CHROMATOGRAPHIC SEPARATIONS USING LIQUID ION EXCHANGERS

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ABSTRACT

A review is made of the last 10 years literature on the application of liquid ion exchangers for chromatographic separations. The details of the various separations are given in Tables.

INTRODUCTION

Liquid ion exchangers have found considerable potential as extractants, both in liquid-liquid extraction as well as in extraction chromatography /1-15/. This technique continues to attract high interest because of its varied field of application, from large scale separation and purification to the preparation of carrier-free trace levels of isotopes, from designing and testing new extraction methods to physico-chemical examination of important systems to determine the underlying extraction mechanism and to evaluate the role of molecular, structural and experimental parameters that will help in the improvement of existing systems. It is an important tool in nuclear fuel reprocessing and hydrometallurgy /16,17/. The use of liquid ion exchangers in ion-selective electrodes is progressing /18,19/ and these extractants also find wide application for the removal of toxic metal ions such as Zn, Cd, Hg, As, Sb from industrial wastes /20-25/ as well as for the determination of traces of elements in geological specimens, soils, sediments and natural waters /26/.

Chromatographic methods in which solvent extraction procedures have been used in a continuous separation process using inert supports impregnated with the extractants combine many of the advantages of both liquid-liquid extraction and ion-exchange chromatography, which are the two most important separation techniques of analytical chemistry. The above technique of extraction chromatography combines the selectivity inherent to solvent extraction and the multistage steps of a chromatographic process. Chromatographic separations with liquid ion exchangers essentially belong to this class. Extraction chromatography with ion exchanger-impregnated columns has many advantages over extraction chromatography with other extractants or the separation achieved with resin exchangers, such as well defined elution curves, narrow peaks, high selectivity and higher exchange rates /27/. These techniques are of the reversed phase chromatographic type where the organic extractant is immobilised on some stationary inert support such as silica gel, kieselguhr, polyethylene, polyglycol, cellulose, styrene-DVB copolymer or simply filter paper, which was introduced first by Fidelis and Siekierski /28/. The incorporation of an extractant into a cross linked copolymer of styrene-DVB to yield a material having useful properties as a column packing was first reported by Small /29/ and he named the technique 'gel-liquid extraction'. Columns containing open-cell polyether type polyurethane foam loaded with an ion exchanger is used for simply sensitive detection /86/ as well as for reversed phase foam chromatographic separations /44/.

Chromatographic separations employing both anion and cation exchangers have been widely reported after the introduction of the various methods of extraction chromatography /30-32/ by Testa and Cerrai. A few reviews have also appeared periodically on the extraction chromatographic separations of liquid ion exchangers /11,13,33,34/. These reviews cover the various extraction chromatographic methods using liquid ion exchangers such as column, paper, tlc, gel-liquid extraction chromatography, etc. Both anion and cation exchangers find wide application for the separation of closely associated elements such as rare earth mixtures, separation of actinides from lanthanides, etc. Solutions of strong monobasic acids and their alkali salts are generally selected as the aqueous phase for elution.

The present review surveys the literature from 1972 to 1983 on the analytical application of liquid ion exchangers for extraction chromatographic separations and includes the various separations carried out on column, thin layer and paper using both liquid anion and cation, exchangers. The various experimental details have been classified and tabulated accordingly (Tables 1, 2 and 3).

TABLE 1

Column chromatographic separations with liquid anion exchangers

Liquid ion exchanger	Separation	Support	Absorption medium	Elution	Other details	Ref.
Alamine 336	Sn & Sb	Celite 350	6 M HCl	Sn – 6 M HCl Sb – 1 M HCl		42
Aliquat 336	Co from Cd, Pb, Zn, Mn Ni, Cu & Fe(II)	Silica gel	Nitroso-R Salt, $HClO_4$	Cd, Pb, Zn, Mn – 0.05M Ni, Cu, Fe(II) – $HClO_4$ Co – 1 M $HClO_4$		43
	Co, Ni, Fe & Cd	Polyurethane foam	HCl	Co, Ni – 3 M HCl		44
Amberlite LA-1	Sc from 20 metal ions	Silica gel	pH 5.0, 0.01 M malonic acid	Sc – 2M HNO_3, 0.5M H_2SO_4 or 1M HCl	Sc separated from Zn, Cd, Hg, Pb, Ni, Sn, Al and La by selective absorption and from Zr, Th, Fe, Ga, In, Ce, Ti, Y and U by selective elution using suitable eluents from mixtures of 3 or 4 components. Extraction mechanism discussed.	45

Amberlite LA-2	Th, Zr, U & rare earths	Silica gel	0.025 M H_2SO_4– 1.0M$(NH_4)_2SO_4$	Th – 0.1 M H_2SO_4 Zr – 4 M HCl U – 1 M $HClO_4$	Rare earths e.g. La, Y, Yb and Sm do not absorb	45
Kelex 100	Cu & Ni	Amberlite XAD-7	pH 1.0	Ni – 1 M NaCl adjusted to pH 1.0 Cu – 2 M HCl	The ion exchanger is an 8-hydroxyquinoline based chelating liquid ion exchanger	47
	Fe & Al	”	pH 1.0-2.0, K Na tartrate	Al – K Na tartrate Fe – 3 M HNO_3		
TBA	As, Cu & Sb	Silica gel	HCl	As, Cu – HCl	Retention of Sb 99.9% As and Cu recoveries 99.6 and 99.8% respectively.	48
TDA	In, Cd, Zn, Pb & Fe(II)	PTFE	5M HCl	Pb, Fe(II) – 5 M HCl In, Zn – 0.01M HCl Cd – 0.1M NH_4Cl-0.1M NH_3	Method used for determining In and Cd in Pb concentrate and In and Cd in pyrite	49

TABLE 1 (cont.)

Column chromatographic separations with liquid anion exchangers

Liquid ion exchanger	Separation	Support	Absorption medium	Elution	Other details	Ref.
TOA	Ga & Al	PTFE	pH 2.5 2M NH_4SCN	Al – 2 M NH_4SCN Ga – 0.1 M HCl	99% recovery	%
	Ga & Fe	Teflon	pH 2.5 2M NH_4SCN	Ga – 0.1 M HCl Fe – 1.5 M HI in 2 M HCl	Spectrographically pure Ga	50
	Co & Ni	Polyurethane foam	8 M HCl	Ni – 8 M HCl Co – 1 M HCl	100% recovery. Applied for measuring the degree of contamination of Ni salts with Co	50
	Mn, Fe, Co, Ni, Cu, Zn & Cd	Silica gel	HCl	Gradient elution by increasing concentration of HCl and HNO_3	Quantitative separation	51
	Ag, Bi, Cd & Zn	Kel – F	2 M HCl	Ag & Bi – 5.5 M HCl Zn – Water Cd – 5 M HNO_3	94-100% recoveries	52

Cr, Mn, Ni, Co, Cu & Zn	Silica gel	8 M HCl	Cr, Mn, Ni – 8 M HCl Co, Cu – 1 M HCl Zn – Water	Applied for determination in Gallium arsenide	53
In & Ga	PTFE	HCl	In – 5.5 M HCl Ga – 0.05 M HCl	––	54
In & Ga	PTFE	HCl	In – 9 m HCl Ga – 0.05 M HCl	Applied for the determination of Ga in metallic In	55
Pd, Pt & Ir	Silica gel	––	Pd – 2.25 M HCl-3M HNO_3 Pt – 2.25 M HCl-4M HNO_3 Ir – 2.25 M HCl-5M HNO_3	Separation of high purity non-volatile platinum group metals from their mixtures and from Au which is strongly retained on the column.	56
B & Fe	PTFE	HCl	B – 8 M HCl	Flame photometric determination of B in steel after separation.	57

TABLE 2

Column chromatographic separations with liquid cation exchangers

Liquid ion exchanger	Separation	Support	Absorption medium	Elution	Other Details	Ref.
HDEHP	Am(V), Am(III) & Np(V)	Celite 545	Weakly acidic	Am(V) – 0.1 M HCl Am(III) – 2 M HNO_3	Am(VI) is reduced to Am(V) and partially to Am(III) when introduced into the HDEHP column. The content of AM(V) decreased slowly in the NO_3^-, OAC^-, SO_4^{2-}, ClO_4^- solution at lower temp. but rapidly decreased in Cl^-, I^-, SO_3^{2-} and H_2O_2 solutions Np(V) passes without absorption.	68
	Rare earths	Silica gel or Hyflo super-gel	0.1 M HCl	Increasing concentrations of HCl	Extraction mechanism discussed	69
	Bk		0.3 M $KBrO_3$, 6 M HNO_3	Bk – 4 M HNO_3- 3% H_2O_2	Separation and purification of Bk	70

Am & Ce	PTFE	pH 3.0, diethylene triamine pentaacetic acid, Conc. NH_3 and cloroacetic acid.	Am – by influent Ce – 5 M HCl	98% recovery. Applicable for the separation of any lanthanide from actinides.	71
Pu (VI), Ce(IV) & Zr(IV)	PTFE	1 M HNO_3	Ce – 0.1 M HCl Pu – 5 M HCl Zr – 0.1 M oxalic acid or HNO_3		72
La, Ce & Nd	Chromosorb W	pH 2-3, HCl	La,Nd – 0.396 M HCl	Ce passes without absorption. Separation of binary mixtures of La-Ce & Nd-Ce is effected by the same eluant.	73
Ce & Nd	Chromosorb W AW-DMCS	HCl	Nd – 0.345 M HCl Ce – 0.09 M HCl		74
Nd	Chromosorb W AW-DMCS	HCl	Nd – 0.36 M HCl		75
Mo & Tc	Kieselguhr	0.1 M HCl	Tc – 5% NaCl Mo – 8 M HCl		76
In from Cd & Ag	PTFE	HNO_3	Cd & Ag – 2 M HNO_3 In – 2-3M HCl	Method used to separate carrier free ^{111}In during activation analysis on the $^{111}Cd(p,n)$ ^{111}In or $^{109}Ag(\alpha, 2n)$ ^{111}In reaction.	77

TABLE 2 (cont.)

Column chromatographic separations with liquid cation exchangers

Liquid ion exchanger	Separation	Support	Absorption medium	Elution	Other details	Ref.
HDEHP	Fe(III) from Co, Ni, Ca, Mn & Mg	PTFE	0.5 M HCl	Fe – 5.5 M HCl	Co, Ni, Ca, Mn and Mg pass without absorption	78
	U(VI), Mo(VI), ^{95}Zr, ^{95}Nb & ^{154}Eu	PTFE or Hyflo super-gel	dil. HCl	Eu – 1 M HCl U & Mo – 8.9 M HCl Zr & Nb – 8% oxalic acid	Applied for the separation of aged spent nuclear fuel solution	79
	Gd & Tb from Y	Silica gel	–	Gd & Tb – 0.5 - 0.9M HCL	Applied for the determination of rare earth metal impurities in high purity yttrium oxide	80
	U(VI) & Th(IV)	Styrene-DVB copolymer	HNO_3	U – 10 M HCl Th – 0.01 M EDTA		81
	Ce(III) & U(VI)	”	”	Ce – 0.1 M EDTA U – 10 M HCl		
	Co(II) & U(VI)	”	”	Co – 0.1 M EDTA U – 10 M HCl		

	Tb & Eu	—	0.7-1 M HCl or HNO_3	Tb – 2-3 M HCl or HNO_3	Eu passes without absorption	82
	U(VI) Np(IV) & Pu(III)	Fluroplast-4	0.5 M HCl	—	Pu passes without absorption whereas U & Np are absorbed completely. Desorption of U & Np with various eluents studied.	83
Bis(2-ethylhexyl) phosphinic acid	Er & Tm	M-type resin	2.5 M HNO_3	Er - 2.5 M HNO_3 Tm – 6 M HNO_3		84
LIX-64N	Cu & Ni	XAD-7	pH 2.8 (NaOAc-HCl buffer)	Ni-buffer (pH 2.8) Cu 2MHCl	Applied for the estimation of Cu in reference bronze and reference brass.	85
	Cu & Co	"	pH 3.5 (NaOAc-HCl buffer)	Co buffer (pH 3.5) Cu – 2M HCl		
	Cu & Mg	"	pH 3.8 (NaOAc-HCl buffer)	Mg – buffer (pH 3.8) Cu – 2 M HCl)		

TABLE 3

TLC/paper chromatographic separations with liquid anion and cation exchangers

Liquid ion exchanger	Technique	Separation	Support	Mobile phase	Other details	Ref.
Liquid anion exchangers						
Alamine 336	TLC	Ce, U & Th	Silica gel	2 M HNO_3	Extraction based on anion exchange, solvation, hydrolysis and interaction with the support.	58
Alamine oxide	TLC	Pb, B & Tl	Silica gel	6 M HNO_3		58
Alamine 336, Amberlite LA-1, Primene JMT, Alamine oxide	TLC	43 ions	Silica gel	HBr – LiBr	The sorption strength increases in the order primene JMT $<$ Amberlite LA-1 $<$ Alamine oxide $<$ Alamine	59
Aliquat 336	TLC	Ni from Cd, Zn, Cu, & Ag	Silica gel	1 M Na NO_2	Probable extraction mechanism discussed.	35
	paper	Y, La, Sc, Nd & Ce	Cellulose	pH 4.0, 0.1 M sodium acetate	Separated from ternary mixtures of various combinations using ascending development	60

Aliquat 336, Alamine 336, Amberlite LA-1 Primene JMT	TLC	Al, Fe(III), Co, Ni, Zn, Ag, Cd, Pb, Th & U(VI)	Cellulose	0.3-7 M SCN^- acidified with 0.01-1.0 M HCl	The sorption strength and extractive ability increased in the order primene JMT < Amberlite LA-1 < Alamine 336 < Aliquat 336. Extraction mechanism discussed.
Aliquat 336 TOA	paper	Os, Ir, Pt, Pd, Ru, Rh & Au	Cellulose	2-2.25 M HNO_3 and 2.25 - 4.5 M HCl	value increases in the order Au, Os, Ir, Pt, Pd, Ru, Rh.
Amberlite LA-1	paper	Au, Os, Pt, Pd, Ru, Rh & Ir	Cellulose	0.5-8 M HCl	Spots detected by spraying reagents. The chromatograms were developed by the circular, descending and wedge-strip methods.
	paper	Fe(III), Ga, In, U(VI), Zn, Mn, Co, Ni & V(IV)	Cellulose	8 M HCl	Identification by spraying suitable reagents
TOA and Amberlite LA-1	TLC	18 metal ions	Silica gel	Lactic acid, tartaric acid, citric acid, iminodiacetic acid, nitrilotriacetic acid, EDTA, glycine.	R_F values of various systems given graphically as a function of pH

TABLE 3 (cont.)

Liquid ion exchanger	Technique	Separation	Support	Mobile phase	Other details	Ref.
TOA	paper	26 metal ions	Cellulose	1-8 M HCl (or HNO_3) with or without $HClO_4$	Chromatograms produced by descending development.	65
TOA, TIOA	paper	Y, Sm, Nd, Ce & La	Cellulose	pH 4.0 0.1 M sodium succinate	Separations from ternary mixtures of various combinations using ascending development.	60
Liquid cation exchanger						
HDEHP	TLC	Rare earths	Silica gel	Ether, HNO_3	Adopted two dimensional chromatographic development.	66
	TLC	Rare earths from fission products.	Silica gel	Ether, HNO_3		67

FOOTNOTE:

HDEHP = Di (2-ethyl hexyl) phosphoric acid; TBA = tribenzylamine; TDA = Tridecylamine; TIOA = tri-iso-octylamine; TOA = tri-n-octylamine.

DISCUSSION

Amongst the various liquid ion exchangers, the anion and cation exchangers TOA and HDEHP, respectively find wider applications than others. The use of HDEHP for the separation of closely associated elements is particularly advantageous in the field of nuclear technology as it has a high potential for the separation and purification of rare earths and radioactive materials.

The basic mechanism of extraction in extraction chromatography with a liquid ion exchanger is essentially the same as that involved in liquid-liquid extraction of elements with liquid ion exchangers. This technique also involves the formation of an ionic species, anionic or cationic, which will be extracted into the corresponding liquid anion or cation exchanger, stationed on an inert support. This can subsequently be eluted selectively using an appropriate eluent. By changing the eluent, or by changing the concentration of the eluent, sequential separation of the various ions may be possible in a manner analogous to ion exchange chromatogrpahy using resins.

De Jong and coworkers /35/ have studied the separations of Mn, Co(II), Co(III), Ni, Cu, Zn, Ag, Cd, and Po by thin layer chromatography with silica gel impregnated with Aliquat 336 (NO_2) in toluene with the use of 0-5 M Na NO_2 as developing solvent. Metala nitrates were applied for separation. Liquid-liquid extractions of the same metal salts from aqueous media into a solution of Aliquat 336 (NO_2) in toluene have also been studied and the determinations were completed by atomic absorption spectrometry. The results of the two techniques were compared and it was found that the extraction efficiency varies in the same order as the sorption strength in extraction chromatography. This result is according to the expectations based on the relationship:

$$D = k\left(\frac{1}{RF} - 1\right);$$

where D is the distribution coefficient of the metal ion in liquid-liquid extraction and k is a constant which has been verified for the Cl^-, Br^-, NO_3^- systems. The nature of the metal-nitrite complex, the species extracted in both techniques, has been studied with Ag, Cd, Co(II) and Co(III). With Ag and Cd, the ratios $[Ag/Aliquat\ 336]_{org}$ and $[Cd/Aliquat\ 336]_{org}$ have been determined and found to have limiting values of 1.0 and 0.5 respectively. That is, the extraction occurs according to the equation:

$$R_4N^+ + NO_2^-{}_{org} + Ag(NO_2)_2^- \rightleftharpoons$$
$$R_4N^+ Ag(NO_2)_2^-{}_{org} + NO_2^-$$

and

$$2 R_4N^+ NO_2^-{}_{org} + Cd(NO_2)_4^{2-} \rightleftharpoons$$
$$(R_4N^+\rightleftharpoons_2 Cd(NO_2)_4^{2-}{}_{org} + 2NO_2^-.$$

For Co(II), the extraction was found to proceed by the following equation

$$2 R_4NO_2^-{}_{org} + Co(NO_2)_4^{2-} \rightleftharpoons$$
$$(R_4N^+)_2 Co(NO_2)_4^{2-}{}_{org} + 2 NO_2^-$$

The composition of the Co-complex was established by Job's method and the mole ratio method. With Co(III), the ratio $[Co(III)/Aliquat\ 336]_{org}$ is 0.5 which shows that the overall composition and the extracted complex is $[Co(NO_2)_3 \cdot 2\ Aliquat^+ NO_2^-]$ and the metal-containing species is probably $[Co(NO_2)_5(H_2O)]^{2-}$. Extraction can be described by the equation

$$2 R_4N^+ NO_2^-{}_{org} + Co(NO_2)_5(H_2O)^{2-} \rightleftharpoons$$
$$(R_4N^+)_2 Co(NO_2)_5H_2O^{2-}{}_{org} + 2 NO_2^-$$

The same workers investigated /36/ the separation of 10 ions Al, Fe(III), Co, Ni, Zn, Ag, Cd, Pb, Th and U(VI), by extraction chromatography from SCN^- medium on thin layers of cellulose impregnated with 4 anion exchangers, Aliquat 336, Alamine 336, Amberlite LA-1 and Primene JMT. The separations were also carried out, under the same conditions, with the same liquid ion exchangers by liquid-liquid extraction. They observed that both the sorption strength and extractive ability increases in the order Prime JMT < Amberlite LA-1 < Alamine 336 < Aliquat 336. They also observed that increasing the acidity of the aqueous phase generally decreases the sorption/extraction of the complex metal-SCN^- anions to a considerable extent. The composition of a few metal-SCN^- complexes was studied. The composition of the Co(II)-containing species extracted into the organic phase is established as $[(R_3R^1\,NH^+)_2\,Co\,(NCS)_4^{2-}]$. Nickel is present in the organic phase as $Ni\,(NCS)_6^{4-}$; however, depending upon the diluent used, $Ni\,(NCS)_4^{2-}$ may also be present. By studying the various aspects of extraction a general equation was formulated to represent the sorption process of all ions under investigation, as given below:

$$nRR^1_3NH^+NCS^-_{org} + M\,(NCS)^{n-}_{p\ aq} \rightleftharpoons$$
$$(RR^1_3NH^+)_n\,M\,(NCS)^{n-}_{p\ org} + n\,NCS^-_{aq}.$$

The anionic species involved in the extraction chromatographic separation of Sc with Amberlite LA-1 from malonic acid has been investigated /45/ and the extraction mechanism represented as

$$Sc\,(NO_3)_3 + 3\text{ malonic acid} \rightarrow$$
$$Sc\,(\text{malonate})_3^{3-} + 3\,HNO_3$$

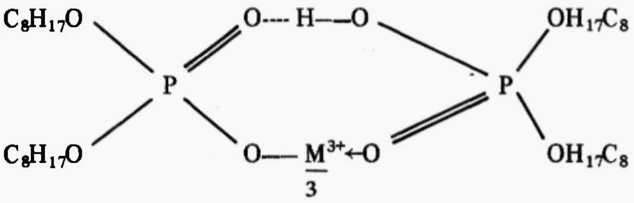
$$3\,(R_2\,NH_2)_2\text{-malonate} + 2\,Sc\,(\text{malonate})_3^{3-} \rightleftharpoons$$
$$2(R_2\,NH_2)_3\,Sc\,(\text{malonate})_3 + 3(\text{malonate})^{2-}$$

The extraction mechanism has been studied in a few cation exchange extractions also. Eckhard and coworkers /69/ have examined the extraction of rare earth metals with HDEHP from HCl medium and found that the extraction behaviour follows the equation

$$M^{3+}_{aq} + 3\,(HA)_2\,^{org} \rightleftharpoons M\,(HA_2)_{3\ org} + 3\,H^+_{aq}.$$

where $A = (C_8H_{17}O)_2\,POO^-_{org}.$

The structure of the chelate complex is visualised as



The distribution coefficient of the extraction is given by

$$D = \frac{[M(HA_2)_3]_{org}}{[M^{3+}]_{aq.}} = \frac{K\,[(HA)_2]^3_{org}}{[H^+]^3_{aq}}$$

Thus the metal cation is extracted by HDEHP by replacing the H^+ from the acid, thereby forming a chelate complex.

The use of chelating liquid ion exchanger /47/ is a favourable step towards selective separation. Polyurethane foam medium is also very promising for sensitive detection and separation.

MISCELLANEOUS

Apart from their applications to the separation of metals and non-metals, liquid ion exchangers are quite often used for the separation of common anions e.g. halides, ClO_4^-, CrO_4^{2-}. Mostly the separations are carried out on paper or thin layers impregnated with liquid anion or cation exchangers. Przeszlakowski and Kocjan have reported a few separations of common anions. The separation of halides has been reported /37/ on silica gel columns impregnated with 0.4 M solution of tri-n-octyl ammonium formate. Cl^- and F^- have been separated by elution with 5 mM of ammonium formate whereas Br^- and I^- can be eluted sequentially by 5 M ammonium formate. The anions were estimated using selective ion electrodes. The same workers studied /38/ the extraction chromatographic behaviour of 30 common anions on paper impregnated with tri-n-octylamine sulphate (or phosphate); the mobile phase was a solution of H_2SO_4 (5 mM-0.5 M), Na_2SO_4 (5 mM5 M), H_3PO_4 (3.5 mM-3.3 M) or NaH_2PO_4 (0.01 M-2 M). The sulphate system exhibited stronger eluting power than the phosphate system, but the latter was found more suitable for separation of anions with a weak affinity for the alkylammonium cations. Several separations have been listed using the above-mentioned eluents. Paper chromatographic separations of these anions have also been tried /39/ using aqueous solutions of acetic, formic, chloroacetic or trifluoroacetic acids and the corresponding sodium salts as mobile phases. The separations were carried out on paper strips treated with tri-n-octyl ammonium salts or Aliquat 336. Separations of anions have been investigated /40/ on paper impregnated with a 0.1 M solution of Aliquat 336, a salt of TOA or a salt of Amberlite LA-1 in benzene. Solutions of anions in the form of acids Na^+, K^+ or NH_4^+ salts were applied on paper. Chromatograms were developed with HCl, HNO_3 or $HClO_4$ or the Na^+ salt of one of the acids. The R_F values were calculated in each case and the affinities of the anions for the anion exchangers were reported. Of the mono, di and tervalent ions, ClO_4^-, CrO_4^{2-} and Fe $(CN)_6^{3-}$ were found to have greatest affinities.

The effects of complexing agents on metal ion separations have been studied /41/ by Muchova and Jokl on thin layers of silica gel impregnated with either anion or cation exchangers. With TOA and Amberlite LA-1, the mobile phases examined for the metal separations were HCl, H_2SO_4, HNO_3, LiCl, NaBr, NaI, KSCN, KCN, lactic acid, tartaric acid, citric acid, glycine, iminodiacetic acid, nitrilotriacetic acid and EDTA, whereas for the cation exchangers HCl, HNO_3 & KSCN were used as mobile phases. The R_F and R_M values of the metal ions were obtained as a function of the pH and the concentration of the mobile phases.

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