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## REVERSED-PHASE EXTRACTION CHROMATOGRAPHY USING SOLUTIONS OF NITRIC ACID AS ELUANTS

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### SUMMARY

Approximately 40 ions have been chromatographed on thin layers of silica gel impregnated with Alamine 336-S, Alamine 336-S oxide, tri-*n*-octylarsine oxide, tri-*n*-octylphosphine oxide or tri-*n*-butyl phosphate, and on non-impregnated silica gel. Solutions of 0.2–15 *N* HNO<sub>3</sub> are used as eluants. *R<sub>F</sub>* spectra and a number of separations are reported. The ions are classified into four groups according to their chromatographic behaviour, which is explained on the basis of anion exchange, solvation, hydrolysis and interaction with the support.

Data on the extraction of HNO<sub>3</sub> and the co-extraction of water are reported. The behaviour of Alamine oxide and tri-*n*-octylarsine oxide parallels that of high-molecular-weight amines: extraction proceeds through anion exchange. Nitric acid taken up in excess of the stoichiometric amount is mainly present in the organic phase as part of the ion [O<sub>2</sub>NO...HONO<sub>2</sub>]<sup>-</sup>. On the other hand, with tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butyl phosphate (TBP), extraction proceeds through solvation; TOPO·HNO<sub>3</sub>, TOPO·2HNO<sub>3</sub> and TBP·HNO<sub>3</sub> are the species present in the organic extracts.

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### INTRODUCTION

In the past decade, reversed-phase extraction chromatography on paper and thin layers impregnated with liquid anion-exchangers and neutral organophosphorus compounds has become a powerful method of analysis<sup>1,2</sup>. More recently, the use of extractants such as oxides of tertiary alkylamines and alkylarsines has also been described<sup>3,4</sup>. Solutions of monobasic strong acids and their salts are chiefly used as eluants. However, literature data on nitric acid are comparatively sparse. Therefore, in the present paper, we report on thin-layer chromatography in HNO<sub>3</sub> systems. Five extractants, which represent the various classes of compounds mentioned above, have been selected to impregnate silica gel and cellulose thin layers. The mechanism of extraction of HNO<sub>3</sub> by these extractants is also discussed.

### MATERIALS AND METHODS

#### *Materials*

Alamine 336-S (General Mills, Kankakee, Ill., U.S.A.), a pale yellow liquid, is a special quality (99–100%) mixture of tertiary amines with alkyl groups that

consist of  $C_8$ - $C_{10}$  straight chains; its mean molecular weight is 392. Tri-*n*-octylphosphine oxide (TOPO; K and K, Plainview, N.Y., U.S.A.) is a white crystalline solid with a molecular weight of 387 and a melting-point of 51-52°. Tri-*n*-butyl phosphate (TBP; BDH, Poole, Dorset, Great Britain) is a colourless liquid with a molecular weight of 266. These three commercially available products contain only a negligible (<0.3%) amount of acidic contaminants and are used as received.

Alamine oxide (AlamO) is prepared<sup>3</sup> by the oxidation of Alamine with  $H_2O_2$ . The synthesis of tri-*n*-octylarsine oxide (TOAsO)<sup>3,5</sup> involves the preparation of tri-*n*-octylarsine from *n*-octylmagnesium bromide and  $AsCl_3$ , and its subsequent oxidation with  $H_2O_2$ . The impure oxide is crystallised from *n*-hexane and treated with absolute ethanol. After rigorous drying, the product has a melting-point of 68-69°.

### *Extraction of HNO<sub>3</sub>*

The extractant (15 ml of a 0.1 *M* solution) in  $CHCl_3$  or toluene is shaken with an equal volume of an aqueous  $HNO_3$  solution of the required normality. The shaking time is 10 min, which is ample for equilibrium to be reached. After separation of the phases, an aliquot of the organic phase is diluted with 70 ml of ethanol and titrated with 0.1 *N* NaOH. The end-point is determined potentiometrically. The water content of the organic extracts is determined by Karl Fischer titration.

Infrared spectra for the region 700-4000  $cm^{-1}$  were recorded on a Grubb-Parsons Spectrometer, Type MK2 Cells with  $AgCl$  windows were used, because  $KBr$  and  $NaCl$  windows are attacked by  $HNO_3$ -containing extracts. Generally, solutions of the extractants in toluene were measured. As this diluent shows several strong absorption peaks in the spectral range investigated, a number of parallel experiments were performed using solutions in  $CCl_4$  and thin films of the toluene extract after evaporation of the diluent. The three sets of measurements yielded closely analogous results.

NMR spectra of TOAsO and TOAsO- $HNO_3$  extracts in  $CCl_4$  were measured on a Varian A-60 Spectrometer.

### *Chromatography*

Solutions of the extractants of concentration 0.1 *M* in  $CHCl_3$ , equilibrated with aqueous 2 *N*  $HNO_3$ , are thoroughly mixed with silica gel (Type DO, Fluka, Buchs, SG, Switzerland, ratio  $SiO_2:CHCl_3$  is 1:6, w/v). When cellulose (Avicel TG 104; Macherey and Nagel, Düren, G.F.R.) is used instead of silica gel, the cellulose: $CHCl_3$  mixing ratio is 1:4 (w/v). Chromatoplates are prepared by dipping microscope slides into the resulting suspension. After evaporation of the  $CHCl_3$ , a series of scores is made in the impregnated support; six chromatograms can then be run on a single plate. The sample solutions contain 1-10 mg of ion per millilitre and are acidified with  $HNO_3$  as far as necessary in order to prevent hydrolysis. With the metal ions, nitrates are selected as salts in all instances.

Ascending chromatography is carried out in Perspex or Hellendahl staining jars (3-cm run). Solutions of 0.2-15 *N*  $HNO_3$  are used as mobile phases. Details of the experimental technique, the procedures for rendering spots visible and the apparatus required, have been described elsewhere<sup>6,7</sup>.

## RESULTS AND DISCUSSION

*Extraction of HNO<sub>3</sub>*

*AlamO and TOAsO.* The acid extraction curves of AlamO and TOAsO, which are shown in Fig. 1, are very similar. Nitric acid is readily extracted from dilute aqueous solutions and a ratio  $(\text{HNO}_3/\text{extr.})_{\text{org.}} = 1:1$  is reached at  $c_{\text{HNO}_3} < 0.3 \text{ N}$ . Data for a tertiary amine, *viz.* Alamine, are included in order to facilitate discussion.

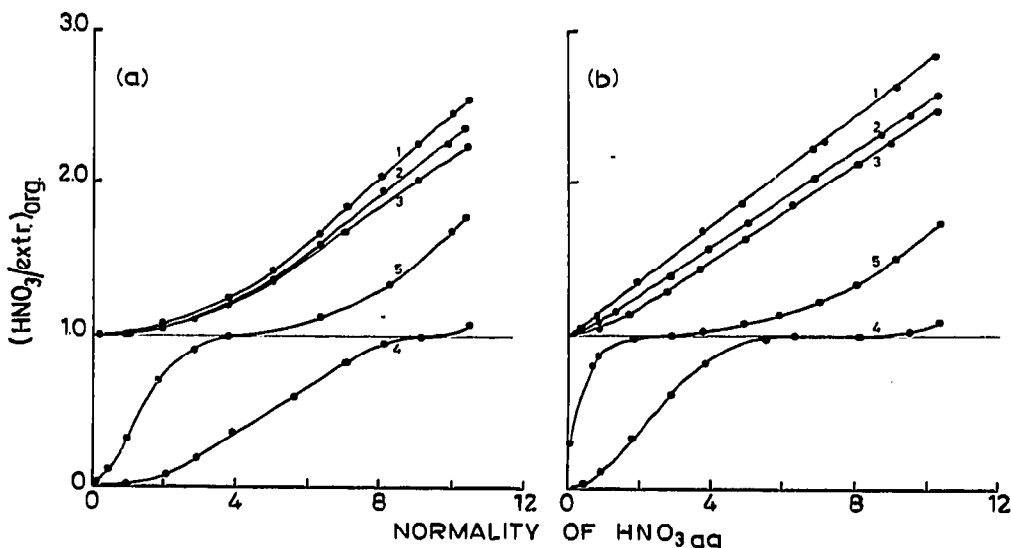


Fig. 1. Extraction of HNO<sub>3</sub> by 0.1 M solutions of various extractants in (a) chloroform and (b) toluene. Extractants Alamine (1); AlamO (2); TOAsO (3); TBP (4); TOPO (5). The data have been corrected for the uptake of HNO<sub>3</sub> by the diluent.

The IR spectra of the simple nitrates of AlamO and TOAsO are closely analogous (see Table I) and can be interpreted with the aid of literature data<sup>8,9</sup>. Nitrate ions show characteristic absorption peaks at 720 and 833 cm<sup>-1</sup>. In our spectra, a possible band at 720 cm<sup>-1</sup> is obscured by the (CH<sub>2</sub>)<sub>n</sub> rocking vibration of the long aliphatic carbon chains. The medium strong, sharp peak found at 823–825 cm<sup>-1</sup>, and the absence of absorptions at *ca.* 935 and 1650 cm<sup>-1</sup> due to molecular HNO<sub>3</sub>, both indicate that nitrate ions only are present in the organic extracts. Hydrogen bonding of these ions to the bulky organic cation is indicated<sup>10,11</sup> by the peak at 1020 cm<sup>-1</sup> and the occurrence of a doublet at *ca.* 1300 and 1390 cm<sup>-1</sup>, a single peak at 1390 cm<sup>-1</sup> being characteristic for the free nitrate ion.

Solutions of high-molecular-weight amines take up nitric acid in excess of the amount necessary for the stoichiometric neutralization of the free base. For the uptake of excess acid, an empirical relationship has repeatedly been confirmed:

$$[\text{HNO}_3]_{\text{excess}} = Q_{12} \cdot [\text{amine}] \cdot [\text{HNO}_3]_{\text{aq.}} \quad (1)$$

with  $Q_{12}$  having values of *e.g.* 0.16–0.18 for tertiary amines and 0.10–0.14 for secondary amines (ref. 12, p. 767). The data in Fig. 1 show that an excess of nitric acid

TABLE I

CHARACTERISTIC IR DATA FOR EXTRACTANTS AND THEIR NITRIC ACID SALTS (ADDUCTS)

Compound	IR frequency (cm <sup>-1</sup> )					
	$\nu_{CN}$ or $\nu_{XO}$ *	$\nu_{2,ONO_2}$	$\nu_{4,ONO_2}$	$\nu_{2,NO_3^-}$	$\nu_{3,NO_3^-}$	
Alamine	1095	—	—	—	—	
Alamine·HNO <sub>3</sub>	**	—	—	824	1280	1390
Alamine·2HNO <sub>3</sub>	**	938	1656	823	1285–1305	1390
AlamO	933	—	—	—	—	—
AlamO·HNO <sub>3</sub>	***	—	—	823	1280	1414
AlamO·2HNO <sub>3</sub>	***	937	1650	824	1304	1390
TOAsO	898	—	—	—	—	—
TOAsO·HNO <sub>3</sub>	760	—	—	825	1310	1418
TOAsO·2HNO <sub>3</sub>	752	936	1658	823	1275–1325	1418
TOPO	1170	—	—	—	—	—
TOPO·HNO <sub>3</sub>	1085	946	1626	—	1272	1400
TOPO·1.5HNO <sub>3</sub>	1085	939	1652	—	1298	1400
TBP	1272	—	—	—	—	—
TBP·HNO <sub>3</sub>	1203	940	1634	—	1302	1389

\* X=N, P or As.

\*\* Peak not observed, perhaps hidden under 1020 cm<sup>-1</sup> absorption of nitrate.\*\*\* NO stretching vibration of AlamO is weak and broad. With tri-*n*-hexylamine oxide, which shows a strong absorption peak at 949 cm<sup>-1</sup>, no shift occurs on salt formation with HNO<sub>3</sub>.

is also taken up by arsine and amine oxides. Eqn. 1 holds for both extractants; as regards TOAsO, this is contrary to the findings of Linder *et al.*<sup>13</sup>, who reported a plateau in the acid loading curve at (HNO<sub>3</sub>:TOAsO)<sub>org.</sub> = ca. 1.5:1.  $Q_{12(\text{toluene})}$  is calculated as 0.15 for AlamO and 0.14 for TOAsO, compared with a value of 0.18 for Alamine. When toluene is substituted by CHCl<sub>3</sub>, the extraction of excess HNO<sub>3</sub> decreases, and a linear relationship between [HNO<sub>3</sub>]<sub>excess</sub> and [HNO<sub>3</sub>]<sub>aq.</sub> is observed at high aqueous acid concentrations only.

The IR spectra of solutions of all three extractants containing an excess of HNO<sub>3</sub> show peaks at 1650–1660 and 936–938 cm<sup>-1</sup> in addition to those already noted above. These are due to the presence of molecular nitric acid, which is present<sup>10</sup> as part of the ion [O<sub>2</sub>NO...HONO<sub>2</sub>]<sup>-</sup>.

The amount of water co-extracted with HNO<sub>3</sub> depends on the amount of acid transferred to the organic phase (Fig. 2). In solutions of AlamOH<sup>+</sup>NO<sub>3</sub><sup>-</sup> and of AlamineH<sup>+</sup>NO<sub>3</sub><sup>-</sup>, water is present in an amount too low to correspond to a definite stoichiometry and hydrates the nitrate ion. When the ratio (HNO<sub>3</sub>: extractant)<sub>org.</sub> surpasses a value of 1:1, part of this water is replaced by molecular HNO<sub>3</sub>. The water uptake decreases and passes a minimum at (HNO<sub>3</sub>: extractant)<sub>org.</sub> = ca. 1.5:1. The subsequent increase in the water content at high aqueous acid concentrations has been ascribed<sup>14</sup> to the extraction of the hydrated dimer (HNO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O into toluene, which is enhanced by the presence of the nitrate salts of the extractants.

The co-extraction of water in the TOAsO–HNO<sub>3</sub> system, as determined

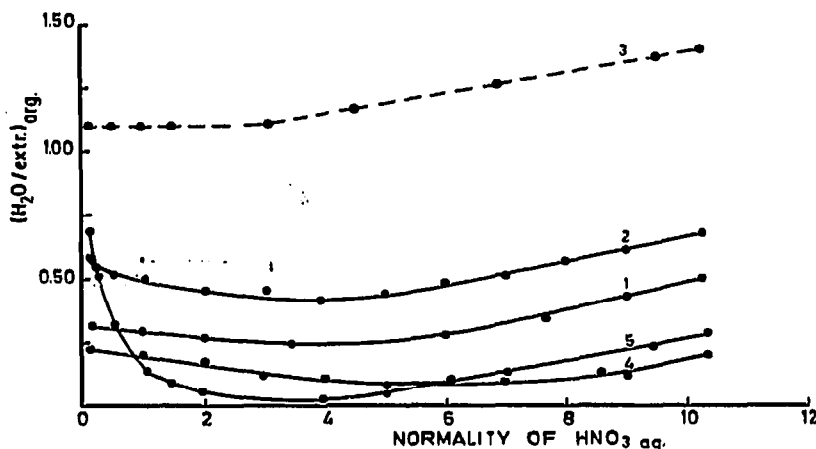


Fig. 2. Co-extraction of water from aqueous 0.1–10.5 *N* HNO<sub>3</sub> solutions by 0.1 *M* solutions of Alamine (1), AlamO (2), TOAsO (3, also see text), TBP (4) and TOPO (5) in toluene. All data have been corrected for the uptake of water by toluene. The ratio (H<sub>2</sub>O:extractant) for water-saturated, 0.1 *M* solutions of the extractants in toluene is: Alamine, < 0.05; AlamO, 2.5; TOAsO, 2.1; TBP, 0.2; TOPO, 0.8.

by Karl Fischer titration, shows a different pattern, *viz.* the ratio (H<sub>2</sub>O:TOAsO)<sub>org.</sub> apparently never falls below unity (Fig. 2; ref. 12). However, in IR spectra of TOAsO–HNO<sub>3</sub> extracts, absorption peaks attributable to water are absent or, at best, very weak. Moreover, the NMR spectra of TOAsO, equilibrated with either water or aqueous HNO<sub>3</sub> solutions, invariably indicate the presence of a total number of non-hydrocarbon protons approximately two less than that expected from titration of the acid and water content of the organic phases. These diverging results are due to the fact that Karl Fischer titration yields too high results, owing to the (probably quantitative) formation<sup>15</sup> of the adduct TOAsO·I<sub>2</sub> in the reaction mixture. In consequence, the values of (H<sub>2</sub>O:extractant) reported for TOAsO in Fig. 2 must be decreased by approximately one.

In summary, the mechanisms of extraction of HNO<sub>3</sub> by AlamO and TOAsO are closely analogous, and can be formulated as:



and



For the sake of simplicity, in eqns. 2–5, water of hydration has been omitted (also see the legend of Fig. 2).

*TOPO and TBP.* The acid extraction curves for TOPO and TBP are shown in Fig. 1. Both compounds form a 1:1 adduct with nitric acid, although the formation is complete at higher aqueous acid concentrations than for Alamine, AlamO and TOAsO. The extraction of HNO<sub>3</sub> by TBP has been extensively studied (ref.

12, p. 669); therefore, in the discussion given below, attention is mainly directed at the TOPO-HNO<sub>3</sub> system.

The IR data in Table I show peaks at 1626 (1634) and 946 (940) cm<sup>-1</sup> for TOPO(TBP)-HNO<sub>3</sub>; this clearly demonstrates the presence of molecular nitric acid. A peak at *ca.* 825 cm<sup>-1</sup>, characteristic for the nitrate ion, is completely absent. This is according to expectations: in non-polar solvents such as toluene and CCl<sub>4</sub><sup>16</sup>, NO<sub>3</sub><sup>-</sup> is a better competitor for the proton than is TOPO, and the latter can coordinate only with the resulting molecular acid. In other words, the rather large shift in the P-O valence vibration of 85 cm<sup>-1</sup> on adduct formation of TOPO with HNO<sub>3</sub> cannot be considered to be proof of an ion-pair structure, as was assumed by Zingaro and White<sup>17</sup>. The data in Figs. 1b and 2 indicate that the adduct TOPO·HNO<sub>3</sub> is essentially non-hydrated. With TBP, a qualitatively similar picture emerges, although the extractant itself is much less hydrated than is TOPO. Hence, the extraction of HNO<sub>3</sub> by TOPO, as well as by TBP<sup>9</sup>, can be formulated as a solvation process:



Solutions of TOPO·HNO<sub>3</sub> readily extract an excess of nitric acid, although to a lesser extent than do AlamO and TOAsO. The suggestion<sup>14</sup> that the excess of acid simply dissolves in the organic diluent as (HNO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O seems to be incorrect in this instance, as solutions of TBP·HNO<sub>3</sub>, which may be expected to have approximately the same polarity as have solutions of TOPO·HNO<sub>3</sub>, hardly extract any excess acid up to 10 N HNO<sub>3</sub> (Fig. 1). Alternatively, Conocchioli<sup>16</sup> has reported data that lend support to the idea of the existence of a TOPO·2HNO<sub>3</sub> complex; that is, extraction proceeds according to:



Indeed, we find a constant value of  $(1.80 \pm 0.05) \times 10^{-3}$  (mole/l)<sup>-2</sup> for the formation constant

$$K_{12} = \frac{[\text{TOPO} \cdot 2\text{HNO}_3]}{[\text{TOPO} \cdot \text{HNO}_3] [\text{H}^+] [\text{NO}_3^-] \cdot \gamma_{\pm}^2} \quad (8)$$

up to 8.5 N HNO<sub>3</sub>; the complex is probably hydrated (Fig. 2). Our results are in good agreement with the findings of Goffart and Duyckaerts<sup>18</sup>, who reported  $K_{12} = (2.9 \pm 0.3) \times 10^{-3}$  (mole/l)<sup>-2</sup> for the formation of TBPO·2HNO<sub>3</sub> in benzene.

### Chromatography

$R_F$  versus HNO<sub>3</sub> normality spectra are presented in Fig. 3; all data pertain to chromatography on supports impregnated with equilibrated extractants. Omitting the equilibration step does not lead to noticeable changes in the  $R_F$  values. However, with dilute (<1 N) HNO<sub>3</sub> solutions, conversion of the extractants, notably Alamine, AlamO and TOAsO, into their nitrate salts during development significantly decreases the acidity of the mobile phase. Besides an increase in the time of run, this causes the occurrence of an acid-free zone, and hence a second front. Some ions that have  $R_F = 1.0$  in Fig. 3 tend to move with this front.

In order to facilitate the subsequent discussion, the ions have been classified into four groups, termed A-D in Table II.

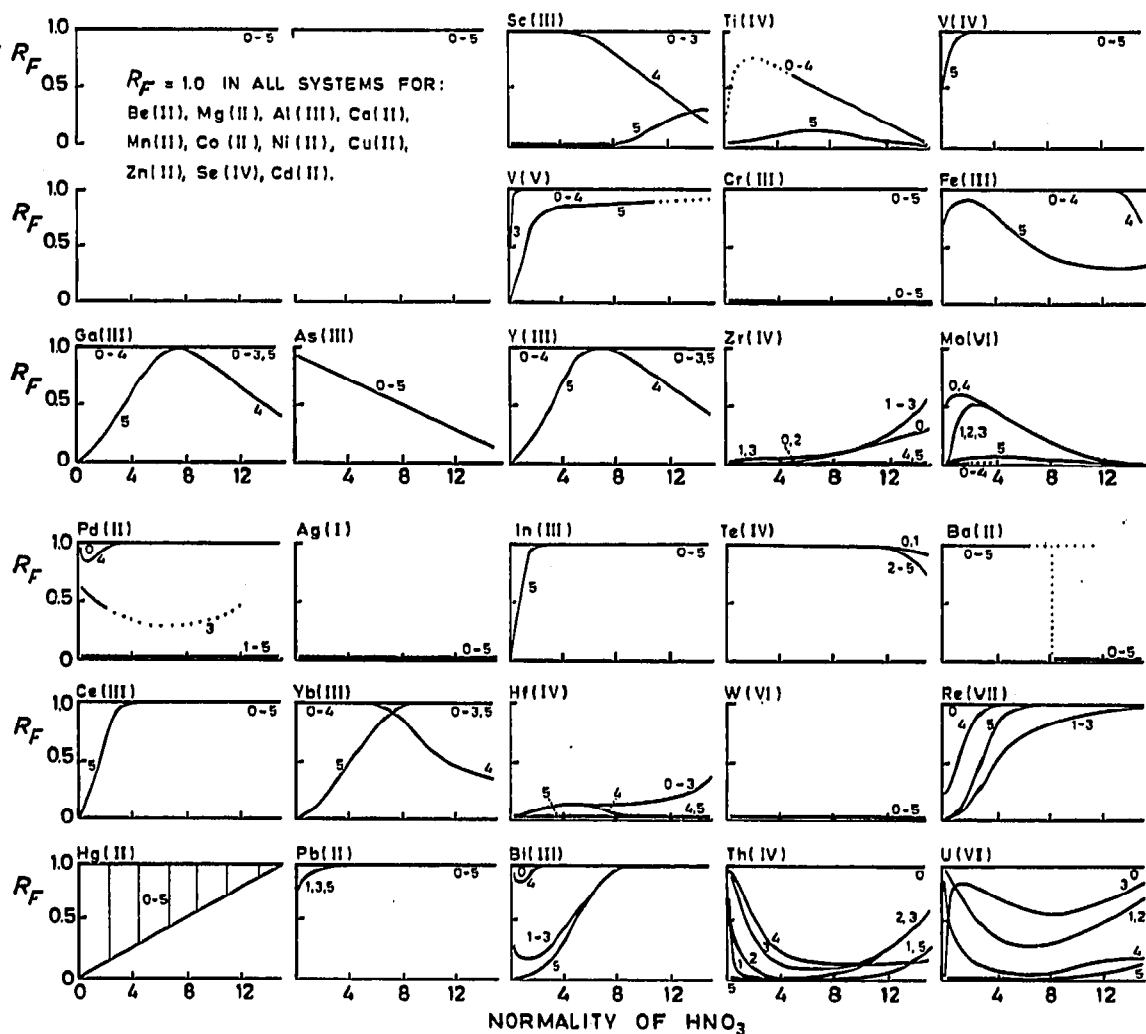


Fig. 3.  $R_F$  versus  $\text{HNO}_3$  normality spectra in thin-layer chromatography, using silica gel impregnated with Alamine (1), AlamO (2), TOAsO (3), TBP (4) or TOPO (5), and non-impregnated silica gel (0). Diffuse spots are indicated by dots.

**Group A;  $R_F \geq 0.8$  in all systems.** The ions in this group show high  $R_F$  values in all systems over the whole  $\text{HNO}_3$  concentration range studied. These results agree with literature data for chromatography on paper impregnated with various liquid anion exchangers<sup>19</sup> or TOPO<sup>20</sup>, and, although somewhat less satisfactorily (Pb and Cd), with data obtained by Ossicini<sup>21</sup> in a study of the sorption of ions from aqueous  $\text{HNO}_3$  on paper impregnated with an anion-exchange resin. Therefore, we may conclude that the ions in question form neither anionic metal-nitrato complexes nor easily solvated metal nitrates to an appreciable extent. Moreover, phenomena such as interaction with the support and hydrolysis appear to be absent.

TABLE II  
PROVISIONAL CLASSIFICATION OF IONS IN EXTRACTANT-HNO<sub>3</sub> SYSTEMS

Group A	Group B	Group C	Group D
Be, Mg, Al, Ca, Mn, Co, Ni, Cu, Zn, Se, Cd, Te, Pb	Sc, V(IV), V(V), Fe, Ga, Y, In, Rare earths	Re, Bi, Th, U	Ti, Cr, As, Zr, Mo, Pd, Ag, Ba, Hf, W

*Group B*;  $R_F < 0.8$  for organophosphorus compounds only. An appreciable number of ions, notably the trivalent rare earths and related ions, show sorption with TOPO, and, to a lesser extent, with TBP. High  $R_F$  values are, however, invariably observed when using Alamine, AlamO or TOAsO as extractant.

The absence of sorption on amine-impregnated supports suggests that the ions in question do not form anionic metal-nitrato complexes. However, one should bear in mind that the rare earths, and also Sc(III) and Y(III), are strongly sorbed<sup>22</sup> on paper impregnated with an amine nitrate if (slightly acidified) LiNO<sub>3</sub> is used as eluant instead of HNO<sub>3</sub>. Sorption increases with decreasing atomic number, as has also been observed<sup>23</sup> in column chromatography using resin exchangers. Weak anionic complex formation probably occurs, which does not lead to significant sorption, if competition due to the extraction of the bulky (O<sub>2</sub>NO... HONO<sub>2</sub>)<sup>-</sup> ion plays a role. Sorption is noticeable only if this competition is diminished by using LiNO<sub>3</sub> instead of HNO<sub>3</sub>. The same phenomenon has repeatedly been observed<sup>1,2</sup> in HCl systems, where desorption is due to the competitive action of HCl<sub>2</sub><sup>-</sup>.

The  $R_F$  spectra on TOPO-impregnated silica gel can be explained in terms of sorption of TOPO-solvated neutral metal (oxy)nitrates, *e.g.*



Competition due to the extraction of (one or two molecules of) HNO<sub>3</sub> decreases this sorption with increasing acid concentration.

A different situation occurs with TBP. With this extractant, the sorption of the Group B ions occurs at high aqueous acid concentrations only, and it increases with increasing concentration. Such behaviour is in agreement with literature data<sup>24</sup> on liquid-liquid extraction. The analogy between TBP and TOPO, not Alamine (*cf.* above), as regards the increase of sorption with increasing atomic number of the rare earths, suggests that extraction occurs by solvation rather than by an anion-exchange mechanism. It is interesting to note that with TBP, competitive extraction of excess HNO<sub>3</sub> is negligible up to at least 10 N HNO<sub>3</sub> (Fig. 1a). Therefore, we tentatively suggest that with increasing nitrate concentration, the formation of neutral nitrates is promoted, which then compete successfully with the single HNO<sub>3</sub> molecule for TBP. With TOPO, the rapid extraction of excess HNO<sub>3</sub> according to eqn. 7 prevents a successful competition and, therefore, increasing sorption at high HNO<sub>3</sub> concentrations.

Mention must be made of the minima in the  $R_F$  spectra of rare earths, Sc(III), Y(III), Fe(III) and Zr(IV) in ascending, but not radial, paper chromatography in the TBP-HNO<sub>3</sub> system reported by O'Laughlin and Banks<sup>25</sup>. The authors themselves suggested as possible reasons inaccurate determination of  $R_F$  values or partial decom-



position of the extractant in the much longer development time involved in the ascending technique. Recently, Cerrai and Ghersini<sup>1</sup> suggested kinetic effects as a reason. However, as neither short-time (this paper; thin layer; TBP) nor long-time (ref. 26; paper; tri-*n*-octyl phosphate) chromatography leads to minima in the  $R_F$  spectra of these ions using ascending development, decomposition or kinetic effects do not appear to be satisfactory explanations.

Lastly, the absence of sorption for Group B ions with AlamO and TOAsO, that is, the analogy with Alamine, not with TOPO or TBP, suggests that sorption (of Group C ions) by amine and arsine oxides from HNO<sub>3</sub> solutions will occur through anion exchange, with solvation playing a negligible role.

*Group C; anion exchange and solvation.* Anion exchange governs the sorption and extraction of Re(VII), Bi(III), Th(IV) and U(VI) when liquid anion exchangers are used as the stationary phase. For the latter three ions, the sorption sequence primary < secondary < tertiary ~ quaternary exchangers has previously been established<sup>27</sup>. With Th(IV) and U(VI), the metal-containing species present in the organic phase<sup>28,29</sup> are Th(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> and UO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub><sup>-</sup>. With Bi(III), the extracted species is probably<sup>30</sup> Bi(NO<sub>3</sub>)<sub>5</sub><sup>2-</sup>. With TBP, on the other hand, extraction often occurs through solvation: the existence of solvates such as UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2TBP and Th(NO<sub>3</sub>)<sub>4</sub>·2TBP in organic extracts has repeatedly been established (ref. 12, p. 702). Data on TOPO are scarce. White and Ross<sup>31</sup> reported the extraction of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2TOPO and Th(NO<sub>3</sub>)<sub>4</sub>·2TOPO from aqueous nitrate solutions; rhenium appears to be extracted as a 1:1 TOPO-HReO<sub>4</sub> complex<sup>32</sup>.

As regards AlamO and TOAsO, no definite conclusions regarding the sorption mechanism can be drawn on the basis of the chromatographic data only: the curves for the Group C ions show essentially the same shape with all five extractants (Fig. 3). However, the data for the Group B ions and the analogous behaviour of amines and amine oxides in halide systems<sup>3,4</sup> suggest that sorption occurs through anion exchange. Current work in our laboratory on the extraction of U(VI) supports this hypothesis.

*Group D; side-effects.* Phenomena such as precipitation of insoluble salts, hydrolysis and interaction with the support play an important role with the ions in Group D. Precipitation of Ba(NO<sub>3</sub>)<sub>2</sub> in concentrated HNO<sub>3</sub> satisfactorily explains the  $R_F$  spectra of Ba(II). With Ti(IV), As(III), Zr(IV) and Hf(IV), interaction with the support determines the shape of the  $R_F$  spectra, especially with the extractants that do not contain phosphorus (see Fig. 3). Parallel experiments have indeed shown that sorption is virtually absent ( $R_F > 0.9$  for all four ions) if chromatography is carried out on cellulose instead of silica gel (see also refs. 19 and 33). The sorption observed with Ti(IV), Zr(IV) and Hf(IV), and also with Mo(VI), on supports impregnated with TOPO (and TBP), is probably due to the formation, and extraction, of solvated metal (oxy)nitrates such as Zr(OH)<sub>*n*</sub>(NO<sub>3</sub>)<sub>4-*n*</sub>·2TBP (*n* = 0-2)<sup>34</sup>. We may add that As(III) streaks to high  $R_F$  values; occasionally, a second spot with  $R_F = 1.0$  occurs, due to the oxidation of trivalent to pentavalent arsenic.

Silver and tungsten remain at the start at all acid concentrations. Streaking occurs, particularly with Ag(I). Substitution of silica gel by cellulose does not improve the results. With Pd(II), a large proportion of the ion remains at the origin, but generally some streaking and/or formation of a second spot occurs. More or less analogous results are obtained for Hg(II): two spots, with intermediate streaks, are generally

observed. The  $R_F$  values invariably increase with increasing acid concentration, but the reproducibility of the data is very poor (shaded area in Fig. 3). However, in contrast with Ag(I) and W(VI), both Pd(II) and Hg(II) show a single well-defined spot at the solvent front on non-impregnated silica gel.

With Cr(III), two spots always appear, with  $R_F$  values of 0.0 and 1.0, irrespective of the acidity and/or age of the sample solution, and the use of silica gel or cellulose as support. A similar observation was made by Sastri and Rao<sup>35</sup> in a study of reversed-phase chromatography on paper impregnated with dinonylnaphthalenesulphonic acid, a cation exchanger. On the other hand, Cerrai and Testa<sup>20</sup> and O'Laughlin and Banks<sup>25</sup>, who both used TOPO-impregnated paper as the stationary phase, reported a spot at the solvent front only.

### Separations

Some interesting separations are recorded in Fig. 4. Also of interest is a recent study by Sherma and Van Lenten<sup>36</sup> of metal ion separations on paper impregnated with ion-exchange resins, using as eluents mixed solvents containing a mineral acid, an organic solvent and a selective extractant (often TOPO). Some of the separations elaborated for this complex chromatographic system can also be achieved by using the relatively simple reversed-phase TOPO- $\text{HNO}_3$  systems described in the present paper. Sc(III) can be separated from the trivalent rare earths on TOPO-impregnated silica gel with 2–10  $N$   $\text{HNO}_3$ , or, alternatively, 0.1  $N$ -conc.  $\text{HBr}$  as eluent<sup>4</sup>. Solutions of 2–7  $N$   $\text{HNO}_3$  are suitable eluants for the separation of Zr(IV) and Hf(IV) from e.g.

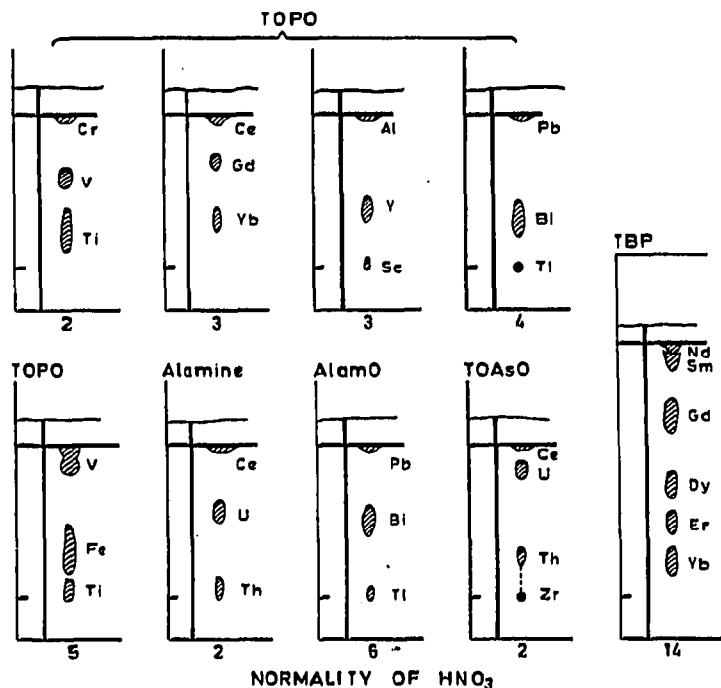


Fig. 4. Examples of separations carried out in various extractant- $\text{HNO}_3$  systems. The separation of the rare earths on TBP-impregnated silica gel requires a length of run of 5 cm. Cr = Cr(III); V = V(V); Ti = Ti(III).

Fe(III), Co(II), Mn(II), Zn(II), alkaline earth and tervalent rare earth ions. Lastly, the separation of Th(IV) from tervalent rare earths, Sc(III) and various transition metals such as Fe(III), Cu(II) and Ni(II) can also be achieved with 2–7 *N*  $\text{HNO}_3$  as eluant, provided that the molarity of the TOPO solution used for impregnation of the support is not too high (*cf.* ref. 20 and this paper). This suggests that in the system used by Sherma and Van Lenten<sup>36</sup>, solvation by TOPO is the phenomenon that predominantly determines the chromatographic behaviour of the ions.

## CONCLUSION

The present results enable us to reach several conclusions.

(1) Contrary to the results obtained for HCl and HBr systems<sup>3,4</sup>, in  $\text{HNO}_3$  systems the behaviour of TOAsO is closely analogous to that of amines and amine oxides: a sudden change in the shape of the  $R_F$  spectra, denoting strong desorption, is completely absent. This result is in accord with the data on the extraction of  $\text{HNO}_3$  by Alamine, AlamO and TOAsO (Fig. 1): the extraction of  $\text{HNO}_3$  in excess of the stoichiometric amount runs parallel for all three extractants. These data suggest that with TOAsO, the mechanism of extraction of  $\text{HNO}_3$  is different from that of HCl and HBr.

Current investigations show that extraction of the second molecule of HCl (HBr) is not due to the formation of  $\text{HCl}_2^-$  ( $\text{HBr}_2^-$ ), as is the case with liquid anion exchangers, but that a trioctylarsine dihalide,  $(\text{C}_8\text{H}_{17})_3\text{AsX}_2$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ), is formed instead. This would explain the low sorption strength of TOAsO at high HCl concentrations very satisfactorily. In the  $\text{HNO}_3$  system, on the other hand, extraction of the second molecule of acid is through formation of the  $[\text{O}_2\text{NO}\dots\text{HONO}_2]^-$  ion, as is the case with amines, and no sudden loss of sorption strength occurs.

(2) The number of elements that shows  $R_F$  spectra with Alamine and AlamO, different from those recorded for TOPO and TBP, is relatively large in the  $\text{HNO}_3$  system, as compared with the hydrohalic acid systems. This is due to the fact that formation of strong anionic metal–nitrate complexes occurs with a few ions only, whereas solvation of neutral metal (oxy)nitrates by the organophosphorus compounds is a much more widespread phenomenon. In this context, we noted earlier<sup>4</sup> that a superficial resemblance of the  $R_F$  spectra for a single, or a few, ions does not imply that the underlying extraction mechanism is the same in both instances. In order to elucidate this problem for nitrate systems, the extraction of U(VI) from aqueous  $\text{HNO}_3$  and  $\text{LiNO}_3$  solutions is currently being investigated in our laboratory.

(3) Comparing our present data with those previously published for halide systems, one notices that a relatively large number of ions show ill-defined  $R_F$  spectra (double spots, streaks, etc.). No doubt this phenomenon can be partly attributed to the high sensitivity of the identification techniques currently used: faint spots or streaks that went unnoticed several years ago now mar the over-all picture [Ag(I), Cr(III), W(VI)]. However, the absence of similar experiences in recent investigations of extractant–HCl systems<sup>3,37</sup> indicates that the problem is at least partly inherent in the use of  $\text{HNO}_3$  as eluent; in the absence of anionic complex formation and solvation, side-effects such as hydrolysis and adsorption play a more prominent role. This may also explain the mutually divergent results obtained by different workers for *e.g.* Cr(III) and Pd(II), and certainly does so for Ti(IV), Zr(IV), Hf(IV) and As(III), as has been shown above.

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