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EXTRACTION CHROMATOGRAPHY WITH LIQUID ION EXCHANGERS

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SUMMARY

After a brief outline of the potential of extraction chromatography involving liquid anion and cation exchangers as a means for the quantitative separation of inorganic substances, the theoretical approaches to the technique are presented and criticized. Known limiting factors to theoretical interpretations of extraction chromatographic results are discussed, and additional factors are suggested.

INTRODUCTION

Suitable solid supports, loaded with liquid compounds normally used for the extraction of metals from aqueous solutions, enable one to obtain chromatographic systems that advantageously reproduce the same processes as liquid-liquid extraction. Although relatively recent, this technique, generally called extraction chromatography, has found increasing popularity in inorganic analytical laboratories, as indicated in several of the many reviews on the subject¹⁻⁶. Columns permit easy and satisfactory separations of microgram to milligram amounts of ions, while treated thin layers or paper are versatile materials for rapid investigations on the behaviour of the different stationary phases or for qualitative analysis.

In this paper, extraction chromatographic systems involving the so-called liquid anion and cation exchangers are briefly considered and compared with conventional ion-exchange resins, and the most recent theoretical approaches to the technique are critically outlined.

LIQUID ANION EXCHANGERS

The salts of long-chain aliphatic amines extract inorganic species from aqueous solution through the exchange of their original anion with an anionic species containing the element of interest, present in the aqueous phase. The nature of the amine affects the overall values of the resulting distribution coefficients, but apparently has little influence on the relative extractability of the different anionic species. Therefore, all extractants of this class display the same selectivity features, strictly comparable to those of conventional anion-exchange resins.

The most popular liquid anion exchangers are tri-*n*-octylamine (TNOA) and Aliquat 336 (methyltricaprylammonium chloride). A large number of other amines

TABLE I
LIQUID ANION EXCHANGERS USED IN COLUMN EXTRACTION CHROMATOGRAPHY

<i>Type</i>	<i>Exchanger</i>
Primary	Primene JM-T (trialkylmethylamine, 18–24 carbon atoms)
Secondary	Amberlite LA-1 (<i>n</i> -dodecyltrialkylamine, 24–27 carbon atoms) Amberlite LA-2 (<i>n</i> -dodecyltrialkylamine, 24–27 carbon atoms)
Tertiary	Alamine 336 (tricaprylylamine; caprylyl = <i>n</i> -octyl, <i>n</i> -decyl) methyldioctylamine tri- <i>n</i> -hexylamine trilaurylamine triisooctylamine tri- <i>n</i> -octylamine (TNOA)
Quaternary	Aliquat 336 (methyltricaprylylammonium chloride) Hyamine-1622 (diisobutylphenoxyethoxyethyltrimethylbenzylammonium chloride) trialkylbenzylammonium nitrates methyltrilaurylammonium salts

have been screened for their behaviour toward metals in laminar extraction chromatography^{2,3}, while relatively few of them have been applied as stationary phases for columns.

Amines and ammonium compounds used in columns are listed in Table I, while Table II lists materials most commonly used as supports. Accurate optimization of chromatographic parameters (amount of extractant loaded on the support; nature, grain-size and porosity of the support material; column packing and dimensions; flow-rate of the eluting solution; temperature) permit 0.2–0.4-mm theoretical plate heights, hydrophobized Kieselguhr or silica gel being the most suitable supports.

Because of their close similarity to conventional anion-exchange resins, amine stationary phases can represent an advantageous alternative to resins only when a

TABLE II
SUPPORTS USED IN COLUMN EXTRACTION CHROMATOGRAPHY

Cellulose powder
Glass beads or powder
Polyethylene: Microthene
Polystyrene: Amberlyst XAD-2
Polytetrafluoroethylene: Fluoroplast-4
Teflon
Polytrifluoroethylene: Hostafion
Kel-F
Plaskon
Voltalef
Polyurethane foams
Poly(vinyl chloride–vinyl acetate) copolymer: Corvic
Silicon dioxide: silanized Kieselguhr
Celite
Hyflo Supercel
Chromosorb W
silica gel
Styrene–divinylbenzene copolymer granules

"tailor-made" retention power or particularly small plate heights are required, when the use of a particular extractant permits a small but important enhancement of the separation factor between closely similar elements (as in the case of several actinides), and in applications to high-pressure column chromatography, as pointed out by Huber⁷.

Among the most interesting column chromatographic separations obtained with liquid anion exchangers, Am-Cm, F⁻-Cl⁻-Br⁻-I⁻ and Cr-W-Mo are particularly noteworthy.

LIQUID CATION EXCHANGERS

Water-insoluble liquid organic compounds that extract by exchanging protons for cationic species originally present in the aqueous phase are generally called "liquid cation exchangers".

The extractants of this class used in column extraction chromatography are listed in Table III; among them, acidic organophosphorus compounds are the most popular, in particular di(2-ethylhexyl)phosphoric acid (HDEHP). Supports used for columns are the same as those mentioned for liquid anion exchangers.

TABLE III

LIQUID CATION EXCHANGERS USED IN COLUMN EXTRACTION CHROMATOGRAPHY

Dinonylnaphthalenesulphonic acid (HDNNS)
Di-*n*-butylphosphoric acid
Di-*n*-octylphosphoric acid
Diisooamylphosphoric acid
Di(2-ethylhexyl)phosphoric acid (HDEHP)
2-Ethylhexylphenylphosphonic acid
2-Ethylhexylphosphoric acid
2,6,8-Trimethylnonyl-4-phosphoric acid

Acidic organophosphorus compounds extract through a mechanism that can be assumed to be cation exchange, but their selectivity is remarkably affected by the solvating properties of their P → O groups, and for strictly related metals generally increases as the ionic radius of the metal decreases. This makes their use very attractive as an alternative to sulphonic resins.

The popularity of HDEHP derives from its very advantageous separation factors for rare earths (the average value for an adjacent pair is 2.5). Using hydrophobized Kieselguhr, silica gel or polytetrafluoroethylene powder as the support material, HDEHP columns having theoretical plate heights as low as 0.1 mm can be obtained. Outstanding examples of separations obtained with HDEHP columns include all rare earths among themselves, transuranium elements, Ba-Sr-Ca and Tl-Ga-In-Al.

2-Ethylhexylphenylphosphonic acid displays even better separation factors than HDEHP for rare earths and was advantageously used for this purpose, supported on Kieselguhr. 2,6,8-Trimethylnonyl-4-phosphoric acid allowed for successful column separations of alkali metals among themselves.

Other cation exchangers, such as carboxylic acids and phenols, have so far found little popularity in extraction chromatography. This applies also to dinonylnaphthalenesulphonic acid (HDNNS), whose selectivity is closely similar to that of conventional cation-exchange resins.

THEORETICAL APPROACHES TO EXTRACTION CHROMATOGRAPHY

Extraction chromatographic systems are generally treated in terms of liquid-liquid extraction phenomena. On the basic assumption that the processes are fundamentally the same in both instances and that the spatial boundaries of the two chromatographic phases are well defined, the distribution coefficient, D , of the eluted species is related to the chromatographic parameters through the classical partition equations

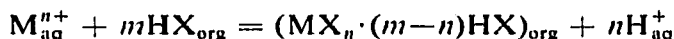
$$D = \frac{V_R - V_m}{V_s} \quad (1)$$

and

$$D = \frac{A_m}{A_s} \cdot \left(\frac{1}{R_F} - 1 \right) \quad (2)$$

eqn. 1 referring to columns (V_R being the volume of eluate to the peak maximum, V_m and V_s the volumes of the mobile and stationary phases in the column, respectively) and eqn. 2 to paper and thin layers (A_m and A_s being the cross-sectional areas of the mobile and stationary phases, respectively, assumed to be constant along the whole chromatogram).

In turn, D can be related to the chemical parameters of the two phases. The extraction of a metal ion M^{n+} by an acidic extractant, for example, can be expressed by a cation-exchange equilibrium:



having an equilibrium constant

$$K = \frac{\gamma_{\text{add}}}{\gamma_M} \cdot \frac{[\text{MX}_n \cdot (m-n)\text{HX}]_{\text{org}} \{\text{H}^+\}_{\text{aq}}^n}{[\text{M}^{n+}]_{\text{aq}} \{\text{HX}\}_{\text{org}}^m}$$

where brackets and braces denote concentrations and activities, respectively, and γ_{add} and γ_M are the activity coefficients of the metal-containing species (adduct and ion) in the two phases.

If the above equilibrium is the only reaction responsible for the extraction of the metal, and M^{n+} and $\text{MX}_n \cdot (m-n)\text{HX}$ are the only metal-containing species present in the system, then

$$D = \frac{[\text{MX}_n \cdot (m-n)\text{HX}]_{\text{org}}}{[\text{M}^{n+}]_{\text{aq}}} = K \frac{\gamma_M}{\gamma_{\text{add}}} \cdot \frac{\{\text{HX}\}_{\text{org}}^m}{\{\text{H}^+\}_{\text{aq}}^n}$$

By combining this equation with eqns. 1 and 2, correlations are obtained be

tween the chromatographic results and the chemical parameters of the two phases, which in a logarithmic form appear as follows:

$$\log \left(\frac{V_R}{V_m} - 1 \right) = \log \frac{\gamma_M}{\gamma_{add}} + m \log \{HX\}_{org} - n \log \{H^+\}_{aq} + \log \frac{V_s}{V_m} + \text{constant} \quad (3)$$

$$\log \left(\frac{1}{R_F} - 1 \right) = \log \frac{\gamma_M}{\gamma_{add}} + m \log \{HX\}_{aq} - n \log \{H^+\}_{aq} + \log \frac{A_s}{A_m} + \text{constant} \quad (4)$$

Such correlations enable information to be gained on the reaction actually responsible for the retention of metals, by slope analysis of the plots of the results obtained varying only one of the chemical parameters involved; in general, the ratio of activity coefficients is assumed to be constant, and straight lines are expected.

Slope analysis has often been applied to extraction chromatographic results, especially when obtained by means of laminar chromatographic techniques. Often, however, these slopes are not in agreement with the reaction coefficients assessed or deduced from liquid-liquid extraction data; sometimes, slopes apparently have non-integer values, or abruptly change within the concentration range studied².

In many instances, reasonable explanations have been given for such poor results, based essentially on the lack of validity of the assumptions implied in eqns. 3 and 4, because of (at least) one of the following causes:

(1) more than one metal-containing species exist in one or both phases; most often, complexing in the aqueous phase is put forward, which reduces the validity of the correlation between distribution coefficients and equilibrium constant;

(2) the metal-containing species extracted in chromatography is not the same as that which appears to be extracted in normal liquid-liquid experiments; this may actually occur, as the aqueous phase concentration range involved in chromatography usually does not correspond to that used in liquid-liquid extraction;

(3) as a limiting case of the preceding item, a completely different mechanism may be responsible for extraction in chromatography, in addition to or instead of the one expected from liquid-liquid extraction experience; this is the case, for example, of the extraction of iron(III) and gallium by HDEHP from concentrated hydrochloric acid solutions⁸, noticed in chromatography and subsequently confirmed by liquid-liquid extraction;

(4) in addition to the extractant, the support materials also display some retention power for a particular metal;

(5) slow kinetics do not permit equilibrium to be reached between the two chromatographic phases; very little is known about extraction rates, especially when the distribution is relatively fast but still sufficiently slow to affect the chromatographic process: slow rates could complicate the interpretation of chromatographic results considerably, especially when obtained by ascending laminar techniques in which the elution speed varies as the eluent front runs up.

In the opinion of the author, other phenomena could be important causes of disagreement between chromatographic and liquid-liquid results in almost all extraction systems.

Liquid-liquid data are generally obtained at very low extractant loadings, *i.e.*, the amount of metal extracted is much lower than that required to saturate the extractant. On the other hand, the very few data available for extractions carried out at high extractant loadings demonstrate that in many instances the extraction process differs remarkably from that which occurs at low loadings; for example, iron(III) can be extracted with HDEHP as $\text{Fe}(\text{DEHP-HDEHP})_3$ and as $\text{Fe}(\text{DEHP})_3$ at low and high extractant loadings, respectively. When the extractant displays a relatively strong retention for a given metal, the whole amount of metal that is chromatographed is retained by a very limited portion of stationary phase, so that high extractant loadings are likely to occur easily. As the retention decreases (*i.e.*, R_F increases or V_R decreases) the system gradually turns to low extractant loading conditions. It is obvious how such a system can hardly fit a simple extraction scheme, and can differ appreciably from low extractant loading liquid-liquid results.

Laminar (and especially paper) chromatographic results can also be affected by appreciable variations of the A_m/A_s ratio along the chromatogram. In some instances, variations in the eluent composition can also take place, near to the front of the eluent. Both of these experimental uncertainties can considerably affect the results of slope analysis.

Extension of slope analysis to a study of the influence of the stationary phase parameters is very difficult because of the lack of knowledge of the actual physical and chemical properties of the combination extractant plus support. Two different approaches have been followed, one regarding the stationary phase as a sort of "solution" of the extractant in the support material, the other one considering the extractant as a well defined liquid phase invading the pores and filming on the surface of the solid support².

In the former case, variations of extractant loading per unit weight of support should change the activity of the stationary phase. If these activities could be estimated, slopes should approach the value of coefficient m in the extraction equation; in any event, log-log plots of results against the amount of loaded extractant need not necessarily give straight lines. In the latter case, the activity should keep constant for any extractant loading within a reasonable range, and log-log plots of results against extractant loading should give straight lines of slope +1, because of the linear variations of V_s (or A_s) in the right-hand sides of eqns. 3 and 4.

The problem has not been studied thoroughly. Most available results support the latter approach, but there are also data that undoubtedly indicate a dependence of the stationary phase activity on the amount of loaded extractant. Attempts have been made to derive a relationship between the activity of the extractant and its amount loaded on the support², but apparently they are not completely satisfactory: the seemingly good results were probably derived from a "vicious circle". Very recently, Siekierski⁹ has discussed theoretically the activity of an extractant that is fixed onto a support as a definite liquid phase. As the outer film of extractant is in equilibrium with that portion of it which enters the pores of the solid material, the activity can be derived from that of the free liquid extractant by calculating the change in chemical potential for forming capillary liquid from free liquid. For supports that have particularly small pore diameters, such as silica gel, the activity of the fixed extractant should be considerably lower than that of the free liquid, but this would have little effect on the distribution coefficient of metals, as a comparable decrease is also expected in the activity coefficient of the extracted species.

In the author's opinion, the actual physical meaning of the stationary phase probably depends on the nature of the supporting material. In most cases, the extractant should be considered as definitely separated from the support, and filmed on it: this applies reasonably to systems involving polytetrafluoroethylene, polytrifluorochloroethylene, polyethylene, Kieselguhr, silica gel, glass and probably cellulose. With other materials, such as styrene-divinylbenzene and vinyl chloride-vinyl acetate copolymers and polyurethane foams, the extractant is likely to be "dissolved" in the support.

The theoretical interpretation of extraction chromatographic results could be even more complicated than outlined above, as the applicability to such systems of the classical partition theories can also be considered. Actually, stationary phases in extraction chromatography have polar groups that give them an electrical nature very similar to that of the aqueous solutions used as the mobile phase, and the ion-containing species that undergo partition between the two phases often result from the simultaneous coordination of ions by molecules of both the stationary and mobile phases. This led Bark and Duncan¹⁰ to express "some doubt concerning the absolute chromatographic and physical boundaries of the two phases", on the existence of which all classical chromatographic equations are based.

From experiments carried out with thin layers loaded with different extractants, Bark and Duncan¹⁰ proposed the following general correlation between R_F and D :

$$D = A \left(\frac{1}{R_F} - 1 \right) - B \quad (5)$$

differing from the Martin and Synge equation not only in the existence of an additional term B , but also in the possible large disagreement between the A values and the corresponding ratio of the cross-sectional areas of the two phases, as determined experimentally.

Bark and co-workers interpreted eqn. 5 in the light of both partial mutual solubility of the two phases and of possible inactivity in the chromatographic process of a part of the active groups of the stationary phase, consumed in binding to the support. Most probably, at least three layers build up (stationary phase-interface-eluent), instead of the two definite layers considered in ideal liquid-liquid chromatographic conditions¹¹. A fourth layer could also exist, consisting of a portion of stationary phase bound to the support and unavailable for extraction. The volumes of stationary and mobile phases should take into account the volume variations that apparently occur in liquid-liquid extraction, and their ratio would therefore depend on the composition of the aqueous phase; the nature of the interface and its role in the dynamic chromatographic process are rather obscure.

The author developed Bark's result in the hypothesis of a portion of mobile phase that does not move with the rest of the eluent, as a reasonable simplification of the interfacial layer model. Although the available data were not sufficient to draw any conclusion, the resulting volumes of the different layers were reasonably consistent among themselves, and with the additional information available from Bark's work and from liquid-liquid extraction experience.

Unfortunately, in spite of the interesting implications of eqn. 5 for both laminar and column chromatography, no further investigation was carried out to

check the above interpretations or to define better the parameters possibly involved in the non-ideality of the system. It is worth pointing out that the term B in eqn. 5, which implies a partial retention also for elements whose distribution coefficient is zero, is in sharp contrast with the experimental evidence of spots running with the front of the eluent in most thin-layer extraction chromatographic systems, if one does not assume that the extracted metal itself is the main species responsible for the existence of the interfacial layer. This assumption finds support in the inverse relationship between R_F values and A_m/A_s ratios ($\approx A$ term) calculated by Bark by comparing distribution coefficients and chromatographic results for each element (see Table IV in ref. 10). Therefore, it is rather unsatisfactory to assess definite A and B values by averaging data obtained with different elements, having different R_F values, as done in ref. 10 and in the above-reported development of those data made by the present author.

CONCLUSIONS

Extraction chromatography with liquid anion and cation exchangers as the stationary phase appears to be a very attractive means for the separation of inorganic substances for analytical purposes, and often gives consistent advantages as an alternative to conventional ion-exchange resins.

Suitable development of extraction chromatographic results will enable useful information to be obtained on the mechanism underlying the distribution of elements between the two chromatographic phases, so as to permit one either to check qualitatively the validity of already well known liquid-liquid extraction processes, or to investigate the chemistry of new extraction systems.

However, theoretical developments are severely limited by several factors (more or less recognized by extraction chromatography investigators), the most important of which are the very scarce knowledge of the actual physical and thermodynamic status of extractant plus support combinations, and reasonable doubts on the applicability of the classical partition equations to such chromatographic systems. The interest that extraction chromatography has, both in itself and because of its potential usefulness as an aid in understanding liquid-liquid extraction processes, should lead to future systematic investigations that could throw light on the many theoretical aspects that are still unexplored.

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