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Extraction chromatography and its analytical application

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ABSTRACT

An overview of extraction chromatography of some metal ions using various extractant during last two decades is presented. The development of this technique since its inception is briefly traced. The various parameters obtained from the previous and present studies such as equilibrium extraction constant K_{ex} , pH, The various influencing parameters such as acid concentrations, effect of flow rate of mobile phase and reagent concentration was studied. The method was free from large number of interferences from cations and anions data are displayed in tabular form. Finally, the current demands, disadvantages and future prospects are also evaluated.

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KEYWORDS

Extraction chromatography;
Metal ions;
Separation.

INTRODUCTION

Extraction chromatography provides a simple and effective method for the analytical and preparative-scale separation of a variety of metal ions. Recent advances in extractant design, particularly the development of extractants capable of metal ion recognition or of strong complex formation in highly acidic media, have significantly improved the utility of the technique. Advances in support design, most notably the introduction of functionalized supports to enhance metal ion retention, promise to yield further improvements. Column instability remains a significant obstacle, however, to the process-scale application of extraction chromatography. Extraction chromatography (EXC) is a type of liquid-liquid chromatography that couples the selectivity of solvent extraction with the multistage character of chromatographic process and the ease of handling associated with ion-exchange resins. Typically, extraction

chromatographic materials are prepared by simple immobilization (adsorption) of an organic extractant onto any of a wide variety of inorganic (alumina, silica) or organic (cellulose, styrene-divinylbenzene copolymers) supports. In contrast to ordinary partition chromatography, in which the partitioning solute undergoes little, if any, chemical change, the sorption of a metal ion in EXC involves the complex chemical changes associated with the don version of hydrated metal ion into a neutral organophilic metal complex, just as in liquid-liquid extraction. This conversion often involves a number of interactions and equilibria, manipulation of which affords opportunities for the design of systems capable of the efficient and selective separations of a variety of metal ions. In this review, we examine recent progress in this field, with particular emphasis on work directed at improving the performance of extraction chromatographic materials and broadening their range of applications. Conventional extraction chromatographic materials are

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prepared by the physical impregnation of an inert substrate with either an undiluted extractant or a solution of the extractant in an appropriate diluent. This impregnation can be accomplished by this any of a variety of techniques. Most commonly, a porous support material is contacted with a solution of the extractant or of an extractant-diluent mixture in a volatile solvent, and the solvent slowly removed by evaporation under vacuum. Alternatively, the support is contacted with a solution of the extractant in a mixture of an organic solvent and water. For very hydrophobic extractants, the most satisfactory results (homogeneous impregnation of the support) have been obtained by contacting a solution of the extractant in a precalculated amount of solvent with a support until all of the liquid has been absorbed. Because none of these methods is particularly well-suited to the preparation of large quantities of EXC materials, procedures have been devised by which the extractant can be incorporated directly into the support during its preparation.

EXTRACTION CHROMATOGRAPHY

Solvent extraction is a versatile technique for the isolation, purification, concentration and separation of solutes. It is popular as it is rapid, simple and easy to operate. It is based on the principle that the solute distributes itself in a certain ratio between two immiscible solvents usually consisting of organic and aqueous phases. This method is applicable at macro gram as well as at trace concentrations. Due to easy availability of various types of new powerful extractants, this technique has been extensively employed in analytical chemistry. In order to achieve efficient separation this technique can be coupled with partition chromatography with some modifications^[1-6]. This technique is called "Reversed phase partition chromatography" or simply "Extraction chromatography". Thus the extraction chromatography is advantageous for the selectivity of organic compounds as well as the multistage character of a chromatographic process, where extraction and re-extraction takes place simultaneously. A chromatographic process is defined as occurring under "reversed phase" conditions whenever the support, either a paper strip or a bed of particles in a column hold the organic phase as the stationary phase while the aqueous

phase is the mobile one (eluent). The applications of the extraction chromatographic techniques in organic chemistry are well known e.g. a system of silica gel with water are useful for separation of hydrophilic substances and substances of medium polarity. Methanol, polyethylene glycol and formamide have been used as a stationary phase and a hydrophobic solvent as the mobile phase for the separation of lipids. It is also useful for the separation of epoxy and hydroxyl esters and polyunsaturated esters. This technique in early days was used for inorganic separations. "Reversed phase extraction chromatographers are to commended for having established so many valuable metal separations schemes on the basis of liquid-liquid extraction data." The statement comes from a well-known liquid-liquid extraction investigator^[7].

Thus solvent extraction and extraction chromatography are closely related. As a rule, extraction systems used in solvent extraction processes can be easily applied to extraction chromatography. The separation of similar elements which otherwise was not possible by a single stage liquid-liquid extraction has become a reality due to availability of extraction chromatographic technique. There have been significant developments in extraction chromatography. A number of authoritative monographs and reviews have appeared in various international solvent extraction conferences^[8-12].

CLASSIFICATION OF EXTRACTION SYSTEM

The classification of various extraction systems is based upon the process of extraction. Usually, when the extraction proceeds with the formation of chelates, it is termed as chelates extraction. Here the chelating ligand replaces the coordinated water molecule from the coordination sphere to form neutral species. Such species are readily soluble in organic solvents. In extraction by ion pair formation a neutral uncharged species is formed by the association of metal ion with bulky organic counter ions like high molecular weight amines. As a result, the metal ion is transferred to the organic phase. In extraction by solvation the oxygen bearing organic solvents, solvate the neutral inorganic species. Finally, in synergic extraction, two different extractants, which are capable of individually extracting a metal ion partially, are employed together, as a result of which

there is considerable enhancement in the extraction. A brief description of the extraction system is given below.

CHELATE EXTRACTION SYSTEM

The theory of chelate extraction has been more thoroughly studied than those of other extraction systems and it is well known that the law of mass action can be applied most successfully to it. Factors that are known to be effective for liquid liquid extraction, with chelate systems such as pH optimization and the use of masking agents. Chelating agents that have been used as stationary phase in extraction chromatography include eriochrome cyanine R, chromazurols, pyrocatechol violet, alizarins, ferroin, chromotropic acid, nitroso-R-salt, sulphosalicylic acid, tiron^[15], bis (salicyladehyde) – dl – stilbenzedimine or bis (salicyladehyde) – mесо – stilbenzediimine^[16] and 1-(2', 3' – dichlorophenyl) – 4, 4, 6 – trimethyl – (1 H, 4 H) pyrimidine – 2- thiol^[17]. Salen(NEt₂)₂^[18] was used as chelating agents for determination of trace copper(II), manganese(II) and zinc(II), 1-(4-Bromophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol^[19] were used for determination of tellurium(IV) and 1-(4-Bromophenyl)-4,4,6-trimethyl (1H, 4H) pyrimidine-2-thiol^[20] for bismuth(III). Some reagents are solid at ordinary temperature and the stationary phase generally consists of their solution in an organic solvent adsorbed on the support.

ION PAIR FORMATION

In this system, the extractable species is formed by interaction between an ion in the aqueous phase and an oppositely charged ion present in either the aqueous or the organic phase. However, the system cannot simply be described by the two ions forming an ion pair and other factors must be taken into account. In the extraction of metal through the formation of ion pair,

- I) A simple cation is extracted into a polar solvent as a pair with a comparatively bulky anion.
- II) A complex ion or a negatively charged chelate complex produced from a metal is extracted together with a bulky pairing cation.
- III) The metal is extracted as a cationic chelate species with a bulky pairing anion.

It is rather difficult to describe the equilibria of formation and partition of extracted complexes in ion-association systems. The law of mass action may also be applied as in chelate extraction system. The reason for this difficulty is that a large number of equilibria, such as higher aggregate formation are involved in the ion association system and that major activity coefficients are uncertain because of the high concentration of electrolytes employed. 2-Octylaminopyridine was used for solvent extraction of bismuth(III)^[21] and indium(III)^[22] from succinate media takes place via anion exchange mechanism. n-octylaniline has been explored as extractant for gallium(III)^[23], indium(III)^[24], thallium(III)^[25], lead(II)^[26] and aluminum(III)^[27], form the ion association species mechanism.

SOLVATION EXTRACTION SYSTEM

In this class the species extracted is solvated by the molecules of the organic solvent. The formation of such species with different types of solvents include weakly basic carbonyl compounds e.g. Ethers, Ketones and other oxygenated compound and also neutral organophosphorus compounds e.g. basic phosphates, phosphonates, phosphinates and phosphine oxides. All these neutral molecules which contains >O, >O=O or =O groups, coordinates to the central metal atom, while the oxygen atoms generally displace water molecules from the coordination sphere but in some cases they coordinate through water molecule bridge. Acid extraction by these compounds takes place through association of the anion with the complex cation formed by protonation of the extractant. For example, the extraction of HClO₄ by TBP (diluted in CCl₄) is assumed to involve an ion associated trihydrated hydronium ion at the highest TBP concentration. That is why these extractants are sometimes classified as ion association system, however, a clear distinction is advisable between them and the more basic ones containing nitrogen, which form ion pairs much more easily. The same treatment of extraction equilibrium as in the chelate extraction system may be applied to these systems that lead to the solvation number. Extraction chromatography with these compounds is of common use and especially TBP has been widely applied from the early days for the technique. Separation of [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ on a TBP

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column is also reported^[28]. Solvent extraction of scandium(III) has been carried out from sulfuric acid media using bis(2-ethylhexyl) phosphinic acid^[29] as extractant in toluene. D2EHPA and PC-88A was used as extractant for scandium(III)^[30], zinc(II) and copper(II)^[31] in perchlorate media.

SYNERGISTIC EXTRACTION SYSTEM

It is sometimes possible that a combination of two extractants results in distribution ratio greater than those obtained individually with either. This phenomenon is called the synergistic effect and is effectively used at present for better extraction. Some synergistic systems have seldom been applied to practical separations. The combination of the extractants includes the use of chelating agents (or acidic organophosphorus compounds) and neutral ligands or two different neutral ligands and two different acidic ligands. There are very few examples of application of synergistic systems to reverse phase

extraction chromatography. Some examples of the column methods include the separation of Sm-Eu and Cf-Cm by means of a mixture of HTTA with dibutyl diethyl carbamoyl phosphonate (DBDECP)^[32,33]. McKay has given the distribution ratio obtained with the column of HTTA, DBDECP and HTTA + DBDECP as stationary phase as 3.1, 3.3, 106.7 respectively and these values clearly demonstrate the synergistic enhancement due to the application of the mixed extractant. These few examples indicate that the synergistic effect takes place not only in the liquid-liquid extraction but also in extraction chromatography. Crown ethers with 8-hydroxyquinoline is used for solvent extraction of lanthanides^[34]. A review of crown ether containing extraction systems has recently been published^[35]. The cobalt(II) extracted with mixtures of 8-hydroxyquinoline and DB18C6^[36,37]. A brief review of different metals studied by various workers by extraction chromatography using different extractant and support are summarized in (TABLE 1).

TABLE 1 : Review of the metals extracted by extraction chromatography using different extractant and support

Extractant	Metals	Support	Mobile phase	Main features	Ref No
n-octylaniline	Ga(III), In(III) and Tl(III)	Silica gel	Distilled water	Separation of Ga(III), In(III) and Tl(III) separated from synthetic mixtures	38
Tributyl phosphate	Ge(IV)	Silica gel	0.01 mol/L HCl	Ge(IV) is separated from multicomponent mixture	39
Carboxylic acid (Versatic-10)	Cu(II)	Silica gel	0.02 mol/L HNO ₃	Separation of Cu(II) from binary mixtures, synthetic mixtures and alloy samples	40
Carboxylic acid (Versatic-10)	Hg(II)	Silica gel	0.02 mol/L HNO ₃	Separation of Hg(II) from binary mixtures and industrial sediment samples	41
Carboxylic acid (Versatic-10)	Tl(III)	Silica gel	0.01 mol/L HCl	Separations from Al(III), Ga(III), In(III), and Tl(III), multicomponent mixtures and synthetic mixtures	42
di-(2-ethylhexyl) phosphoric acid (HDEHP)	⁹⁵ Zr(IV), ⁹⁵ Nb(IV) and ¹⁷⁵ , ¹⁸¹ Hf(IV)	Kieselguhr Whatman no.1	6 N H ₂ SO ₄ + X N Oxalic acid + H ₂ O ₂ (Where X= 0.1, 0.5, 2.0 and 18 N H ₂ SO ₄ + 0.1 N Oxalic acid + H ₂ O ₂)	Quantitative recovery of metals using paper and column chromatography	43
Tributylphosphate	Cr(VI)	Silica gel	-	Separated from binary, multicomponent mixtures and from alloys	44
Versatic 10	Cd(II)	Silica gel	0.1 mol/L HNO ₃	Separated from synthetic mixture, alloys, removal and recovery of industrial waste.	45
SRS-100	Ga(III)	Silica gel	0.02 mol/L H ₂ SO ₄	Separated from Al(III), In(III), Tl(III) and multi-component mixtures	46
Versatic-10	Pb(II)	Silica gel	0.01 mol/L HNO ₃	Pb(II) separated from Cu(II), Sn(II), Hg(II) and Cu(II), Cd(II) and Bi(III). Alloys and industrial effluents.	47
Poly(acrylic acid)	Ce(IV)	Silica gel	0.02 mol/L HNO ₃	Separated from real samples viz. Monazite, bastnasite, and Al-Ce alloy. Ce(IV) separated from toxic and heavy metals.	48

Extractant	Metals	Support	Mobile phase	Main features	Ref No
Capric acid	Hg(II)	Silica gel	0.05 mol/L HNO ₃	Separated from Zn(II), Cd(II), Cu(II), Fe(III), Ni(II), Tl(I), Pb(II) and Zr(IV)	49
SRS-100	Hg(II)	Silica gel	0.1 mol/L HNO ₃	Separated from Mg(II), Cr(III), Mn(II), Co(II), Ni(II), Zn(II), La(III), Pr(III), Nd(III), Sm(III), and U(VI)	50
Amberlite LA-1	Th(IV)	Silica gel	-	Separated from U(IV), Zr(IV), Sc(III), Ce(IV), La(IV) and from monazite	51
Tributyl phosphate	Mn(II)	Silica gel	-	Separated from alkali metals, soils and minerals samples	52
Trioctylphosphine oxide	Zn(II)	Silica gel	4.0 mol/L HCl	Separated from alloys, alkali and alkaline earth metal, trivalent rear earths and platinum group metals.	53
Tri-octylphosphine oxide (TOPO)	Be(III), Al(III)	Silica gel	0.5 mol/L HCl for Be(III) 3.0 mol/L HNO ₃ for Al(III)	Separation of Al(III) and Be(III) from multicomponent mixtures and real samples viz. devardas alloy and monel alloy.	54
Triisobutylphosphine sulfide (TIBPS)	Hg(II)	Silica gel	-	Separated from waste effluent	55
Organophosphorous extractants	Pu(IV), Am(III) and Eu(III)	Silica gel	-	Separation of actinides from waste solutions	56
Aliquat 336 and Thorin I	Fe(III), Co(II), Ni(II)	Silica gel	-	Separation of nicle, cobalt and iron	57
Acetylacetone (AA)	Cr and Ni	Kel-F	-	Separation of nickel from alloys.	58
N,N,N',N'-tetraoctyl diglycolamide (TODGA)	La(III), Pr(III), Pm(III), Eu(III), Tb(III), Ho(III), Er(III), Yb(III) and Lu(III)	Chromoso rb-W	2.5 mol/L HNO ₃	-	59
Aliquat 336	Niobium and Tantalum	Kieselguhr	M HF 10 mol/L HNO ₃	Require low concentration of Aliquat 336	62
Quaternary ammonium salt and Aliquat 336	molybdenum and tungsten	Kieselguhr	0.05 mol/L and 0.1 mol/L HCl	Quantitative recovery	63
TODGA+TBP	Actinides	-	-	Actinides and lanthanides separated from fission products	64
Adogen-381	-	Celite	-	Separation of radiotracers from one another	65
Aliquat 336	Cr(VI), Cd(II) and Zn(II)	Polystyrene	-	-	66
Aliquat 336	Cr(VI)/Cd(II) and Cr(VI)/Zn(II)	Polystyrene	-	-	67
Aliquat-336	La(III) and Gd(III)	XAD-4	-	Removal of La(III) and Gd(III) with nitric acid media	68
di(2-ethylhexyl)phosphoric acid (DEHPA) and tri-n-octylphosphine oxide (TOPO)	Zn(II), Cu(II) and Cd(II)	Amberlite XAD2	-	-	69
Morpholine dithiocarbamate (MDTC)	Cu(II), Cd(II), Zn(II), Pb(II), Ni(II) and Mn(II)	Amberlite XAD-4	-	Separation of trace metals in seawater.	70
Petroleum sulfoxide	Yttrium and Lanthanides	Silica gel	-	Separation of yttrium from lanthanides, rare-earth ores	71
Bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid	Ti(IV)	Silica gel	-	Titanium from red mud. Binary separation from associated metals	72
Quinalizarin [1,2,5,8-tetrahydroxyanthraquinone]	Cu(II), Cd(II), Co(II), Pb(II), Zn(II), and Mn(II)	Amberlite XAD-2	4.0 mol/L HNO ₃	Cobalt separated from vitamin tablets	73
Tri-n-octylphosphine oxide (TOPO)	Th(IV)	Silica gel	0.01 mol/L H ₂ SO ₄	Separation of Th(IV) from monozite ore	74

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Extractant	Metals	Support	Mobile phase	Main features	Ref No
2-hydroxy-propiofenone-4-phenyl-3-thiosemicarbazone (HPPPTSC)	Co(II), Cu(II), Pb(II), Ni(II) and Zn(II)	Amberlite XAD-7	-	Separation of trace metals in river water and plant leaves	75
Cyanex 921 (tri-octyl phosphine oxide, TOPO)	Cadmium	Amberlite XAD-7	3.0 mol/L HCl	Equilibration time 8 hr	76
Tri-octylphosphine oxide (Cyanex 921)	Fe(III)	Amberlite XAD-7	0.1 mol/L HNO ₃	Extraction capacity increases with temperature	77
Cyanex 301	Cadmium	Amberlite XAD-7,	5.0 mol/L HCl	Recovery of cadmium from industrial phosphoric acid	78
TBP	Eu(III) and Am(III)	XAD-4	-	-	79
Xylenol Orange	Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III)	Amberlite XAD-7	2.0 mol/L HCl	Analysis of metal ions from river water, vitamin tablets	80
di(2-ethylhexyl)phosphonic acid (EHEHPA)	Rare earths Metals	Styrene-divinylbenzene	-	-	81
Primene JM-T	-	Silica gel	-	-	82
Aliquat 336S	Germanium	Silica gel	0.5 mol/L HCl	Separated from coal fly ash	83
Aliquat 336S	Bismuth	Silica gel	0.1 mol/L H ₂ SO ₄	Separated from binary, ternary mixtures and low fusible alloy	84
Bis(2-ethylhexyl) phosphate	Lead	Silica gel	-	Separated from alloys, sediments and wastewater	85
Tri-octylphosphine oxide	Se(IV) and Te(IV)	Silica gel	4.0 mol/L HCl and 1.0-2.0 mol/L HCl	Separation from multicomponent mixtures	86
Tri-octylphosphine oxide	Gallium	Silica gel	-	Separated from binary, multicomponent mixtures and bauxite ore	87
Tri-n-octylamine	Lead	Polytetrafluoroethylene	-	-	88
Tri-octylphosphine oxide	Sb(III)	Silica gel	0.5 mol/L HCl	Separated from multicomponent mixtures alloys transition metals	89
Tri-octylphosphine oxide	Germanium	Silica gel	-	-	90
Tri-octylaminetriisooctylamine or Aliquat 336	Rare earth metal	Paper	NaOAc, Na malonate, Na succinate	Separation of ternary and quaternary mixtures	91
Bis(2-ethylhexyl) phosphoric acid	Sb(III)	Silica gel	2.0-8.0 mol/L HCl	Arsenic, antimony, bismuth and tin was separated	92

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