

CHROM. 5251

The use of tri-*n*-alkylamine and -arsine oxide in reversed-phase extraction chromatography

In the past decade, considerable attention has been paid to the chromatography of inorganic ions on supports impregnated with high-molecular-weight amines and substituted quaternary ammonium salts¹⁻⁴. It has been observed that the R_F vs. N HCl diagrams obtained with these so-called liquid anion exchangers often show a distinct resemblance to those obtained with neutral organophosphorus compounds such as tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butylphosphate (TBP)^{5,6}. It seems worthwhile to widen the range of vision by investigating the extraction properties of some related compounds. To this end, tri-*n*-octylarsine oxide (TOAsO) and a tri-*n*-alkylamine oxide, Alamine 336-S oxide (AlamO), were selected. In the present paper reversed-phase extraction chromatography on silica gel layers impregnated with TOAsO and AlamO is described. Chloride solutions are employed as eluants.

Materials and methods

The procedure described by KENNEDY AND PERKINS⁷ was adopted for the preparation of AlamO from Alamine 336-S (General Mills, Kankakee, Ill., U.S.A.), a special quality (99-100 %) tertiary amine, having alkyl groups which consist of C₈-C₁₀ straight chains; its mean mol.wt. is 392. A solution of Alamine in abs. ethanol is added with stirring to a solution of 30 % H₂O₂ in absolute ethanol over a period of a few hours. After keeping the mixture at 45° for 3 days, the clear solution is poured into 5 vol. of distilled water. The AlamO, which separates as an oily upper layer is diluted with toluene and repeatedly washed with 0.5 *N* NaOH and distilled water. Stock solutions of AlamO in CHCl₃ are prepared after evaporation of the toluene at a temperature below 50°. The aliphatic amine oxide contains only traces (< 1 %) of unreacted tertiary amine, as was demonstrated by chromatography on Al₂O₃ with benzene as the eluant⁸.

The synthesis of TOAsO involves⁹ the preparation of tri-*n*-octylarsine by the addition of AsCl₃ to the Grignard reagent formed by the reaction of *n*-octylbromide with magnesium turnings. After the addition of excess HCl, tri-*n*-octylarsine is oxidized with 30 % H₂O₂ to form TOAsO. The impure oxide is crystallised from *n*-hexane, and dissolved in absolute ethanol. A white colloidal residue is filtered off and the ethanol is evaporated. After rigorous drying a melting point of 68-69° is obtained (literature: ref. 9, 60°; ref. 10, 69.5-71°).

Solutions of AlamO and TOAsO in CHCl₃ are standardised by equilibration of an aliquot portion with an equal volume of approx. 2 *N* HClO₄, and subsequent determination of the amount of acid taken up by the organic phase.

Reversed-phase chromatography is carried out as described by BRINKMAN *et al.*³. 0.1 *M* solutions of the oxides in CHCl₃ are equilibrated with 3 vol. of 2 *N* HCl, and the organic solution is mixed thoroughly with silica gel (Type DO, Fluka, Buchs, S.G., Switzerland). Chromatoplates are prepared by dipping microscope slides into the suspension. Superfluous material is wiped off the back of the plates and small margins are made along the edges; the thin layers are of good quality. 2-6 spots are applied on each plate, using sample solutions containing 2-10 mg of ion per ml, and acidified as far as

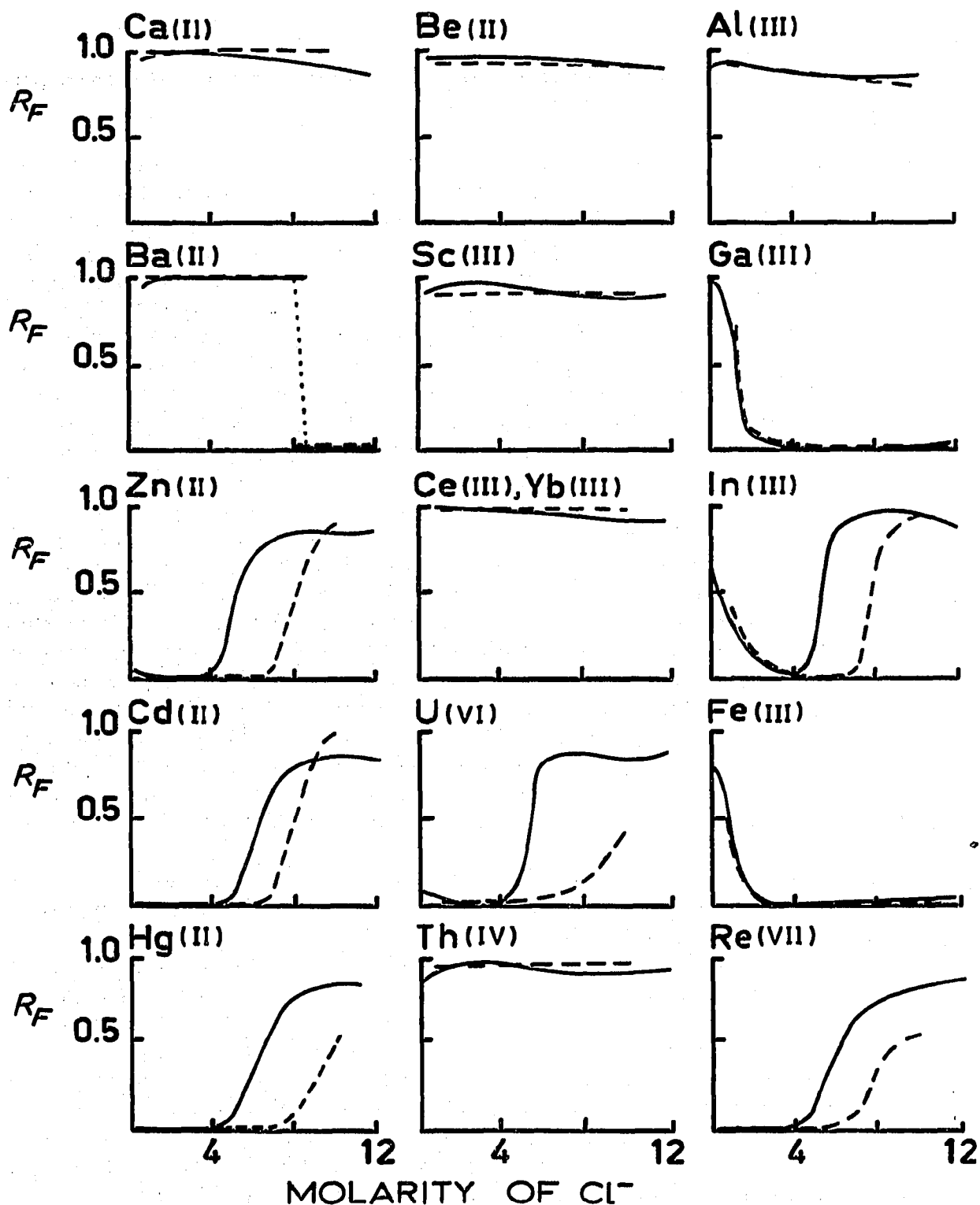
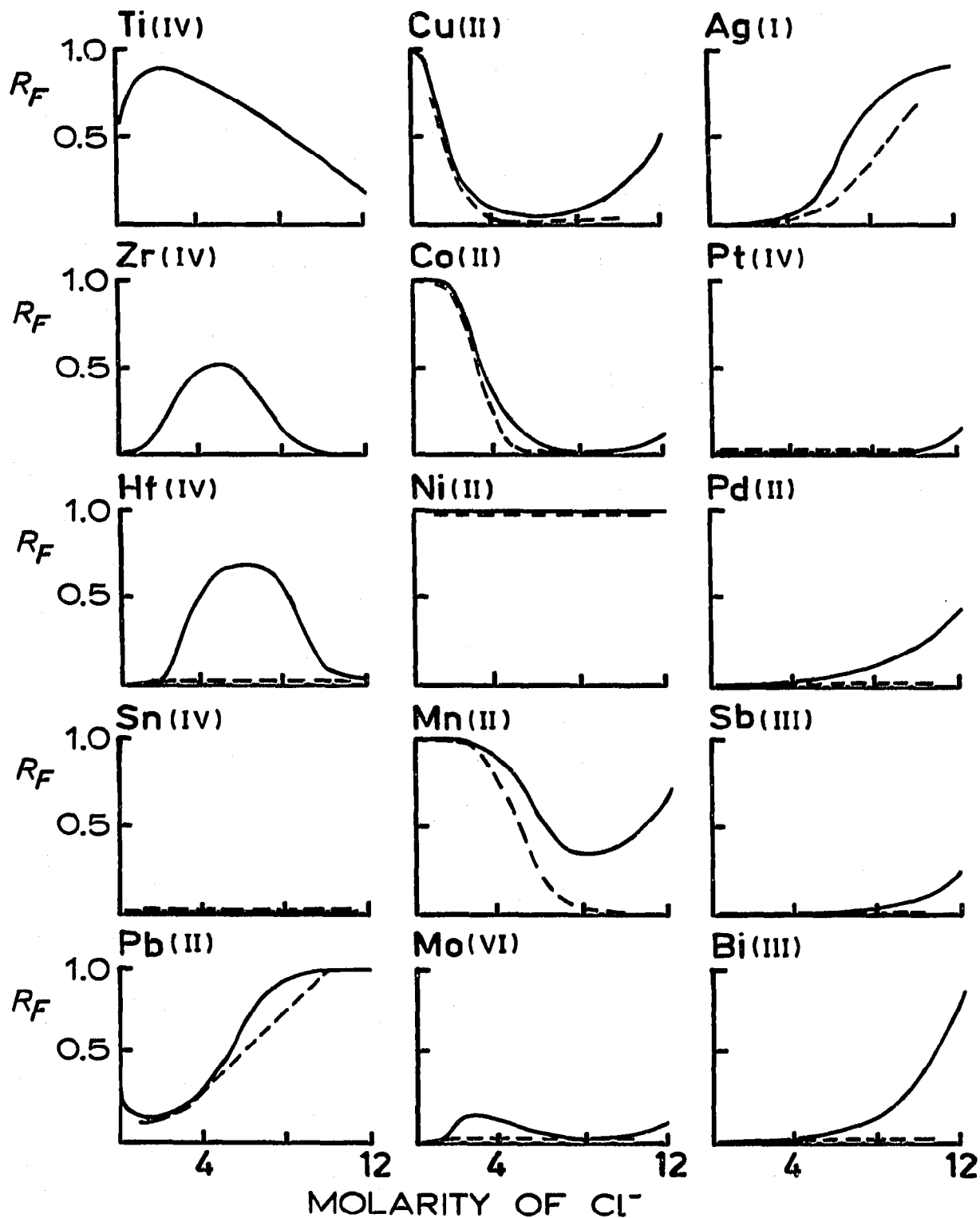


Fig. 1. R_F vs. $M Cl^-$ spectra for 30 ions using silica gel impregnated with AlamO as the stationary phase. (—) HCl; (---) acidified LiCl. Details not mentioned in the text: streaking occurs with Ti(IV) and Zr(IV) at all LiCl concentrations. The curves for Ba(II) may be explained in terms of insoluble salt formation; hydrolysis and/or adsorption to the support determine the form of the curves for Ti(IV), Zr(IV) and Hf(IV), at least to a considerable extent (cf. ref. 3).



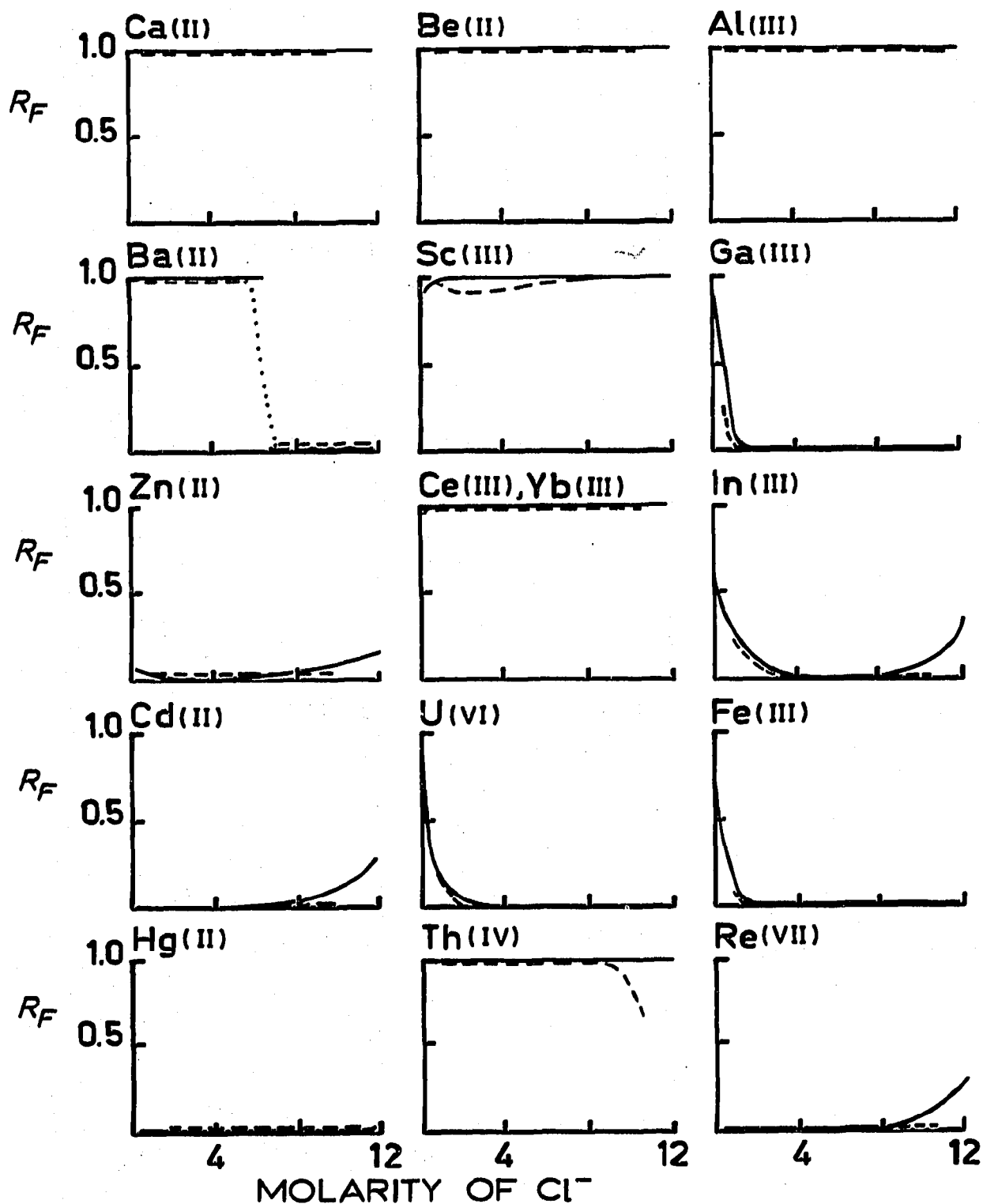
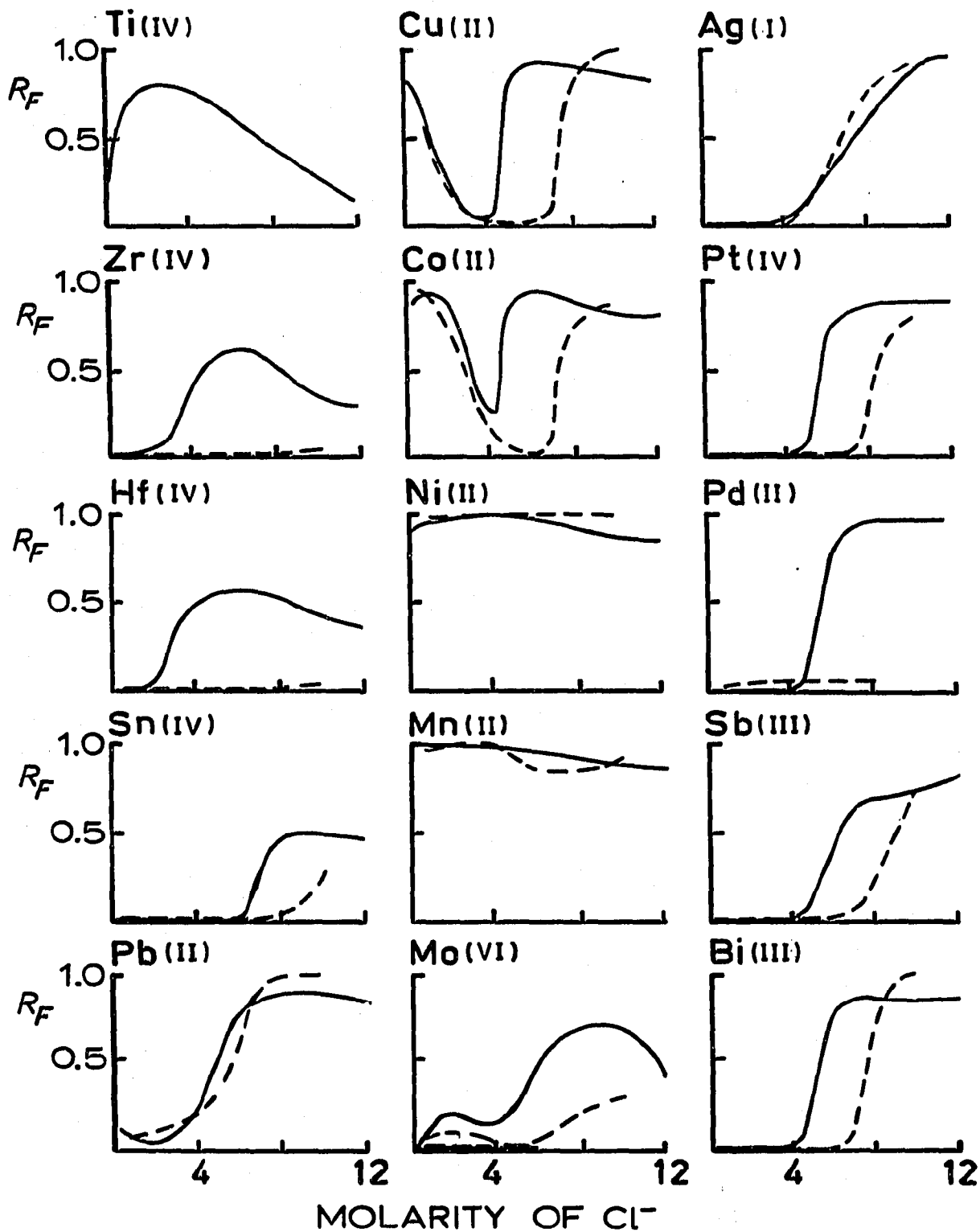


Fig. 2. R_F vs. $M Cl^-$ spectra for 30 ions using silica gel impregnated with TOAsO as the stationary phase. (—) HCl; (---) acidified LiCl. Details not mentioned in the text: streaking occurs with Zr(IV) with HCl, and is very severe for Ti(IV) with LiCl.



necessary to prevent hydrolysis. Ascending chromatography (3.0 cm run) is carried out in Hellendahl staining jars. Development times generally are between 8 and 15 min when employing HCl as the eluant. The use of LiCl instead of HCl leads to a considerable increase of the elution time, especially at high salt concentrations. For detection of the spots the visualisation procedures described in refs. 3 and 4 are used. All further details concerning the chromatographic technique are reported in the same papers.

Results and discussion

Chromatography has been carried out for 30 ions, employing solutions of 0.1–11 N HCl and 0.1–9.5 M LiCl acidified with 0.5 N HCl as eluants; the results are summarised in Figs. 1 and 2.

AlamO. The data presented in Fig. 1 for AlamO show a very close analogy with those published previously for liquid anion-exchangers such as Alamine and Amberlite LA-1 (ref. 3), the sorption strength of AlamO being roughly comparable to that of the latter amine.

KENNEDY AND PERKINS⁷, from a study of the extraction of U(VI) and Pu(IV) from nitric acid solutions by AlamO, also conclude that there are only small differences between Alamine and AlamO as extractants; the slopes of $\log D$ vs. $\log c_{\text{AlamO}}$ plots are consistent with the extraction of the species $\text{UO}_2(\text{NO}_3)_3^-$ and $\text{Pu}(\text{NO}_3)_6^{2-}$, as in the case of extraction by amines. A similar conclusion is drawn by TORGOV and co-workers¹¹. On the basis of results with the extraction of U(VI) by trioctylamine oxide and its parent amine from aqueous chloride and nitrate solutions, these authors conclude that the U(VI)-containing anions present in the organic amine and amine oxide phases are identical. (The formulation¹¹ of these anions as UO_2X_3^- ($\text{X} = \text{Cl}$ or NO_3) may be erroneous, however, in the case of the chloride system (*cf.* refs. 12 and 13).)

The quoted data do not completely rule out the possibility of the extraction of a coordinately solvated salt, $\text{UO}_2\text{X}_2 \cdot n\text{R}_3\text{NO}$ (*cf.* ref. 11); however, as far as chloride systems are concerned, current research¹⁴ has demonstrated the presence of complex metal anions for *e.g.* Co(II), Cu(II), and Fe(III). For each of these three metal ions, the spectra of its metal-containing toluene extracts are identical, irrespective of the Cl⁻ concentration of the aqueous phase, and the use of HCl or (acidified) LiCl. The complex metal anions have been identified as CoCl_4^{2-} (629, 667 and 699 nm), CuCl_3^- and CuCl_4^{2-} (300 and 470 or 410 nm), and FeCl_4^- (317, 366, 450 (sh.), 533 and 620 nm), respectively. The anions probably constitute part of an associated electrolyte $(\text{R}_3\text{N}^+\text{OH})_n \cdot \text{MCl}_p^{n-}$. The results are in good agreement with data on the extraction by liquid anion exchangers, where CoCl_4^{2-} , CuCl_4^{2-} (but not CuCl_3^-), and FeCl_4^- are present in the organic extracts at all acid concentrations¹⁵. Complex metal anions are also identified in organic phases obtained after extraction with TOPO¹⁶ and TBP¹⁷ from relatively concentrated aqueous HCl solutions; at low acid concentrations, however, divalent cobalt and copper are extracted as solvated metal chlorides $\text{MCl}_2 \cdot n\text{S}$ (refs. 17 and 18).

Moreover, it has been shown¹⁴ that the extraction of HCl by AlamO is a process almost identical to the extraction by Alamine — which sharply contrasts with the behaviour shown by TOPO and TBP. At low aqueous acid concentrations, extraction corresponds to the formation of 1:1 acid:AlamO adduct. With increasing concentration, the extraction of HCl gradually proceeds beyond the amount necessary to neutralise the AlamO. An IR band at 1110–1190 cm^{-1} , observed for solutions of

AlamO and Alamine, known to contain an excess of acid, indicates the presence of HCl_2^- in both cases (*cf.* refs. 15 and 19) For amine- Cl^- systems, the formation, and competitive extraction, of HCl_2^- is repeatedly mentioned^{15,19,20} to explain the desorption observed for many metal ions at high HCl — but not LiCl — concentrations. The shape of the R_F spectra presented in Fig. 1 for ions such as Cu(II), Mn(II), Cd(II), and Bi(III) favours an identical explanation for the AlamO- Cl^- system.

Lastly, it may be added that for the ions for which the R_F *vs.* N HCl spectra obtained with TOPO- and TBP-impregnated thin layers do show differences compared with those recorded for thin layers treated with Alamine⁶, *e.g.* Sc(III), Th(IV), and to a lesser extent Zr(IV) and Hf(IV), the R_F spectra observed with AlamO-impregnated silica gel closely resemble those found in the amine-HCl system.

In conclusion, the extraction/sorption properties of AlamO, *i.e.* of amine oxides, in the Cl^- system, are closely analogous to those of amines—which probably, as regards base strength, are comparable to the amine oxides (*cf.* ref. 7). There are distinct differences in extraction/sorption properties, however, between AlamO and the structurally related TOPO.

TOAsO. The R_F spectra obtained for TOAsO-impregnated layers only show a superficial resemblance to those reported for supports treated with high-molecular-weight amines³ or neutral organophosphorus compounds⁶. The shape of the curves is roughly the same, but the sharp increase of the R_F values occurring with TOAsO at approx. 5 N HCl is never observed with amines or TOPO.

The use of TOAsO as an extractant has been investigated by BLAIR AND MICHAEL⁹, who studied the extraction of HNO_3 and trivalent Am, Cm and Pm from aqueous HNO_3 and LiNO_3 solutions. The authors claim that the extraction properties of TOAsO are comparable with those of high-molecular-weight amines, but markedly differ from those of TOPO. The conclusions are based upon an analysis of the shape of $\log D$ *vs.* \log concentration plots, but no details are given regarding the composition of the extracted species. Differences in behaviour between TOAsO and TOPO have also been observed by LINDER and coworkers^{21,22}. The former compound excellently extracts metal ions such as Zn(II), Cd(II) and Fe(III) from aqueous Cl^- -containing solutions having $\text{pH} > 0.2$, but the amount of metal extracted with TOAsO from more concentrated HCl solutions is considerably less than with TOPO. According to the authors, the said metal ions are extracted as molecular adducts $\text{ZnCl}_2 \cdot 2\text{TOAsO}$, $\text{CdCl}_2 \cdot 3\text{TOAsO}$ and $\text{FeCl}_3 \cdot \text{TOAsO}$; the low extractability from solutions having $\text{pH} < 0.2$ is due to the preferential extraction of HCl at this level of acidity, which sharply rises to a limiting ratio of $(\text{HCl}/\text{TOAsO})_{\text{org.}} = 2/1$ at approx. 2 N HCl aqueous concentration*. At the same time, however, the results quoted imply that the extraction behaviour of TOAsO is widely different from that of liquid anion exchangers: the latter compounds efficiently extract Zn(II), Cd(II), and Fe(III) from aqueous HCl-containing solutions, the species present in the organic phase after extraction being formulated as $(\text{R}_3\text{NH}^+)_2\text{MCl}_4^{2-}$ for Zn(II) and Cd(II), and $\text{R}_3\text{NH}^+ \cdot \text{FeCl}_4^- \cdot n\text{R}_3\text{NH}^+\text{Cl}^-$ ($n = 0$ or 1) in the case of iron.

The rapidly decreasing extractability of metal ions due to the preferential extraction of excess HCl has a parallel in the strong desorption occurring at approx. 5 N HCl in reversed-phase chromatography (Fig. 2). The distinct shift of the ascending

* According to LINDER, the $(\text{HCl}/\text{TOAsO})_{\text{org.}} = 2/1$ adduct is presumably of the type $\text{TOAsOH}^+\text{HCl}_3^-$. However, no IR bands attributable to HCl_2^- are reported in the text.

branch of the R_F curves to higher aqueous chloride concentrations upon substitution of HCl by solutions of LiCl acidified with 0.5 *N* HCl, supports this hypothesis. Admittedly, there is a rather large difference between this HCl concentration and the one at which the limiting ratio $(\text{HCl}/\text{TOAsO})_{\text{org.}} = 2/1$ is reached, but it must be borne in mind here that the behaviour of undiluted TOAsO on silica gel and the 0.1 *M* solution in benzene, used by LINDER, may show some divergence.

A more complete evaluation of the sorption mechanism will have to await further research on liquid-liquid extraction in the TOAsO-Cl⁻ system.

Free Reformed University,
Chemistry Laboratory,
Amsterdam (The Netherlands)

H. R. LEENE
G. DE VRIES
U. A. TH. BRINKMAN

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Received January 12th, 1971

J. Chromatogr., 57 (1971) 173-180