 6 (see also ref. 22). With regard to the analysis of these relatively simple 3- or 4-component mixtures, paper-chromatographic techniques, such as the radial method described for Cu, Cd and Bi by BHATNAGAR et al.[25], cannot be recommended.

Pb–Bi–Sn(IV)–Cd

The components of Wood's metal cannot be separated readily all at one time in a HCl system, However, by combining the results obtained on Amberlite-impregnated layers using 5 N and conc. HCl, the mixture can be satisfactorily analysed. With the former eluant, Pb (R_F 0.9) and Bi (R_F 0.65) are well separated, while Sn and Cd both yield R_F values of 0.0–0.1. With conc. HCl, the former two ions both have R_F 1.0, but Cd (R_F 0.55) now separates from Sn, which still remains close to the origin. A reasonable result may also be acquired by using a two-dimensional procedure, as shown in Fig. 7, though it is preferable to use square (50 × 50 mm²) diapositive plates.

Zn–Cd–Hg(II)

This mixture can be separated on Amberlite with 10 N HCl as eluant, when the elliptical spots of Zn (R_F 0.49) and Cd (R_F 0.36) are practically contiguous, while Hg remains close to the origin. A better result is obtained with a two-dimensional technique, first using 0.1 N HCl and subsequently 10 N HCl.

Zn is easily separated from the other two ions with 0.1–0.5 N HCl, when it has R_F values of 0.6–0.2 on Amberlite, while both Hg and Cd yield R_F values close to 0.0.

As(III)–Sb(III)–Sn(IV)

The H_2S-I group of classical analysis does not easily yield to complete separation. The best results are obtained by two-dimensional chromatography on Primene, using 0.1 and 2.0 N HCl. Occasionally, however, some As remains at the origin when eluting with 0.1 N HCl.

As(III)–Sb(III)–Bi

A very satisfactory separation is given by elution with 4 N HCl on Amberlite-impregnated thin layers.

Miscellaneous

Various other separation procedures mainly pertaining to 2-component mixtures, appear promising from Figs. 5 and 6. Good examples include the separation of SeO_3^{2-} from TeO_3^{2-} (*cf*. ref. 26) and that of U from Th or rare earth elements, which compares favourably with the time-consuming separation of a similar mixture described by GUPTA AND MUKERJEE[27] (on the other hand, a separation combining a liquid anion-exchanger with HNO_3 as eluant is better still[28]). Lastly, separations of Hg(I) from Hg(II), Br^- from I^-, and Zr from Hf also range among the possibilities.

CONCLUSIONS

The results presented in this paper show that for most ions the various liquid and solid exchanger-treated supports behave very similarly. A number of exceptions do occur, but for the greater part these are not due to interaction between ion and exchanger. In this context, two aspects need further attention: (a) the analogous behaviour of the neutral TOPO and the other—really anionic—exchangers; and (b) the relative importance of *e.g.* anion-exchange and adsorption to the network of the exchanger, when comparing the liquid anion-exchangers and the solid resins. On the other hand, the role of the support itself and of phenomena such as hydrolysis has by now been fairly clearly established in HCl systems (refs. 15 and 16 and this paper).

Concerning the adsorption sequence previously proposed, it is shown that the (anion-)exchangers (including the solid-resin papers, TBP and TOPO) can be broadly divided into three groups of different adsorption strength. However, discrepancies do occur (*cf*. ref. 11) and a more subtle subdivision cannot easily be introduced, as is shown by the behaviour of Aliquat[1,2,10,11].

Supports impregnated with liquid anion-exchangers yield an inexpensive and easily accessible route to paper and thin-layer chromatography, which can be carried out over a wide range of HCl concentrations. Therefore, they may be preferred to supports containing solid resin or TOPO, though these come in useful in special cases[18,20]. As demonstrated in this paper, the moderately (Amberlite LA-1) and strongly (Alamine 336) adsorbing high-molecular-weight amines and substituted ammonium salts are both very useful, with some emphasis on the latter class, but Primene JM-T and similar weakly adsorbing compounds (such as TBP[18]) will be of limited importance, even with fairly strongly complexing eluants such as HCl.

The thin-layer technique—preferable on account of its short elution time—will generally be very suitable for qualitative work, as has been amply demonstrated in one of the preceding sections. Here it must be admitted that although many interesting separations are easily accomplished, other groups of elements, notably the alkaline earths and the ions of the IIIA and IVA group, are not readily separated, partly because of identical R_F values and partly due to streaking of the spots. In these cases, however, liquid anion-exchangers may still prove valuable, *e.g.* when using the nitrate system for the separation of rare earth mixtures[30, 31].

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SUMMARY

Using thin-layer chromatography on silica gel impregnated with Alamine 336, Amberlite LA-1 or Primene JM-T, the behaviour of approx. 55 ions in an HCl system has been systematically investigated. Data have also been collected on the behaviour of most ions on the non-impregnated support. When comparing the R_F spectra obtained with literature data concerning related methods, a satisfactory overall agreement is found. Moreover, for some elements tentative conclusions about the exchange mechanism are reached.

The thin-layer technique previously described has been standardized and suitable apparatus developed.

A number of successful separations are reported and in a few cases the advantages of these methods over those described in the literature are indicated.

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