CHROMATOGRAPHIC TECHNIQUES USING LIQUID ANION-EXCHANGERS

II. STRONG MONOBASIC ACID SYSTEMS*

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INTRODUCTION

In our previous paper[1] dealing with the use of high-molecular-weight amines and substituted ammonium salts in paper and thin-layer chromatography, the investigation was limited to HCl systems. The results so obtained showed the necessity to test further some of the selected liquid anion-exchangers with respect to their behaviour with other strong monobasic acids.

This paper deals with systems using HNO_3, HBr, HI, HSCN and $HClO_4$, and some conclusions are given regarding the value of the "adsorption sequence" tentatively proposed by us and the possible applicability of the systems considered here for further qualitative and quantitative work.

MATERIALS AND METHODS

For a full description of materials and methods, one is referred to ref. 1. Ions not mentioned there were also applied using solutions containing 2–8 μg cation per μl. The ions chosen for each acid system were selected with regard to their expected divergent behaviour and results already known in the literature on anion-exchange and neutral organophosphorus systems.

All high-molecular-weight amines and substituted ammonium salts were converted into the appropriate salt form by equilibrating a 0.10 (thin layer) or 0.15 (paper) molar solution in $CHCl_3$, or occasionally benzene, for 10 min in a separatory funnel with 3 vol. of approx. 2 N acid. The ammonium salts — purchased as chlorides —were converted into the desired salt form by shaking the solution in $CHCl_3$ for some minutes with a 5-fold excess of freshly precipitated Ag_2O, decanting the supernatant solution and treating the hydroxide with the acid in question.

All solutions of acids except those of HSCN were made by diluting the concentrated acid of p.a. quality to the desired normality and subsequent standardization. Concentrated HBr and HI contained only traces of Br_2 and I_2, respectively; these were not removed prior to use. This omission caused no difficulties even with concentrated hydriodic acid, because any I_2-I^- complexes formed in low concentration were tightly held by the liquid anion-exchanger-treated support (*cf.* RESULTS).

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* For the first part of this series, see ref. 1.
** This paper forms part of the work done by U. A. TH. BRINKMAN for his Ph. D. Thesis.

HSCN solutions were made by acidifying KSCN solutions of appropriate molarity with $HClO_4$ to a final acid concentration of 0.1 N (*cf.* ref. 2) and filtering off the precipitated $KClO_4$; HSCN was standardized after this treatment.

RESULTS AND DISCUSSION

HNO_3 was selected as a first choice for our present investigation, mainly because some work had already been done in this direction by CERRAI, TESTA and coworkers[3-6] and others[7,8].

Based on the results previously obtained in HCl systems[1], seven high-molecular-weight amines and substituted ammonium salts were investigated using HNO_3 as an eluant. In consequence of this work (see below), the number of liquid anion-exchangers tested with the remaining four strong monobasic acid systems was limited to five.

HNO_3 systems

Systematic investigations were carried out using 8 ions, *viz.* $UO_2(II)$, $Th(IV)$,
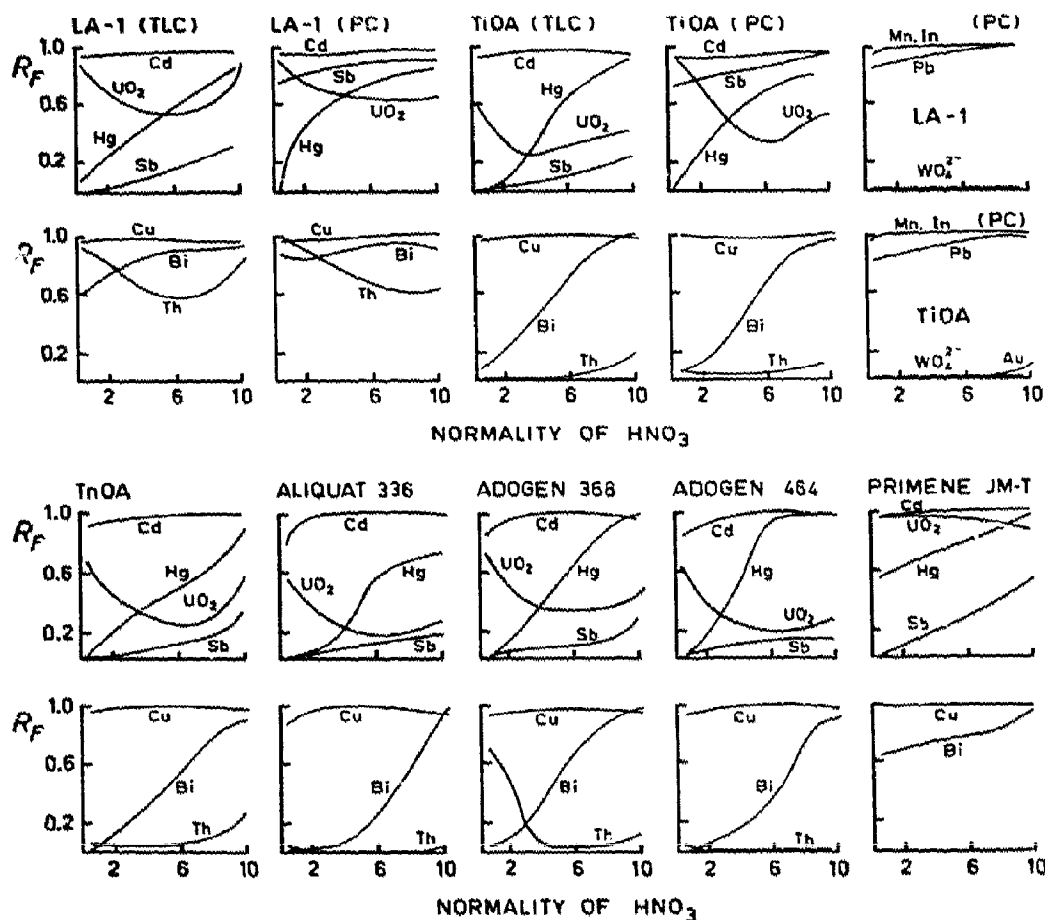

NORMALITY OF HNO₃

NORMALITY OF HNO₃

Fig. 1. R_F spectra for 12 ions using various amine-HNO_3 and quaternary ammonium nitrate systems in thin-layer (TLC) and paper (PC) chromatography; the lower set of diagrams entirely pertains to TLC. To complete the data presented in the diagrams the following is observed. Detection of UO_2 and Th was difficult with Primene JM-T; the UO_2 curve here was found in PC, and Th (omitted) most probably had an R_F of 0.9–1.0 over the whole range. Slight streaking of the spots was occasionally observed with Hg. Sb generally gave fairly long spots, while WO_4^{2-} showed weak comets attached to the main portion at R_F 0.0.

Sb(III), Cu(II), Cd(II), Bi(III) and Hg(II), with 0.5–10 N HNO$_3$ as an eluant. Incidentally, R_F curves were also recorded for some further ions, WO$_4^{2-}$, Pb(II), Mn(II), In(III) and Au(III). The corresponding data, obtained for both thin-layer and paper chromatographic experiments, are summarized in Fig. 1. Results found with both techniques for TiOA* and Amberlite LA-1 show good mutual analogy except for Sb(III). This last phenomenon was also encountered in experiments with HClO$_4$, i.e. another case where Sb has high R_F values in paper chromatography. In the HNO$_3$ system the use of chloride and nitrate solutions of Sb yielded similar results, so that the differences between paper and thin-layer chromatography cannot be explained by the presence of chloro complexes of Sb.

The data on Th and UO$_2$ correspond well with those published by CERRAI AND TESTA[3] when using TnOA. When our experimental work had been finished, SASTRI et al.[9] published R_F spectra for HNO$_3$ systems in paper chromatography using among other things Aliquat 336 and dilaurylamine. Their results also correspond favourably with those given by us; this holds for both the absence of adsorption found with Cu, Cd, Pb, Mn and In and for the more interesting curves obtained with Th, UO$_2$, Au, Bi and Hg. The data for most ions tested moreover correspond well with those given by FARIS AND BUCHANAN[10] for solid anion resins, though large discrepancies occur with Bi and Hg. On the other hand, the curves for Bi (and for most other elements) closely agree with those published by O'LAUGHLIN AND BANKS[11,12] and CERRAI AND TESTA[13] when using neutral organophosphorus compounds; with Hg, though there is less agreement.

Attention may also be called to a study by OSSICINI[14] on the adsorption of metal ions on solid anion resin paper Amberlite SB-2 using 0.5–8.0 N HNO$_3$. Her data confirm essentially those reported by us, though deviations do occur, especially with Bi.

We may conclude, therefore, that in HNO$_3$—as in HCl—systems, the chromatographic data found when using various liquid anion-exchangers are closely analogous (refs. 3, 9 and this paper). On the other hand, discrepancies between results so obtained, and those found for either solid anion resins or paper treated with neutral organophosphorus compounds, seem to be somewhat more serious than in HCl systems[1]. Secondly, as regards the "adsorption sequence" of the liquid anion-exchangers tested, Primene JM-T again has the weakest adsorption strength, while Amberlite LA-1, though being much stronger, clearly falls behind the five others, which do not show significant differences; Aliquat 336 being probably slightly stronger than the other four. Therefore, the sequence recently given for HCl systems seems to be reliable for general guidance. Minor variations occurring when going from one (acid) system to another (see also below), may be due to small experimental inconstancies.

For qualitative and quantitative separations, HNO$_3$ systems are most probably of limited value only. However, UO$_2$ and Th, Sb and Bi or Hg, some noble metals[9] or a limited number of rare earths elements[4] may be separated from each other and from many other elements. Moreover, in quantitative analysis, many ions will easily be eluted by changing the composition of the eluant to dilute HNO$_3$ or nitrate (cf. refs. 5 and 6).

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* Abbreviations: TnOA = tri-n-octylamine; TiOA = triisooctylamine; HDEHP = hydrogen di(2-ethylhexyl) phosphate.

HBr systems

Systematic investigations were carried out using the 12 ions previously selected for HCl systems[16]. Al(III), Cd(II) and Hg(II) were, however, only examined with Amberlite LA-1, where their R_F curves hardly differed from our earlier results with HCl as an eluant (R_F = 1.0, 0.0 and 0.0, respectively). Elution was done with 0.5–8.0 N HBr.

Thin-layer data for the HBr system are graphically represented in Fig. 2; paper chromatographic experiments carried out with 2 and 4 N HBr as an eluant for Cu, Zn and Pb did not show any significant discrepancies and this technique therefore was not applied further. The thin-layer data show a rather close agreement with those previously published by us for HCl systems[1, 16], though Cu is distinctly more strongly adsorbed in the bromide system, which effect is to a lesser extent apparent with Pb and Bi and seems to be reversed with Co and Fe.

Comparison of our data can best be done with those of BAGLIANO *et al.*[15], who reported R_F values of metal ions on various anion-exchange papers using 0.5–6.0 N HBr. The curves found for Cu, Cd, Pb, Bi, Hg and Fe closely resemble those given by us. Thin layers impregnated with Aliquat 336, TiOA and the Adogens have approximately the same adsorption strength as the strong base resin paper Amberlite SB-2, which clearly surpasses layers treated with Amberlite LA-1; Whatman DE-20 and AE-30 cellulose anion-exchange papers fall far behind (*cf.* ref. 1). In connection with these results, there seems to be no motive for a differentiation between adsorption in the network and ion-exchange as detailed as was given by BAGLIANO *et al.*[15], except in the case of Au.

As regards the picture outlined above for some ions in HBr systems, further reference may be made to a study by HERBER AND IRVINE[17]. Using Dowex-1, these
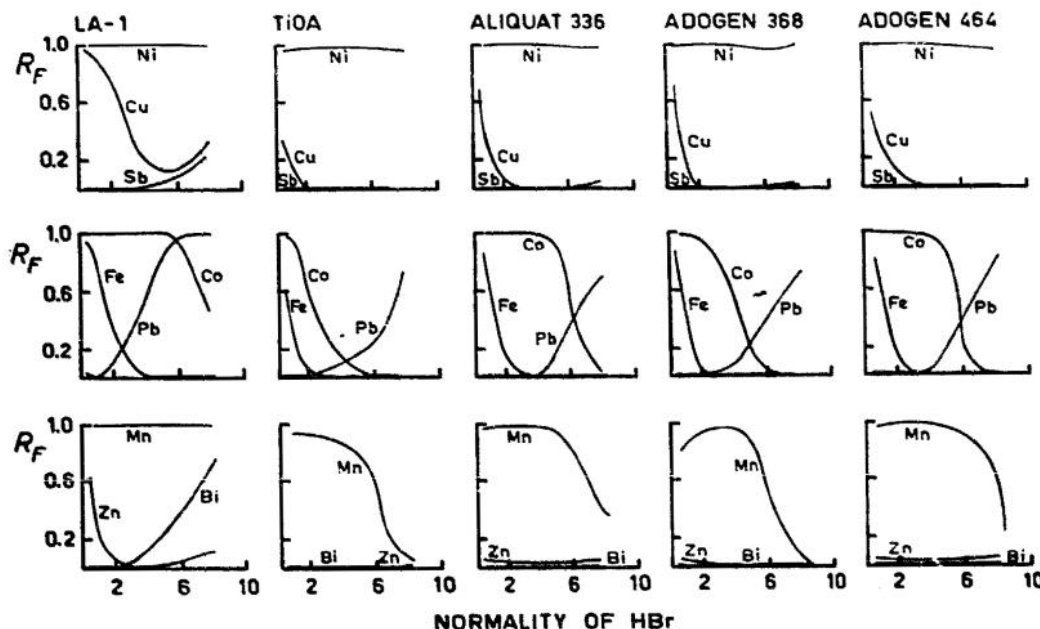

Fig. 2. R_F spectra for 9 ions using various amine·HBr and quaternary ammonium bromide systems in thin-layer chromatography. Owing to partial reduction to Fe(II) (R_F 1.0), Fe(III) showed weak comets to the solvent front. Partial reduction of Cu(II) to Cu(I) yielded tailing spots for Cu at low acid strengths.

authors found only small deviations between the behaviour of Ni, Cu, Co and Zn in HCl and HBr media, respectively.

No special conclusions concerning the adsorption sequence of the liquid anion-exchangers seem possible, TiOA and Adogen 368 being this time slightly more strongly adsorbing than Adogen 464 and Aliquat 336, with Amberlite LA-1 again clearly in the last place. As an analytical tool, the HBr systems in general will closely resemble the HCl analogues. However, higher cost, a limited concentration range and especially reduction of oxidizing ions (*e.g.* Cu^{2+} and Fe^{3+}; see legend to Fig. 2) present serious drawbacks. Apart from the last aspect use of the HBr system will not meet with any practical difficulties, making incidental application possible.

HI systems

Systematic investigations were carried out using the ions previously tested in HCl systems[16], excepting Al(III), Cd(II) and Hg(II), which still showed fairly constant R_F values of 1.0, 0.0 and 0.0, respectively, with Amberlite LA-1. Elution was generally done with 0.5–7.4 N HI, made by appropriate dilution of conc. HI p.a. However, in one instance, *viz.* with Amberlite LA-1, comparative experiments were carried out using $KI–H_2SO_4$ solutions for both equilibration and elution. The results of all thin-layer experiments have been recorded in Fig. 3. Paper chromatography, done at 2 and 4 N HI for reasons of comparison, did not show any advantage and was therefore abandoned.

As regards the experimental aspects of the use of HI solutions, some results are worth mentioning. Though the HI solutions turn their colour to brown-red on standing owing to oxidation of I^- to I_2, the thin-layer plates are only lightly coloured. Moreover, in all identification procedures involving either H_2S or NH_3, these re-
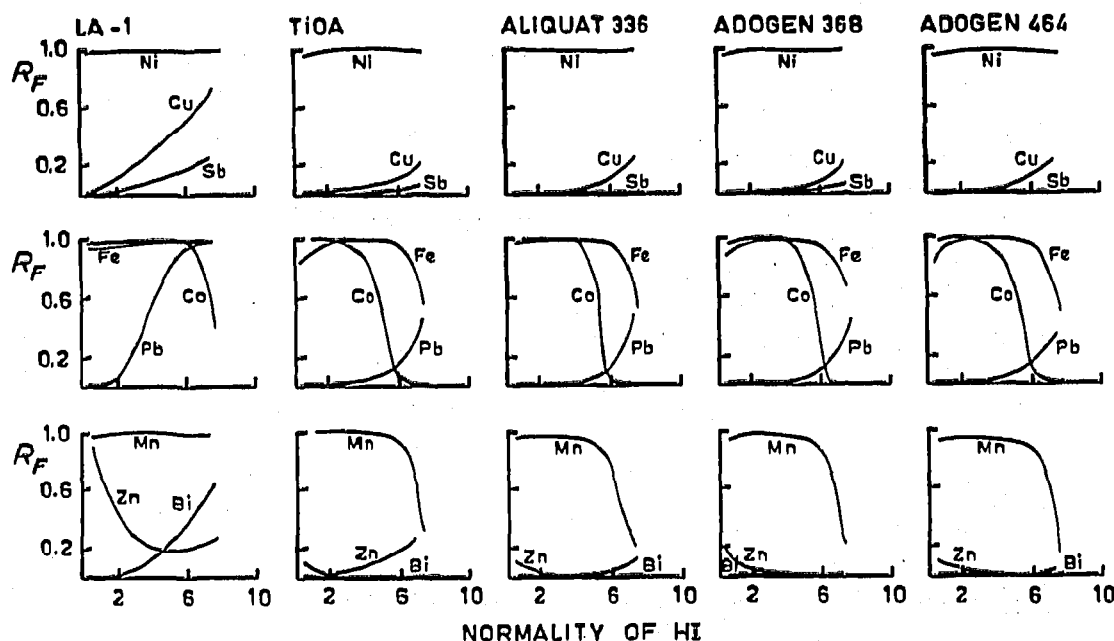

Fig. 3. R_F spectra for 9 ions using various amine·HI and quaternary ammonium iodide systems in thin-layer chromatography. The curves for Cu and Fe represent those of Cu(I) and Fe(II), respectively; at low acid strengths, the Fe(II) spots tailed weakly to the origin, reduction obviously not being complete.

ductants cause a complete disappearance of the disturbing colour. Secondly, it was observed that any I_2-I^- complexes present in the eluant are held tightly by the anion-exchanger-treated support, forming a small 2–3-mm wide zone at the lower end of the plate. When, therefore, the spots are applied a few mm higher than usual, no further precautions are necessary as regards the presence of traces of I_2 in HI. The use of the more concentrated HI solutions generally interferes to some extent with the identification procedures of the ions tested, but no insurmountable difficulties are encountered.

The spectra in Fig. 3 are generally quite analogous to those obtained with either HCl or HBr systems; good agreement also exists between the HI and the $KI-H_2SO_4$ data. The results found for Cu(II) and Fe(III) are, however, noteworthy. Here reduction to Cu(I) and Fe(II), respectively, appears to be fairly complete, which satisfactorily explains the greatly changed R_F curves.

Summarizing, we may state that generally the anion separation of iodo complexes of the elements studied—and most probably of many others—does not offer special advantages over those reported for the more convenient chloride system, while placing an upper limit of approx. 7.5 N (conc. HI) on the acid concentration which can be employed in the separations. Moreover, with both HI and HBr systems, the ions have a tendency to streak. On the other hand, the handling of the HI system appears to be relatively simple, thus encouraging further investigation, e.g., in cases where procedures using other (acid) systems are not successful.

HSCN systems

Systematic investigations were limited to six ions, Cu(II), Cd(II), Pb(II), Co(II), Mn(II) and Ag(I), but in the case of Amberlite LA-1 most ions tested with the HCl system were studied. Thin-layer experiments were carried out using NH_4SCN acidi-
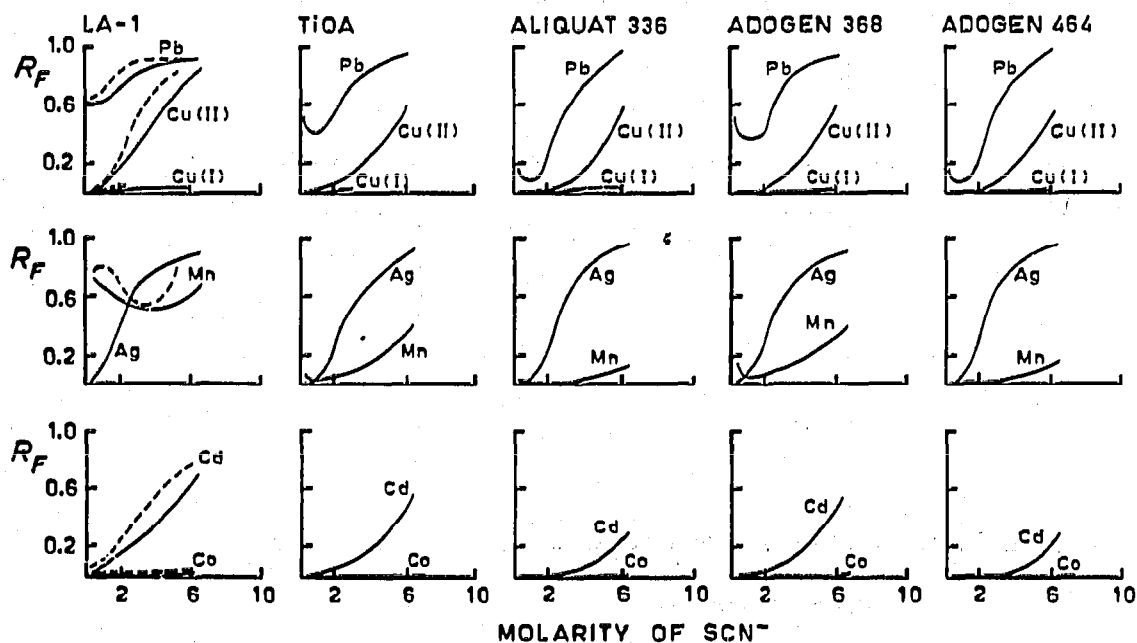

Fig. 4. R_F spectra for 6 ions using various amine·HSCN and quaternary ammonium thiocyanate systems in paper (————) and thin-layer (— — —) chromatography. At low and high thiocyanate molarities, some tailing occurred with Pb and Cu(II), respectively.

fied with HCl and KSCN–HClO$_4$ solutions of varying composition as eluants. In all cases fairly irregular solvent fronts were observed, while identification was more difficult than with e.g. HCl systems. Another slight disadvantage of the silica gel thin-layer system concerns the presence of traces of Fe(III) in the treated support, which imparts a red colour to the thin layer. Therefore, though the data obtained are decidedly reliable as regards the general outline of the curves (see below), they are less reproducible than with other acid systems. Contrary to the procedure generally followed, the main portion of the systematic work was therefore carried out using paper chromatography, where reproducible R_F values were obtained and no special difficulties were encountered.

The results of the experiments are summarized in Fig. 4. They were carried out using the KSCN–HClO$_4$ solutions described in MATERIALS AND METHODS, but incidentally a HSCN solution was made by adding an equivalent amount of HClO$_4$ to the KSCN solution and filtering off[2]. Results so obtained were qualitatively comparable to those given in Fig. 4 and therefore the latter technique was rejected, because the more concentrated HSCN solutions are subject to a fairly rapid deterioration. Some results of thin-layer experiments using Amberlite LA-1 are included in Fig. 4 and it is seen that these indeed correspond agreeably with those reported for the paper chromatographic system. Thin-layer chromatography of the ions not represented in Fig. 4 showed that Ni and Al give R_F values of 1.0, while Zn, Hg and Sb have R_F = approx. 0.0 over the whole concentration range. The curve found for Bi closely resembles that of Cd.

As regards the R_F curves found for the ions tested, attention may be called to the two clearly distinguished curves found for Cu, which must be ascribed to Cu(II) and Cu(I), the latter ion originating from a partial reduction of Cu(II). Secondly, it is emphasized that for some ions the adsorption in the HSCN system is significantly different from that found in the halogenide systems. For instance, Co, Mn and Zn are more strongly adsorbed in the thiocyanate system, while the opposite holds for Cd and Pb. Therefore, the HSCN system certainly may be of value for qualitative analytical work, e.g. when separating Co, Mn and Ni or Cd and Zn.

Further research of the HSCN system appears to be more justified than that where HBr or HI are used as eluants. The paper chromatographic technique may be used as such, but more work will have to be done on the thin-layer experiments. As regards the liquid anion-exchangers tested, the data in Fig. 4 clearly indicate that with HSCN as an eluant Aliquat 336 and Adogen 464 are somewhat stronger than Adogen 368 and TiOA.

HClO$_4$ systems

Systematic investigations were carried out using the ions UO$_2$(II), Th(IV), Cu(II), Pb(II), Hg(II), Sb(III), Zn(II), In(III) and Fe(III). Thin-layer experiments were done using 0.5–10 N HClO$_4$ as an eluant, but paper chromatography had to be limited to 0.5–8.0 N acid, because 10 N HClO$_4$ clogs the paper.

The experiments as a whole had no really satisfactory results. No difficulties were encountered with UO$_2$, Cu, Zn, Fe and In, which gave R_F values of 0.85–1.0 in all paper and thin-layer experiments; Th also yielded a fairly consistent picture of slight adsorption, though here tailing of the spots occurred in thin-layer work at

high acid strengths. The remaining three ions, however, showed a somewhat irregular behaviour (cf. Fig. 5). As was the case in HNO_3 systems, Sb gave low R_F values in thin-layer work contrasted with fairly high ones on paper. Pb yielded satisfactory R_F spectra on paper, but the thin-layer experiments were less successful. Here, and still more with Hg, long tailing spots were observed in most instances, so that the
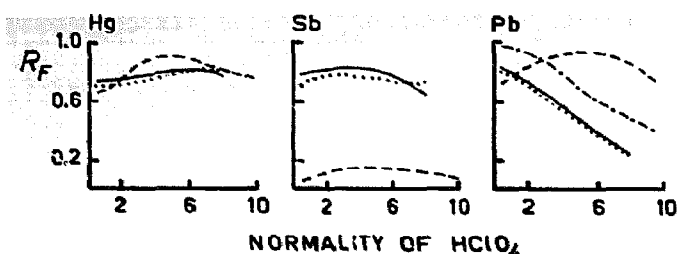

Fig. 5. R_F spectra for Hg(II), Sb(III) and Pb(II) in $HClO_4$ systems using supports treated with liquid anion-exchangers and supports merely dipped in $CHCl_3$ and dried. – – – = thin-layer and ———— = paper chromatography using Amberlite LA-1; –·–·–· = thin-layer chromatography using Adogen 464; ··· = paper chromatography using paper not treated with a liquid anion-exchanger. The curve on Adogen 464 demonstrates the divergent behaviour of Pb in thin-layer work, simultaneously showing good agreement with the paper chromatographic curves.

R_F values reported are not too significant. For that matter, it was observed that especially on paper, where the most reliable results were obtained, hardly any R_F differences were noted between papers treated with each of the five anion-exchangers tested and paper not treated with anion-exchanger, but merely dipped in $CHCl_3$ and dried. Obviously, the role of the basic exchangers generally is negligible here; i.e., the fairly complete absence of complex formation in the $HClO_4$ system precludes the possibility of anion-exchange playing an active part. Other factors will now determine the R_F picture, sometimes giving rise to unexpected (and badly defined) curves.

In this context, a tentative comparison may be made with the results of O'LAUGHLIN AND BANKS[11,12] who used 0.5 and 3.0 N $HClO_4$ only for most ions. With the notable exception of UO_2, which had fairly low R_F values in sharp contrast to the complete absence of adsorption found by us, their paper chromatographic data reasonably correspond with those recorded by us. However, we must still conclude that as yet liquid anion-exchanger·$HClO_4$ systems appear to be rather unsuccessful in thin-layer and paper chromatography. To a certain extent, this result parallels that of O'LAUGHLIN AND BANKS, who obtained some striking discrepancies when investigating various neutral organophosphorus compounds.

CONCLUSION

The results presented in our recent papers show what can be accomplished in the field of chromatography when using supports impregnated with liquid anion-exchangers and eluting with various strong monobasic acids.

It has been shown that the great majority of the liquid anion-exchangers tested gives satisfactory results both in paper and thin-layer chromatography, irrespective of the acid system used. The adsorption sequence previously given is moreover useful for general guidance, at least for the strong monobasic acid systems tested. The sharp changes in R_F values noted by SASTRI et al.[9] when comparing

tertiary and quaternary basic extractants, are distinctly absent from our work. Technical-grade products may be recommended, though some purification will be necessary when contaminants mar the identification procedures at the solvent front, as was found *e.g.* with Primene JM-T in the HNO_3 system. For the rest, practical aspects such as quality of the impregnated support and short elution time will determine the ultimate choice. In this connection, both the favourable results generally obtained in thin-layer experiments and the practical advantages with regard to the solid resin-impregnated supports (*cf.* ref. 1) may be once more emphasized.

Secondly, as regards the acid system(s) to be recommended, preference must be distinctly given to the HCl system, this being more convenient than both the HBr and HI system, which generally gave comparable results. On the other hand, HSCN may be recommended for further research, though it has some practical disadvantages (see foregoing section). Moreover, it is feared that a rather large number of elements will be held at or close to the origin owing to strong complexation with SCN^-*. Lastly, HNO_3 must be clearly preferred to $HClO_4$ when selecting a system with comparatively low adsorption; HNO_3 will also be a good choice in problems concerning rare earth separations[4].

Therefore, liquid anion-exchangers and acid systems having been fairly thoroughly investigated, a few selected combinations may now be tested for a large number of cations. Work in this direction is in progress now and has already shown that the HCl system is indeed advantageous for primary investigation. A subsequent paper[19] will deal more systematically with this aspect and some interesting qualitative separations will be recorded.

Next, the tentative interpretation of the R_F curves previously given[1] is briefly considered again. As regards the HCl system, the data in ref. 1—especially in combination with those on the notable absence of adsorption found for supports merely dipped in $CHCl_3$ and dried—clearly point to the role of the basic extractants as anion-exchangers. This theory is supported on broad lines by our present work, *viz.* by the good mutual analogy between the data on the HCl, HBr and HI systems, which is presumably caused by the opposing action of the general increase of complex formation and competition of excess ligand, when increasing the ligand size, *i.e.* when going from Cl^- to I^-. The correspondence between our data and those reported in the literature on solid anion-exchangers points in the same direction. Strong adsorption (*i.e.* complexation) in the HSCN system fits onto the picture and the same holds for the HNO_3 system, where adsorption, though being generally low, is found with UO_2 and Th, both known to form negatively charged nitrato complexes. Lastly, the correspondence between data on impregnated and untreated supports in the $HClO_4$ system, where generally high R_F values are found, may be mentioned.

On the other hand, several important aspects need further investigation. Among these range: (1) The composition of the species involved in the ion-exchange process, especially that of the complex metal anions. (2) The factor(s) governing the desorption of the adsorbed complex metal anions, *e.g.* competition of excess ligand, formation of higher charged negative ions and formation of undissociated complex metal acids. (3) Various points such as the discrepancy between the Sb curves in

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* When preparing this manuscript, a paper[18] came to our notice which briefly summarizes results obtained with SCN^- systems for many ions. Agreement with our data is good, and most of the ions having interesting R_F curves with HSCN as an eluant are included in our present work.

HNO$_3$ and HClO$_4$ systems when using either paper or silica gel as support; the adsorption found for Bi and Hg in the HNO$_3$ system, which does not correspond too well with some of the literature data; and the adsorption found for Pb in the HClO$_4$ system. In these and similar cases the influence of hydrolysis and precipitation cannot simply be neglected.

When trying to solve some of the problems outlined, comparative experiments using supports treated with cation-exchangers, anion-exchangers and neutral supports[20,21] may be enlightening, i.e. the use of liquid cation-exchangers such as HDEHP and the stronger acidic dinonylnaphthalene sulphonic acid will be valuable. In a preliminary study some interesting observations regarding the role of the anion in the case of supports treated with liquid cation-exchangers have been made by us and it is hoped that these investigations will be continued shortly. Involvement of these cation-exchangers is also interesting because excellent results have already been achieved when using them in the field of e.g. rare earth[6] and alkaline earth[21] separations. Therefore, a more thorough investigation of these acidic extractants in chromatography, especially for the more commonly encountered ions, is certainly justified.

ACKNOWLEDGEMENTS

SUMMARY

Paper and thin-layer chromatography—which generally give analogous results—have been carried out in HNO$_3$, HBr, HI, HSCN and HClO$_4$ systems, using supports impregnated with high-molecular-weight amines and substituted ammonium salts. Based on results previously obtained in the HCl system, 5–7 liquid anion-exchangers were investigated, using approx. 10 cations for each acid system.

The HBr and HI systems generally give results comparable to those found with HCl as an eluant. A more divergent picture is shown by HSCN, with which eluant it is preferable to use paper chromatography for the time being. The HNO$_3$ system shows fairly low adsorption for most ions, but some interesting applications are outlined. Results with HClO$_4$, on the other hand, are not particularly successful. The use of HI and HBr solutions containing some free I$_2$ and Br$_2$, respectively, has no unfavourable effects.

The R_F spectra in the HBr and HNO$_3$ systems show good agreement with literature data on solid anion-exchangers. Most curves may be explained assuming an anion-exchange mechanism, adsorption to the support being important incidentally.

The adsorption sequence previously reported for the liquid anion-exchangers appears to be reliable for general guidance.

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