This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Use of Impregnated Silica Gel Layers and Modified Celluloses in Thin-Layer Chromatographic Analysis of Inorganic Mixtures

Jameel Ahmad[a]
[a] SENIOR ANALYTICAL LABORATORY, DEPARTMENT OF APPLIED CHEMISTRY, Z. H. COLLEGE OF ENGINEERING AND TECHNOLOGY, ALIGARH MUSLIM UNIVERSITY, ALIGARH, INDIA

To cite this Article Ahmad, Jameel(1995) 'The Use of Impregnated Silica Gel Layers and Modified Celluloses in Thin-Layer Chromatographic Analysis of Inorganic Mixtures', Separation Science and Technology, 30: 12, 2429 — 2454
To link to this Article: DOI: 10.1080/01496399508021394
URL: http://dx.doi.org/10.1080/01496399508021394

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **30**(12), pp. 2429–2454, 1995

REVIEW

The Use of Impregnated Silica Gel Layers and Modified Celluloses in Thin-Layer Chromatographic Analysis of Inorganic Mixtures

JAMEEL AHMAD
SENIOR ANALYTICAL LABORATORY
DEPARTMENT OF APPLIED CHEMISTRY
Z. H. COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202002, INDIA

Downloaded At: 11:59 25 January 2011

ABSTRACT

This review of literature covers salient features on the use of impregnated silica gel layers and modified cellulose layers as applied to the analysis of inorganic mixtures. One hundred and ten references have been cited from the literature published from 1963 to 1993. Although plain silica gel is commonly used for thin-layer chromatography of inorganics, silica gel impregnated layers play an important role for achieving particular separations of analytical importance and are more frequently used than plain adsorbents except for silica gel. Modified celluloses have received proper attention in the recent past, particularly for rare earths.

INTRODUCTION

A large number of stationary phases are used for thin-layer chromatography (TLC). No perfect adsorbent has been found. Some have great retaining power whereas others hold the adsorbate loosely. The adsorbing power of a substance varies greatly according to its fineness, method of preparation, activation process, etc. A good adsorbent must not chemically interact with the adsorbate. It should be colorless so it does not interfere with the chromatogram. The adsorbent should be noncatalytic, i.e., should not catalyze the decomposition of the substances, and insoluble in the solvent to be used. The physical and chemical properties of adsorbent should not change under the experimental conditions used.

Copyright © 1995 by Marcel Dekker, Inc.

Most workers have used silica gel (plain, chemically modified, and chemically bonded reversed phase layers) as the stationary phase. Cellulose (powdered, fibrous, microcrystalline, cellulose derivatives, and impregnated cellulose layers), alumina, synthetic inorganic ion exchangers with or without binder, silufol, glass powder, soil, NaX molecular sieves, and polyamide have also been used but to a lesser extent. Marlowska and Lepri et al. introduced chitosan (1, 2) as a new adsorbent. Macrocyclic polyethers have also been used as stationary phases (3). Stahr et al. used CRP-Whatman HP plates combined with densitometry for the analysis of selenium in biological tissues (4). Thin-layer sticks instead of plates have also been used for the separation of anions (5). Besides the possibility of changing the selectivity of a sorbent by chemical modification, improvement of selectivity can also be achieved by impregnating the matrix with suitable organic or inorganic substances (physisorption).

Downloaded At: 11:59 25 January 2011

ORGANIC IMPREGNANTS

Silica gel has been impregnated with diethylene triamine, sulfaguanidine, 8-hydroxyquinoline, *t*-butylamine, 2,2-dipyridal iminodiacetic acid, tributyl amine primene JM-T, Amberlite LA-1, Alamine 336, Aliquat 336, EDTA pyridinium tungstoarsenate, *p*-toluidine, etc. Microcrystalline cellulose has been impregnated with chitosan formate, bis-(2-ethyl hexyl) orthophosphoric acid, trioctyl phosphine oxide-bis-(2-ethyl hexyl) orthophosphoric acid, dibutyl phosphonate, etc.

INORGANIC IMPREGNANTS

Ceric molybdate, sodium molybdate, NH_4Cl, $Ba(NO_3)_2$, $NaNO_2$, $NaNO_3$, potassium ortho dihydrogen phosphate, NH_4SCN, $CuSO_4$, etc. have been used as impregnants for silica gel.

The two possible methods for impregnating the sorbent are the following.

Prechromatographic Impregnation of the Porous Matrix

The slurry is prepared with an aqueous solution of an acid, base, or salt, or in this way the support is impregnated with a solution of the liquid stationary phase of an organic, water-soluble compound instead of water, and subsequently the solvent is evaporated. This method has the advantage of exactly defined loading of the support with a stationary phase up to complete filling of the pores. Furthermore, in this case the composition and the film thickness of the liquid stationary phase are constant over the entire migration distance.

Self-Adjusting Impregnation during Chromatographic Development

1. By immersing the plate in a solution (usually 5–10%) of the involatile impregnation agent in a volatile solvent. The latter is then evaporated off.
2. By spraying the impregnation agent uniformly on the plate, removing the solvent as in 1.
3. By a type of ascending development with the impregnation solution, removing solvent as in 1.

Only the first method ensures that the stationary phase will be well defined with respect to both qualitative and quantitative composition. This is true both for addition of the impregnating agent to the suspension before plate preparation and for impregnating the precoated layer with an appropriate solution containing the liquid stationary phase.

Layers have been impregnated with buffers, chelating agents, metal ions, or other compounds to aid selectivity and resolution or detection of certain compounds. If plates are prepared in the laboratory, the reagent is usually added to the stationary phase slurry. Reagents are applied to precoated plates by spraying, brushing, or dipping. Plates impregnated with 0.1 M NaOH are used for the resolution of organometallics. Mohammad et al. showed that for metal ions, the impregnated silica gel layers were more selective than plain silica gel layers. More compact spots for metal ions were obtained when aqueous salt solutions were used as impregnants rather than as the mobile phase. A systematic TLC study of a number of inorganic ions on cellulose impregnated with liquid exchangers in HCl-NH_4SCN had been carried out by Kuroda et al. (8). Cellulose derivatives have been found useful for the separation of rare earths (9–11).

High molecular amines, substituted quaternary ammonium salts, heterocyclic amines (12), tetra-substituted pyrazol (13), and neutral organophosphorous compounds (14) have been extensively used as impregnants of the stationary phase.

During development with a solvent mixture, a liquid stationary phase is formed within the pores of silica gel, which changes in composition and amount along the development direction. The formation of such a gradient is a particularity of thin-layer chromatography. It can be attributed to different affinities of the solvent components to the surface of the silica gel.

Data available in the literature demonstrate that suitable impregnated silica gel (Table 1) and modified celluloses (Table 2) are used for virtually all mixtures of inorganic mixtures of interest. A selective review of literature published in various journals on TLC of inorganic cations, anions, and

Downloaded At: 11:59 25 January 2011

Downloaded At: 11:59 25 January 2011

TABLE I
Work Done on Impregnated Silica Gel Layers

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel impregnated with TBP (20% solution in benzene)	NH_4SCN, 2.5–10% oxalic acid, 4–8 N HCl (1 g:10:10), 2 N HCl	Nb, Ta, Rh, Ru, Pd, Au	—	—	15
Silica gel impregnated with TBP–benzene (1:1)	TBP–benzene (1:1), TBP–benzene (1:3), cyclohexanone, acetone, butanone, 4 N HCl	Au, Pt, Pd, Rh, Ir(III), Ir(IV)	Saturated chamber	The behavior of Fe, Co, and Cu on the separation of Pt, Pd, Rh, Ir(IV), and Au has been studied. Semiquantitative determination using reflectance densitometry. Standard mean deviations is 3–20%	16
Silica gel D-O (Fluka) impregnated with 0.1 or 0.05 M solutions of Amberlite LA-1, Alamine 336, or Adogen 464 in $CHCl_3$	1–11 N HCl, 1–11 M LiCl (acidified)	Cu, Co, Fe(III), Mn, Zn	Hellendahl jar, 3 cm run in ~10 min (HCl) or 0.5–3 h (LiCl)	Discussion of sorption mechanism in reversed phase chromatography	17
Silica gel impregnated with TiOA or TBP. Impregnation: 2 mL TiOA or TBP, dissolved in 25 mL ether, is equilibrated with appropriate acid. The extractant is mixed with 16.8 g silica gel, the ether is evaporated off. After the addition of 2.4 g $CaSO_4 \cdot 2H_2O$ the mixture in homogenized in 30 mL water	3 and 8 N HCl, 2 N H_2SO_4, and 5 N HNO_3	Cu, Ni, Co, Zn, Mo, Ti, Cr, U, Zr, Th, Mn	Run 3–8 cm in 5–40 min	—	18
HDEHP, DBP, or TBP impregnated silica gel (acid washed Wakogel B-O), and aluminum oxide DS-O (Camag)	1–12 N HCl, 1–16 N HNO_3	La, Pr, Eu, Dy, Gd, Er, Sm, Tb, Ho	Sandwich chamber, run 10 cm	R_F values decrease as the temperature decreases from 25 to 15°C. 0.02–0.25 μmol Gd can be determined semiquantitatively	19

Downloaded At: 11:59 25 January 2011

Impregnated silica gel (Wakogel B-5, 20 g) impregnated with 12% HDEHP in butanol (40 mL)	0.1–5 N HNO_3	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yp, Du	Sandwich chamber, run 8 cm in 3 h	Ni, Co, and Cu (R_F 1.0) are separated from rare earths by using 0.1 N HNO_3 as the mobile phase. U, Th, Sc, and Zr (R_F 0.0) are separated from the rare earths by using 10 N HNO_3 as the mobile phase	20
Silica gel (Wakogel B-5) impregnated with 1–7 N HNO_3. 1–10 N HNO_3, silica gel (Wakogel B-5, 15 g) impregnated with 0.08 M TOPO in butanol (32 mL)	100% TBP	Tb, Dy, Ho, Er, Tm, Yp, Th, U, Sc, Zr	Sandwich chamber	—	21
Silica gel D (Chemiewerk G-D) impregnated with HDEHP. Impregnation: 30 g silica gel is slurried with 6 mL HDEHP dissolved in 44 mL butanol-1	HCl and HNO_3 of several normalities	La, Ce, Pr, Sm, Nd, Gd, Eu, Tb, Dy, Ho, Er, Y, Yb	Run 9–10 cm in 2–3 h	—	22
Silica gel D impregnated with HDEHP	Aqueous solution of HNO_3 and HCl	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er	—	—	23
Silica gel impregnated with 1 N $HClO_4$	TBP–benzene (1:1), TBP–benzene (1:10)	Am(III), Cm(III), Pu(IV), U(VI)	Run 12–13 cm in 45–90 min	—	24
Silica gel H (Merck), Silica gel H (Merck) impregnated with olethylamine (25 mg/g silica gel)	Water, 0.1 N acetic acid	Na, K	Run in ~2 h	—	25
Silica gel H, Silica gel G, Silica gel H impregnated with tryptamine (25 mg/g silica gel), Silica gel G impregnated with tryptamine (25 mg/g) silica gel)	Water	Na, Rb, K, Cs	—	—	26
Silica gel D-O (Fluka) impregnated with 0.1 M solution of Amberlite LA-1 in	0.5–11 N HCl	Transition metal ions	Hellendahl jar, run 3 cm in 10 min	R_F data (for 12 ions) are reported	27

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
$CHCl_3$. Impregnation: Solution of amine equilibrated with 3 volumes of 2 N HCl					
Silica gel D-O (Fluka) impregnated with 0.1 M solutions of primary, secondary, or tertiary amine HCl salts and quaternary ammonium chlorides in $CHCl_3$	0.1–11.5 N HCl	Mn, Sb, Bi, Fe, Ni, Co, Cu, Pb	Hellendahl jar, Run 3 cm in 10–15 min	—	28
Silica gel D-O (Fluka) impregnated with 0.1 M solution of various anion-exchangers in $CHCl_3$	0.5–10 N HNO_3, 0.5–8 N HBr, 0.5–7.4 N HI, 0.5–7 M NH_4SCN acidified with HCl, 0.5–10 N $HClO_4$	Cd, UO_2, Hg, Sb, Cu, Bi, Th	Run 3 cm in 10–20 min	—	29
Silica gel (Wakogel B-O) impregnated with dithizone. Impregnation: 10 g silica gel slurried with 30 mL 0.3% dithiazone in $CHCl_3$	1 or 2 N acetic acid–acetone (1:1) or 2 or 4 N acetic acid–acetone (1:0.66)	Hg, Cu, Cd, Ni, Zn	Run 2 h, 28–30°C. Circular development	—	30
Silica gel G (Merck 30 g) slurried with a solution of Amberlite La-2 in $CHCl_3$ (70 mL)	0.1–7 M NH_4SCN	Ag, Cu, Cd, Bi, Mn	Double saturated chamber. Run 12.5 ± 0.5 cm, 25 ± 0.1°C	—	31
Silica gel (Whatman SG-41) or granulated PVC (Corvic D_{55}/3, ICI), impregnated with TBP, HDEHP, or TiOA. Impregnation: A solution of the extractant in a volatile	0–12 N HCl	Ni, Cu, Co, An, Gd, Tb, Ho, Er, La, Eu, Sr, Y, Mn, Zn, Fe	Run 10 cm in 40–50 min, horizontal ascending and descending development techniques used	—	32

Downloaded At: 11:59 25 January 2011

solvent is allowed to run over the thin layer					
Silica gel MN N-HR impregnated with TBP and nonimpregnated. Impregnation: 30 g silica gel with 70 mL TBP or CCl_4	1–9 N HCl	Transition metal ions	Double saturation chamber. Development time 1–3 h, 25 ± 0.5°C	—	33
Silica gel G (Merck) washed with HCl or EDTA	0.3 N HCl in methanol, TTA solution in MeOH, 0.1 M NH_4SCN in MeOH, 0.4 N HCl in MeOH, 0.025 M EDTA in MeOH, containing 8% water	Ba, La, Sr, Y, Sn, Ce, Cd	Run 10–15 cm in 20–55 min	Two-dimensional chromatography separation of Ba, Nb, Hf, Zr, Sn, La, and In	34
Silica gel D-O (Fluka), impregnated with TOPO or TBP. Impregnation: Solution of TOPO or TBP in $CHCl_3$ equilibrated with 3 volumes of 2 N HCl and mixed with silica gel: Silica–$CHCl_3$ (1:2 v/v)	0.5–10 N HCl	Sc, Ti, Th, Cr, Mn, Fe, Co, Cu, Zn, Ga, Y, Zr, Mo, Ag, Cd, In, Sn, Sb, Hc, Re, Au, Hg, Pb, Bi	Hellendahl jars, run 3 cm	—	35
Silica gel D-O (Fluka), impregnated with Primene JM-T, Amberlite LA-1, Alamine 336-S, or Aliquant + HSO_4^- and nonimpregnated	0.01–10 N H_2SO_4 0.1–8 N $(NH_4)_2SO_4$	Sc, Ti, V, Fe, Zr, Mi, Ce(III), Ce(IV), Hf, Re, Bi, Th, U(IV), U(VI), Be, Mg, Al, Mn, Co, Ni, Cu, An, Gu, Y, Cd	Hellendahl jars	—	36
Silica gel D-O (Fluka) impregnated with 0.1 M solution of primene JM-T, Amberlite LA-1, or Alamine 336 in $CHCl_3$ or nonimpregnated	0.1–11.5 N HCl	Be, Mg, Al, P, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Cn, Ga, Ge, As, Se, Br, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Ba, La, Er, Hf, W, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U	Hellendahl jars	—	37

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel D-O (Fluka) impregnated with Primene JM-T, Amberlite LA-1, Alamine 336-S, AlamO, TOPO, or TOAsO	0.2–9 N HBr, 2–10 M LiBr acidified with 0.5 N HBr	42 ions	Run 3 cm	—	38
Silica gel D-O (Fluka) impregnated with 0.1 M solutions of AlamO or TOAsO in $CHCl_3$	0.1–11 N HCl, 0.1–9.5 M LiCl acidified with 0.5 N HCl	Transition metals	Run 3 cm in 8–15 min	—	39
Silica gel (5–30 μm, Velvary) impregnated with 0.1 M solutions of TnOA (-) or Amberlite LA-1 (-) in C_6H_6	Aqueous solutions of strong acids and alkali salts	Be, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg, Cd, Sn(II), Sb, La, Hg, Pb, Bi, U	Saturated chamber, run 10 cm in 30–135 min	—	40
Silica gel (Velvary) impregnated with 0.1 M solutions of TnOA (-) or Amberlite LA-1 (-) in C_6H_6	Lactic acid, tartaric acid, citric acid, glycine, iminodiacetic acid, nitrilotriacetic acid, hydroxyethylene, iminodiacetic acid, EDTA	Mg, Be, Al, Hg, Bi, Fe, Cu, Ag, Hg, Pb, Mn, Co, Ni, Zn, Cd, La, Cr, Sb, U	Saturated chamber, run 10 cm in 30–120 min	—	41
Silica gel D-O (Fluka) impregnated with 0.1 M Amberlite LA-1 in $CHCl_3$	2–10 N HCl	Fe, Co, Ni, Cu, Sn, Sb, Bi, Mo	Metal contents in mineral powders	The analysis of 30 sulfide minerals is reported	42
Silica gel D-O (Fluka) impregnated with 0.1 M Amberlite LA-1 in $CHCl_3$	2, 6, and 10 N HCl	Be, Pt, U, Cr(VI), S, Sr, Y, Zr, Mo, Ba, Re, W, Th, U, rare earths	Metal contents in powdered minerals	—	43
Silica gel H (Merck) impregnated with 3% $AgNO_3$ (10 mL/4 g silica gel)	Water (saturated with isobutanol), 10–15% aqueous ammonium acetate. Water (saturated with isobutanol)–40% ammonium acetate (4:1)	I^-, Br^-, Cl^-, PO_4^{3-}	Plates accommodated to water vapor. Horizontal and ascending development on 2.5 mm wide thin layer strips	—	44

Downloaded At: 11:59 25 January 2011

Silica gel impregnated with EDTA 2Na	EtOH–1% NaOH (80:30) and (80:40)	Cu, Ag, Cd, Hg, Pb, Bi, As, Sb	Developed at constant temperature (30 ± 1°C)	—	45
Silica gel impregnated with ceric molybdate	C_6H_6–ethyl acetate–CH_3COOH–HCl (60:30:10:0.5) and (60:30:10:1)	Cu, Ag, Cd, Hg, Pb, Bi, As, Sb, Se, Al, Cr, Fe, Co, Ni, Zn	Developed at 30 ± 1°C	—	46
Silica gel impregnated with *p*-toluidine	BuOH–ethyl acetate–CH_3COOH–H_2O (60:40:30:50) and (80:40:30:50). 0.1 M HCl (3:1:1). Ethyl acetate–ethanol–1 M HCl (3:2:2)	Ag, Cu, Cd, Hg, Pb, As, Sn, Se, Mo	—	—	47
Silica gel KSK + NH_4NO_3 is salting out agent + starch (1:0.1:0.01), equilibrium mixture 10%-	0.11 M HSCN in methyl ethyl ketone	La, Ce, Pr, Nd, Sm, Eu, Gd, Y, Er, Yb	Ascending technique, run 10 cm	Mixtures of 10–12 REE at the submicrogram level are separated quantitatively	48
Silica gel (Velvary) impregnated with 0.2 M solutions of HDEHP in C_6H_6	Aqueous solutions of HCl, HNO_3, and KSCN (+ 0.1 N HNO_3)	Be, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, Sn, Sb, Ba, La, Ce, Hg, Tl, Pb, Bi, U	—	—	49
Silica gel impregnated with TBP–benzene (3:7), silica gel impregnated with 1 M thiourea	TBP–benzene (3:7–7:3) saturated with concentrated HCl, 1–8 N HCl, and 1–3 N HBr	Se, Te	Ascending and horizontal technique, 12–15°C	For semiquantitative determination after TLC, the appropriate zones are scraped off and eluted with HCl. Se and Te are determined photometrically	50
Silica gel impregnated with pyridinium tungustoarsenate	Butanol–acetic acid ethyl alcohol–acetone–water (60:10:30:40:10). Isopropanol–acetic acid–acetone (65:5:35)	Cu, Ag, Hg, Pb, Sb, Al, Ti, V, Fe, Co, Ni, Zn	Ascending technique	—	51

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel impregnated with diethylene triamine	1,2-EtOH:acetone $-CH_3COOH$ (70:50:20) and (40:50:20)	Ti, UO_2, VO, Th, Zn, Zr, Ni, Co, Fe, Ag, Cu, Cd, Hg, Pb, Sb, Se, Sn, As	—	—	52
Silica gel (BDH) impregnated with 0.5% sulfuguanidine	Isopropanol–ethyl acetate–DMF–acetic acid–H_2O (60:30:5:5:10) and (60:30:3:5:10)	Ni, Co, Fe, Ag, Th, UO_2, V, Cu, As, Pb, Cd, Ng, Pd, Sb, Se, Sn, Ti, Mo, Pt	Ascending technique, layer thickness 0.5 mm, plates dyed at 60 ± 1°C for 24 h	Detection limit of metal ions on chromatoplates was 1.0–7.0 μg	53
Silica gel impregnated with 8-hydroxyquinoline silica gel impregnated with dibenzoylmethane Plain Silica gel G	BuOH–ethyl acetate–HOAc (4:1:1). Ethyl acetate–CH_3COOH $-H_2O$–pyridine (3:1:1:0.5)	Pb, N, Zn, Ni, Co, Cu, Fe, Mg, Al, V, UO_2, Th	Ascending technique, run 10 cm, layer thickness 0.5 mm, plates dried at 60 ± 1°C for 24 h	Dibenzoylmethane impregnation offers a method for the removal of iron from silica gel G	54
Silica gel impregnated with 0.3 M aq sodium molybdate	1 M HCOOH–1.0 M HCOONa mixtures	Fe, Cu, Cd, Zn, Ni, Co, Cr, Pb, Al, VO, Zr, Th, UO, Ag	Ascending technique, run 10 cm, development time 12–15 min, layer thickness 0.25 mm	Semiquantitative determination of nine cations on stationary phase has been achieved by spot area measurement method	55
Silica gel impregnated with 30% *S*-butylamine. Silica gel impregnated with 30% *t*-butylamine	1.0 M aq HCOOH, 1.0 M aq HCOONa (1:1, 2:8, 4:6, 6:4, 8:2)	VO, Fe, Al, Fe, UO_2, Bi, Tl, Mo, Cd, Cr, Pb, Zn, Ni, Cu, Th, Se, Ag, W, Zr	Ascending technique, run 10 cm, development time 15–20 min	*S*-Butylamine impregnated silica gel layers were more selective for metal ions at lower pH value of the mobile phase (pH 1–2.5) than *t*-butylamine impregnated silica gel layers and vice versa	56
Silica gel impregnated with 0.5% aq solution of 2,2-dipyridyl. Silica gel impregnated with 0.75% aq solution of iminoacetic acid	Isoamyl alcohol–H_2O–AcOH (20:10:10). MeIH–C_6H_6–AcOH (20:10:15)	Pb, Mg, Cu, Cd, Zn, Fe, Mn, Hg, UO_2, As, Th, V	The impregnated silica gel plates were activated at 60 ± 1°C for 24 h, run 10 cm	—	57
Silica gel impregnated with 0.5 M NH_4Cl. Silica gel impregnated with saturated aq solution of $Ba(NO_3)_2$	Aqueous formic or acetic acid and sodium formate or acetate	Ag, Al, Cu, Th, Mo, Pb, Cd, Fe, Ni, Zr, Tl, Se, W, UO_2, VO	Ascending technique, run 10 cm, development time 12–15 min,	The method is used for semiquantitative determination of Pb, Ag, Se, Cd, Al, and Th by spot area measurement.	58

Downloaded At: 11:59 25 January 2011

			layer thickness 0.25 mm, activation temperature 100 ± 5°C, time 2 h	Quantitative separation of uranium from numerous metal ions	
Silica gel impregnated with 0.1 M $NaNO_2$, 0.1 M $NaNO_3$, 0.1 M sodium molybdate, 0.1 M potassium orthodihydrogen phosphate	1.0 M HCOOH–1.0 M salt solution (1:9, 9:1) and 0.1 M formic acid	Al, Fe, Co, Ni, Cu, Zn, Ag, Cd, Hg, Hg_2, Tl, Pb, Bi	Ascending technique, run 10 cm	Quantitative separation of Ni from Fe, Zn, Cd, and Pb has been achieved at microgram and milligram levels	59
Octadecyl silica gel. Aminopropyl silica gel	MeOH–H_2O (90:10 v/v) + acetylacetone (5–10) + diethylamine (0.5–1%)	Metal complexes of tetraphenylporphine with Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	—	Most of the complexes can be successfully developed without undesirable demetallation of the complexes. On octadecyl silica gel plates, the mobility (R_F) of the complexes of lanthanide metals tends to decrease in the order of the atomic number of the metals whereas on aminopropyl silica gel plates the reverse order occurs	60
Silica gel soaked in a solution of glycidoxypropyl trimethoxysilane in toluene at 110°C	—	A series of strictly related *trans*-($PdCl_2L_2$) complexes where L = hydrazone	After soaking 45 min, the plates were washed with C_6H_6, then with MeOH, and dried	The plates were also used to study the reaction of ligand exchange in solution between Pd complexes with different ligands	61
Silica gel impregnated with hydroxy benzoic acids	—	Transition metals	Ascending technique	The results obtained can be used to gain a better insight into the behavior of metals under the proposed chromatographic conditions	62
Silica gel + starch + ammonium nitrate	Trialkylammonium chloride (N263)–*n*-octyl alcohol–petroleum ether–concentrated HNO_3 (6.0:70:25.0:1.0)	La, Ce, Pr, Nd, Sm, Eu, Gd	—	The R_F values of rare earths decrease with an increase in atomic number	63

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel + starch + ammonium rhodanate (2.8:0.15:0.5 by weight)	Trialkylmethyl-ammonium chloride (N263/*n*-octyl alcohol/petroleum ether/HCl system (2.0:60:30:1.2) and (2.0:10.0:30.0:1.0)	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tn, Yb, Lu	—	The R_F values increase with an increase in the volume ratio of N263 and the number of rare earth elements. The R_F values of rare earths decrease with an increase in the volume ratio of *n*-octyl alcohol, petroleum ether, and concentrated HCl	64
Silica gel impregnated with 3 N HNO_3	Tri-*n*-butyl phosphate synthine (23:77)	Ru(III), Pu(IV), Pu(VI)	Ascending technique	Separation of Pu(III) (R_F 0.0) from Pu(IV and VI) (R_F 1.0) achieved. Disproportionation of Pu(IV) in HNO_3 and $HClO_4$ solutions	65
Silica gel H + ammonium nitrate (4%) + sodium cellulose (1%)	Dilute 2-ethyl hexyl phosphate–diisopropyl ether–diethyl ether–nitric acid (0.4:8:8:0.07)	Y, Sm, Nd, Pr, Ce, La	—	Densitometric determination of individual rare-earth metals (La, Ce, Pr, Nd, and Sn) in monazite sand	66
Oxalic-acid-treated silica gel layers	Ethyl acetate–acetone –formic acid–water (8:7:4:1)	Hg, Pb, Ni, Cu	—	Determination of microquantities of Hg(II) with TLC separation from Hg(I), Pb, Ni, and Cu on acid-treated layers and recovery of Hg(II) from river water and industrial wastewater	67
Silica gel G + *p*-toludine (50:1, w/w)	Acetonitrile–methanol (1:1)	5-Chloro-2,3-dihydroxy-pyridine complexes of Mn^{2+}, Co^{3+}, Cr^{3+}, and Fe^{3+}	Ascending technique, layer thickness 5 mm, drying of plates at 40°C for 24 h, run 11 cm, development time 30–40 min	The R_F values are in the order of Co > Fe > Mn > Cr. RPTLC separation of the complexes was also carried out on Zorbax ODS column with acetonitrile–methanol–water (6:1:3) eluent using UV-visible detector	68
Silica gel impregnated with 1) 1% sodium lauryl sulfate, 2) tetrabutyl ammonium bromide, 3) 1% Triton X-100.	Benzene, toluene, xylene, chloroform–benzene, xylene–benzene, toluene–benzene,	Pb, Cd, Cu, Fe complexes with piperidinedithio-carbamate	Ascending technique, chromatoplate (20 × 10 cm), layer thickness 0.75	Iodine vapors used for detection. Limits of detection ranged from 0.8 to 1.5 μg. Pb, Cu, Cd, and Fe complexes are quantitatively formed in the pH ranges 3–5,	69

Downloaded At: 11:59 25 January 2011

	xylene–chloroform, xylene–toluene, and chloroform–toluene, each in the two ratios (80:20 and 20:80)		mm, activation at 60°C for 24 h, run 16.5 cm, development time 45–70 min, loading volume of complex 0.1 mL	1.5–4.5, 3.5–5.0, and 3.5–8.0, respectively	
Silica gel precoated with fluorescent indicator (Silufol UV_{254}, Kavalier, CSFR)	Acetonitrile–benzene (31:69), methanol ether (1:4.1:1), pentone, acetonitrile, dichloromethane –pentane in different ratios	Zn(II) compounds: $Zn(CH_3COO)_2(X)_n \cdot (H_2O)_l$. X = caffine, thiourea, phenazone, nicotinic acid; n = 1 or 2; l = 0.5 or 1.5.	Layer thickness 0.1 mm, loading volume 5 μL, development in horizontal HPTLC chamber. Plates were developed thrice with each eluent to 5 cm distance	Best separations were achieved on silica gel layer with acetonitrile–benzene (31:69). Separations on cellulose were inferior to those obtained on silica gel	70
Precoated HPTLC silica plates after preliminary development with 2.5 M ammonium nitrate	4-Methyl-2-pentanone (MP)–tetrahydrofuran (THF)–nitric acid (NA)–mono-2-ethyl-hexyl ester of 2-ethyl hexyl phosphoric acid (P507) in the following ratios 300:150:40:42, 300:150:76:42, 300:150:94:14, 300:150:76:46, 300:150:112:42, 300:150:58:14, 300:150:94:70, 300:150:58:70	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er	Linear development, sample volume 200 μL spotted by Pt-Ir pointed glass capillary, run 50 mm, computer studies on a model HP-220 microcomputer, plates were heated at 70°C for 1 h for activation	For detection: Spray first with saturated alizarin-ethanol solution and then treat with ammonia vapor, followed by gentle heating. Rare earths as violet spots on pale yellow background were visualized. A useful computer-assisted method is proposed for simultaneous two-factor (acidity and extractant concentration) optimization for the separation of mixture of 10 rare earths by HPTLC. Good agreement was observed between the predicted data and experimental results. The R_F values increase with increasing concentration of P507 and decrease with increasing concentration of HNO_3. The predicted R_F values are in close agreement with the observed values	71

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel impregnated with 1) $CuSO_4$, 2) $ZnSO_4$, 3) $NiCl_2$, 4) $CoCl_2$, 5) hexamine cobalt(III) chloride	0.1 M formic acid–DMSO–acetone (1:1:8), (5:1:4), 0.1 M H_2SO_4–DMSO–acetone (1:1:8), 0.1 M $HClO_4$–DMSO–acetone (1:1:8), 0.1 M HCl–DMSO–acetone (1:1:8), DMSO–acetone (1:8)	I^-, Br^-, IO_3^-, BrO_3^-, NO_2^-, NO_3^-, VO_3^-, SCN^-, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, $C_2O_4^{2-}$, MoO_4^{2-}, WO_4^{2-}, PO_4^{3-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	—	IO_3^- separated from neutral alkaline natural or synthetic water samples containing I^-, NO_2^-, and BrO_3^- without close control of sample pH	72
Silica gel impregnated with DMSO	*n*-Butanol–acetone –HNO_3 (6:6:1), diisopropylether –DMSO (10:1), diisopropyl ether–DMSO–THF (9:1:1), diisopropyl ether–DMSO–THF (5:1:5), diisopropylether DMSO–THF (1:1:9)	Ag, Mn, VO, Co, Ni, Cu, Zn, Pd, Cd, Hg, Cr, Fe, Rh, Ru, La, Au, Ti, Zr, Pt, Nb, Ta, Mo, W	Ascending technique, activation at 100 ± 5°C for 2 h, run 11 cm. The activated silica gel layers were impregnated with a 1:1 mixture of DMSO and sulfur-free toluene, heated in an oven until the dampness disappeared and then cooled in an airtight glass cabinet before use	The R_F values of metals on impregnated layers developed with DMSO–THF (1:10) were proportional to their atomic numbers	73
Silica gel impregnated with 3% primene and JM-T (3, 5, and 15%)	Citric acid 0.05, 0.1, and 1.0 M	Ce^{3+}, Ce^{4+}, Nd, Eu, Gd, Tb, Yb, Y, V, Zr, Th, U	Ascending technique, layer thickness 0.5 mm, loading volume 5 μL of 2.5% metal ion solution	Effect of eluent and impregnant concentration on the R_F values of metal ions have been investigated. An inverse correlation between R_F values and the percent extraction of the	74

Downloaded At: 11:59 25 January 2011

				metal ions is observed. Silica gel impregnated with 3% primene JM-T with 0.1 M citric acid as eluent is identified as the best system	
Silica gel impregnated with 0.1 M NaCl, 0.1 M KBr, and 0.1 M KI	1.0 M formic acid (FA)–1.0 M KI (1:9, 9:1), 1.0 M FA–1.0 M NH_4Cl (1:9), 1.0 M FA–0.1 M KBr (1:9), 1.0 M FA–0.1 M NaCl (1:9, 9:1)	Cu, Ni, Co, Zn, Al, Cd, Bi, Hg, Fe, Ti, Ag	Ascending technique, run 10 cm, layer thickness 0.25 mm, plate activation 100 ± 5°C, 1 h	Impregnation enhances the selectivity of silica gel layers toward metal ions. Cd^{2+} is separated from synthetic samples (pH range 1–3) containing Cu^{2+} and Zn^{2+} with formic acid–KI, 1.0 M each (1:9), solvent system. The ternary separation of Fe^{3+}, Al^{3+}, and Ti^{4+} is achieved up to a loading amount of 10 mg of metal salts of each cation	75
Silica gel impregnated with 1) 5% nitrobenzene in petroleum ether, 2) 5% phenol in benzene, 3) 5% phenol in petroleum ether, and 4) chlorobenzene	Ethyl acetate–methanol (1:1, 1:2, 2:1)	Oxalato and thicyanato complexes of Co, Hg, Fe, Cr, Cu	Precoated and preimpregnated silica gel G plate (20 × 20 cm), development time 35 min, drying of plates	Best separations were achieved on silica gel impregnated with chlorobenzene using ethyl acetate–methanol (1:1) as mobile phase. After TLC separation the concentration of the complexes was determined spectrophotometrically with a maximum error of 8%	76
Silica gel impregnated with 1) 5% ethanolic solution of phthalic acid, 2) 5% ethanolic solution of salicylic acid, and 3) 5% ethanolic solution of syringic acid	Distilled water, tap water	Pb, Hg, Fe, Cu, Co	Ascending technique, run 8–11 cm	Detection by spraying with bromocresol green indicator and observing under UV light or by exposure to ammonia followed by H_2S vapor. Best separations on impregnated layers. The mobility (R_F values) of metals generally increases on impregnated layers in the order phthalic acid > salicyclic acid > syringic acid, indicating the complexation affinity of the metals for the functional groups of the impregnants	77

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel impregnated with 1 and 0.1% copper sulfate	0.1 M NaCl–acetone (1:9, 9:1), 0.1 M NH_4OH–acetone (1:9, 9:1), 0.1 M HCl or HBr or formic acid–acetone, 1:9 each	NO_2^-, NO_3^-, Br^-, I^-, VO_3^-, SCN^-, MoO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, PO_4^{3-}, $Fe(CN)_6^{4-}$	Development time 45–70 min	The optimum impregnant concentration with 2.5% copper sulfate solution is deformed during development. Mobile phases containing 90% acetone gave better results. The limits of detection obtained on a 0.1% copper sulfate impregnated silica gel layer were 0.1–10 μg	78
Silica gel impregnated with 3% pretreated 1) Primene JM-T, 2) Alamine 336, and 3) Aliquat 336	0.03 M aqueous citric acid	Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Ti^{4+}, V^{5+}	Ascending technique, layer thickness 0.5 mm, loading value 10 μL of 1% metal ion solution. The amines were converted into citrate form by treating with 1.0 M citric acid followed by washing with water to attain a wash solution of pH 3	Detection by spraying with 1% solution of 8-hydroxyquinoline in alcohol–water (1:1) followed by exposure to ammonia vapors. Examination of the effects of amine, concentration of amine (0.1–6%), and the concentration of citric acid (0.015–0.15 M) on R_F values of metal ions. Best system for effective separations was 3.0% Primene JM-T and 0.03 M citric acid mobile phase	79
Silica gel impregnated with 1) 1% and 3% mono(2-ethyl hexyl) phosphoric acid, 2) 3% of di-(2-ethyl hexyl) phosphoric acid (DEHPA), dibutyl phosphonate and a mixture [DT-23, DEHPA, and trioctyl phosphine oxide (TOPO)]	1.0 M nitric acid	U, Ti, V, Zr, Th, Ce^{4+}, Ce^{3+}, Nd, Sm, Gd, Ho, Yb, Y	Ascending technique, layer thickness 0.5 mm, loading volume 5 μL of 0.25% metal ion solution, sample application by Hamilton syringe, run 10 cm,	Effective system for separation of metal ions was silica gel impregnated with 3% mono-(2-ethyl hexyl) phosphoric acid and 1.0 M HNO_3. An inverse correlation between the extraction percent and reversed phase chromatographic behavior (R_F values) of metal ions was found	80

Downloaded At: 11:59 25 January 2011

			development time 35–40 min		
Silica gel loaded with tributyl amine	1.0 M aqueous formic acid (FA)–1.0 M aqueous sodium formate (SF), (2:8, 4:6, 1:1, 6:1, 8:2), FA (10^{-3}–2.0 M), aq SF (10^{-3}–5 M)	VO, Ti, Al, W, Ni, Fe, UO, Mn, Cu, Bi, Zn, Se, Pb, Cr, Cd, Ag, Tl, Hg	Ascending technique, run 10–12 cm, development time 1–2 h	Plates developed with 5.0 M aq SF (pH 7.15) during the period of drying at room temperature	81
Silica gel + 10 wt% Dowex 50W-X8 (200–400 mesh, K^+)–4 wt% CH_3COOK	*t*-BuOH–acetone –H_2O (9:35:6), ethanol–propanol-1–glacial acetic acid–acetone–H_2O (37:5:37.5:5.1:20)	SO_3^{2-}, $S_2O_8^{2-}$, S^{2-}, $S_2O_3^{2-}$, Cl^-, Br^-, I^-, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_6O_6^{2-}$, $S_7O_6^{2-}$, PO_3^-, PO_4^{3-}, $P_2O_7^{4-}$	S and BN chambers, development time 30–40 min	—	82
Silica gel + 10 wt% Dowex 50W-X8 (200–400 mesh, K^+)–2 wt% CH_3COOK	*t*-Butanol–acetone –water (9:35:6)	SO_3^{2-}, $S_2O_8^{2-}$, S^-, $S_2O_3^{2-}$, Cl^-, Br^-, I^- $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ $S_6O_6^{2-}$, $S_7O_6^{2-}$.	Combined C and B cells and glass tanks with ground caps. Run 10 cm, development time 30–40 min	—	83
Silica gel impregnated with methanolic solution of fluorescein	Toluene–HOAC (10:2)	Br^-	—	Br^- forms red-colored spots on the plate	84
Silica gel G impregnated with 3% solution of the following amines: Primene JM-T, Amberlite LA-l, Alamine 336, Aliquat 336	0.01 M aqueous succinic acid	Mn, Ni, Co, Cu, Zn, Fe, Cr, Ti, V	Layer thickness 0.5 mm, loading 10 μL of 1% metal ion solution	R_F values were lower in plates impregnated with Primene JM-T compared to other amines. The R_F values decreased as the concentration of Primene JM-T increases. With an increase in succinic acid concentration, R_F values tend to increase. 1% solution of 8-hydroxy quinoline in a mixture of alcohol and water (1:1) followed by exposure of spots to ammonia vapors was used for detection	85

(*continued*)

Downloaded At: 11:59 25 January 2011

TABLE 1 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Silica gel impregnated with NH_4SCN (0.1–2%) and 0.1–1% $K_4Fe(CN)_6$	H_2O, 10^{-2} to 1.0 M aqueous formic acid (FA), 10^{-2} to 1.0 M aq sodium formate (SF), 1.0 M aq SF–1.0 M aq FA (1:9, 3:7, 1:1, 7:3, 9:1), 1% aq $K_4Fe(CN)_6$–1% aq FA (1:9, 3:7, 7:3, 9:1, 10:0)	Ni, Co, Zn, Cd, Sn, Mo, Fe, Al, Ti, VO^{2+} Cu, Ag, Hg, Tl, Pb, UO_2^{2+}	Ascending technique, layer thickness 0.25 mm, activation at 100 ± 5°C for 1 h	The effect of carboxylic acids on the separation of Ni, Al, UO_2^{2+}, and VO^{2+} from other cations was examined. The separation of Ni^{2+} and Co^{2+} at milligram levels from microgram quantities of Zn^{2+}, Ti^{4+}, Fe^{3+}, and UO_2^{2+} on 1% NH_4SCN impregnated layers using 1.0 M FA–1.0 M SF (3:7) systems	86

Downloaded At: 11:59 25 January 2011

TABLE 2
Work Done on Modified Cellulose Layers

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Cellulose impregnated with polyethyleneimine	0.05–3.0 M LiCl	Various phosphates	—	The method was used to estimate the relative chain length of unknown polyphosphates	87
DEAE–cellulose in chloride form	Aqueous solutions of HCl (1–5 M), LiCl (1–9 M), $CaCl_2$ or $MgCl_2$ (2.5 M), NaCl (1–5 M), saturated NaCl, and 1.6 M $AlCl_3$–0.1 M HCl	Pd, Ir^{3+}, Ru, Rh, Au, Pt	Ascending technique, run 10 cm, layer thickness 0.25 mm, development time 1–6 h	An additional weak streak is occasionally observed for Ir^{4+} and Rh^{3+} with a few solvent systems	88
Cellulose phosphate (Whatman P-41, England) in thiocyanate form, P-cellulose + microcrystalline cellulose (2:1) in free hydrogen form	Aqueous HCl (0.01–2.0 M), NH_4SCN (0.01–2.0 M), HCl was always added to the NH_4SCN solutions to give 0.1 M in free acid	W, V, In, Ba, As, Ti, Be, Mn, Re, U, Dy, Pt, Nb, La, Ru, Sc, Sm, Au, Te, Se, Ni, Bi, Pb, Zn, Ag, Fe, Cd, Ca, Hg, Al, Mg, Ga, Mo, Sr	Ascending technique, run 170 mm, layer thickness 0.25 mm, development time 20–35 min	Sharper spots for most inorganic ions are obtained in the thiocyanate media than in HCl	89
Sulfoethyl cellulose (Serva, Heidelberg, GFR)	H_2SO_4 and NH_4SCN solutions over the range 0.01–2.0 M. H_2SO_4 was always added to the NH_4SCN solutions to give 0.025 M free acid	Sr, Y, Hg, As, Sc, W, La, Re, Cr, Pb, Ce, Cu, Fe, Mo, Au, Ru, Ba, Bi, Tl, Zn, Cr, Pd, Pt, Ge	Ascending technique, run 170 mm, development time 45–60 min at room temperature, layer thickness 0.5 mm. After development, the plates were dried under an infrared lamp	Best results were obtained with acid sulfate solution eluent	90
Cellulose phosphate (Whatman P41, England) and cellulose phosphate + microcrystalline cellulose (3:1)	Aqueous acetic acid (0.1, 1.0, 2.0, 3.0 $mol \cdot dm^{-3}$), CH_3COOH–CH_3COO-NH_4 solutions, where CH_3COOH was always added to acetate solutions (0.1, 1.0, 2.0, 3.0 $mol \cdot dm^{-3}$) to give 0.1 $mol \cdot dm^{-3}$ in free acid	W, Sn, Cr, Zr, Sb, Be, Fe, Th, V, Pb, Cd, Ag, Mn, Hg, Ni, Co, Cu, Mg, Tl, Te, Mo, As, Ge, Re, Se	Ascending technique, run 17 cm, development time 35–45 min, layer thickness 0.25 mm	R_F values were calculated from chromatograms of multicomponent separations in mixed solvent systems. Several quaternary and five to six metal ions separations have been achieved	91

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 2 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Sulfoethyl cellulose (Serva, Heidelberg, FRG)	Aqueous acetic acid (0.1, 1.0, 2.0, 3.0 M), CH_3COOH + $CH_3COOHNH_4$ solutions (pH 4.7, 5.7, 6.5, 6.7)	As above	Ascending technique, run 17 cm, development time 40–60 min, layer thickness 0.5 mm	—	92
Sulfoethyl cellulose (Serva, FRG) in H-form	0.05 M H_2SO_4–MeOH or acetone (100:00, 80:20, 60:40, 40:60)	As above	As above except development time of 60–100 min	—	93
Cellulose phosphate (Whatman P41, England) in H-form	As above	As above	As above	—	94
Cellulose impregnated with bis-(2-ethyl hexyl) or the phosphoric acid, cellulose impregnated with trioctyl phosphine oxide–bis-(2-ethyl hexyl) orthophosphoric acid (17:83), cellulose impregnated with dibutyl phosphonate	MeOH–6 N HNO_3–acetyl acetone (20:15:5)	Th, Zr, Ti, Dy, Gd, Nd, La, Pr, Tb, Sm, Th, Ti, Zr, Y	Ascending technique, run 12 cm, plate thickness 0.5 mm. Impregnation concentration 1% in EtOH–H_2O (70:30), plates dried for 24 h at 40 ± 1°C, development temperature 22 ± 1°C	1% alcoholic solution of alizarin after exposure to ammonia used for detection. Trioctyl phosphine oxide–bis-(2-ethyl hexyl) orthophosphoric acid impregnated adsorbent was most effective for efficient separation of Th, Ti, Zr, Y, and seven lanthanides	95
PEI-cellulose (Serva, FRG)	Aqueous HCl (0.01, 0.10, 1.0 M)	51 inorganic ions	Ascending technique, run 17 cm, development time 100–110 min, layer thickness 0.25 mm, plates dried under infrared lamp after development	PEI-cellulose treated with 0.5 M NaOH solution was slurried with 1.0 M NH_4Cl solution after complete washing with deionized water	96
PEI-cellulose (Serva, Heidelberg, FRG)	Aqueous H_2SO_4 (0.01, 0.1 and 1.0 M) H_2SO_4–$(NH_4)_2SO_4$ (0.01–1.0 M solutions where H_2SO_4 was always added to $(NH_4)_2SO_4$ solutions to give 0.025 M in free acid	49 inorganics ions	Ascending technique, run 17 cm, development time 100–120 min	PEI-cellulose was treated with 0.5 M NaOH solution, washed with deionized water, saturated with 1.0 M $(NH_4)_2SO_4$ solution followed by water washing, slurried with water, and coated over glass plates. The plates were air dried (12 h) and then dried at 40°C for 3 h. Stored	97

Downloaded At: 11:59 25 January 2011

				over saturated KBr solution	
Cellulose with azopyrocatechol group	Butanol-l–acetone–glacial acetic acid–5% ammonia solution–water (7:5:3:3:2)	Transition metals	—	Determination of Ni, Cu, and Cr in wastewaters from an electroplating process before their treatment	98
Polyethylene imine cellulose	HCl–NH_4SCN in various ratios	Several cations including all rare earths	—	Correlation between R_F values and the paramagnetic moment of rare earths was established	99
Polyethylene cellulose in chloride form	Eight mobile phases containing different concentrations of HCl, NH_4Cl, and their mixtures	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Ascending technique, layer thickness 0.25 mm (plates were first air dried for 12 h and then activated at 40°C for 3 h and stored in a tank over saturated KBr solution), run 17 cm, loading volume of ion 1 mm^3, test solution 0.01 $mol \cdot dm^{-3}$, development time 90–120 min. Drying of plates under an infrared lamp	The sorption of rare earth elements decreases with increasing concentration. Correlation of R_F values to atomic number and the paramagnetic moment of the trivalent rare earths is proposed. Separation of Zr^{4+} from Nd^{3+}, Sm^{3+}, Yb^{3+}, and Lu^{3+}, and of Th^{4+} from Eu^{3+} and La^{3+} with 0.01 $mol \cdot dm^{-3}$ HCl is established. 0.05% aqueous solution of Arsenazo III was used for detection	100
Polyethylene (PEI) cellulose treated with 1.0 $mol \cdot dm^{-3}$ ammonium sulfate solution	H_2SO_4 (0.1 $mol \cdot dm^{-3}$ acetone or methanol (10:0, 7:3, 3:7, 5:5)	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	As in Ref. 75	The R_F values of most ions are higher in acetone-containing systems then in methanol systems. Acid–methanol (7:3) and acid–acetone (1:1) were best for analytical separations of rare earths. Detection as in Ref. 71	101
PEI-cellulose	Different concentrations of HCl with dioxane in 1:1 and 7:3 ratios	Be, Mg, Al, V, Cu, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Sr, Y, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, W, Re, Pt, La, Hf, Ta, Au, Hg, Tl, Pb, Bi, Ce, Sm, Dy, Lu, Th, U	As in Ref. 75	Adsorption relation with precipitation by hydrolysis and the formation of anionic chloro complexes	102

(continued)

Downloaded At: 11:59 25 January 2011

TABLE 2 Continued

Stationary phase	Mobile phase	Ions studied	Conditions	Remarks	Ref.
Diethyl-(2-hydroxypropyl)-aminoethyl cellulose	H_2SO_4 and H_2SO_4–$(NH_4)_2SO_4$ of various concentrations in several ratios	Be, Mg, Al, V, Ca, Se, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd	Ascending technique, layer thickness 1.0 mm, drying at room temperature for 12 h, activation at 40°C for 3 h, and storing the plates in a tank oversaturated with KBr solution. Development time 100–110 min for a 17-cm run	Many separations of multicomponent mixtures containing 1–4 μg of each ion	103
ECTEOLA-cellulose	2.5 mol/L HCl–2.5 mol/L NaCl–0.6% (w/v) H_2O_2 solution, DMSO–THF (1:10)	Au, Pt, Pd, Cr, Mn, Fe, Co, Cu, Ni, Mg, Ba, Al, Bi, Pb, Zn, Ag	—	R_F values in DMSO–THF system were proportional to their atomic numbers. The method was applied to synthetic mixtures in the form of alloys	104
Polyethylenemine cellulose	Binary mixtures containing H_2SO_4 and dioxane	Several inorganic ions	—	Separations of multicomponent mixtures of the ions are presented	105
Aminoplast (carbamide formaldehyde polymer), cellulose MN 300	Water, ethanol–water (2:3), ethanol–2-propanol–5 M HCl (2:2:2, 2:1:2), 1-butanol–5 M HCl (2:1)	Sc, Ti, O, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mg, Ca, Sr, Ba, Pt, Pd, Au, Hg(I), Hg(II), Cd, Ag, Al, Bi, As(III), Sb, Pb	Ascending technique, glass plates (20 × 20 mm). Coated with slurried aminoplast powder in water (2 g aminoplast per plate) and dried at room temperature	Metal ions with different valency states are resolved clearly on aminoplast layers. The total molecular structure of polymer controls the retention mechanism of metal ions	106

Downloaded At: 11:59 25 January 2011

Diethyl-(2-hydroxypropyl) amino ethyl (QAE) cellulose, a strongly basic anion exchanger obtained from James River Corp., USA	0.10 mol·dm^{-3} HCl, 0.05 mol·dm^{-3} HCl–1.0 mol·dm^{-3} NH_4Cl	Ag, Au, Mo, Ru, W, Pt, Hg, Nb, Bi, Re, In, Cd, Te, Th, Zn, Fe, Al, As, V, Mn, Ta, Ga, Se, U, Ba, Pd, Ge	Ascending technique, layer thickness 1.0 mm, plates dried in air for 12 h followed by heating at 40°C for 3 h and finally stored in a tank over saturated KBr solution. Loading volume 1 mm, run 17 cm	Selective separation of Re^{7+} from many inorganic ions in aqueous HCl and in HCl–NH_4Cl (0.01 to 1.0 mol·dm^{-3})	107
p-Aminobenzyl (PAB) cellulose (Serva, Heidelberg, FRG) treated with 1.0 mol·dm^{-3} NH_4Cl solution	HCl in difference concentrations, HCl–NH_4Cl in various concentrations. HCl was always added to NH_4Cl_3 to give 0.05 mol·dm^{-3} free acid	All cations as in Ref. 77	As in Ref. 75	R_F values as a function of total chloride ion concentration in the range 0.01 to 1.05 mol·dm^{-3} were discussed. Re^{7+} and Se^{6+} were separated from other cations successfully	108
Polyethlene (PEI) cellulose (for TLC, Serva, Heidelberg, FRG) treated with 1.0 mol·dm^{-3} NH_4Cl solution	Mixed solvents containing 0.1 mol·dm^{-3} HCl and acetone or methanol in volume ratios of 100:0, 70:30, 50:50, and 30:70	All cations as in Ref. 77	As in Ref. 75	Separation of Pb^{2+} from other ions achieved	109
PAB cellulose treated with 0.5 mol·dm^{-3} ammonium sulfate	H_2SO_4 (aq) in various concentrations. H_2SO_4–$(NH_4)_2SO_4$ prepared by adding H_2SO_4 to the $(NH_4)_2SO_4$ solutions to give 0.025 mol·dm^{-3} free acid	All cations as in Ref. 82	Ascending technique, layer thickness 1.0 mm, metal concentration 0.01–0.1 mol·dm^{-3}, development time 15–20 min for 170 mm run	Acid concentration enhances the R_F of cations. 0.025 mol·dm^{-3} H_2SO_4–0.01 mol·dm^{-3} $(NH_4)_2SO_4$ and 0.10 mol·dm^{-3} H_2SO_4 systems were best for rare earth and bismuth separation	110

organometallics on different impregnated silica gel and modified cellulose layers is presented. Details are given in tabular form to include the stationary phase, mobile phase, substance studied, conditions with the technique, remarks, and reference number. The literature shows that the majority of the work has been performed on cations compared to anions. Rare earths and organometallics have also received attention. It is concluded that impregnated layers are more selective than plain adsorbent layers for the TLC separation of inorganic mixtures.

REFERENCES

1. J. Maslowska and Z. Mlodzikowski, *Chem. Anal.*, *31*, 193 (1986).
2. L. Lepri, P. G. Desideri, and G. Tanturli, *J. Chromatogr.*, *147*, 375 (1978).
3. M. M. Movsumzade, I. Abdullabekov, and S. F. Karaov, *Dokl. Akad. Nauk SSSR*, *42*, 41 (1986); *Chem. Abstr.*, *105*, 1451493 (1986).
4. H. M. Stahr, J. Kinker, D. Nicholson, and W. Hyde, *J. Liq. Chromatogr.*, *5*, 1191 (1982).
5. K. Kawanabe and K. Maruyama, *Yakugaku Zasshi*, *101*, 912 (1981).
6. S. Srivastava and V. Dua, *Z. Anal. Chem.*, *282*, 137 (1976).
7. S. Srivastava and V. Gupta, *Chromatographia*, *17*, 496 (1979).
8. R. Kuroda, K. Oguma, and K. Nakamura, *Nippon Kagaku Zasshi*, *91*, 1155 (1970).
9. T. Shimizu, H. Kashima, and K. Watanabe, *Chromatographia*, *11*, 517 (1978).
10. T. Shimizu, Y. Nakamura, and K. Inami, *Ibid.*, *14*, 83 (1981).
11. T. Shimizu, Y. Suzuki, and C. Inose, *Ibid.*, *23*, 648 (1987).
12. V. M. Dziomko, V. N. Avilina, O. V. Ivanovin, J. G. Gregory, B. Evans, and P. C. Weston (Eds.), *Proceedings of International Solvent Extraction Conference, ISEC 71, The Hague, April 1971*, Vol. II, Society of Chemical Industry, London, 1971, p. 1913.
13. U. A. Th. Brinkman, J. H. Taphoorn, and G. De Vries, *J. Chromatogr.*, *84*, 407 (1973).
14. M. Qureshi, B. M. Sethi, and S. D. Sharma, *J. Liq. Chromatogr.*, *6*(1), 165 (1983).
15. C. H. Hu and C. L. Liu, *Hua Hsueh Hsueh Pao*, *31*, 267 (1965).
16. M. P. Volynets, A. N. Ermakov, and L. P. Nikitina, *Zh. Anal. Khim.*, *25*, 294 (1970).
17. U. A. Th. Brinkman, G. De Vries and E. Van Delen, *J. Chromatogr.*, *31*, 182 (1967).
18. P. Mark and F. Hecht, *Mikrochim. Acta*, p. 970 (1963).
19. T. H. Chang and T. L. Chow, *Hua Hsueh*, No. 1–2, 18 (1969).
20. K. Higashi and Y. Miyake, *Osaka Kogyo Gijutsu Shikensho Kiho*, *22*, 6 (1971).
21. K. Higashi and Y. Miyake, *Ibid.*, *22*, 282 (1971).
22. H. Holzapfel, L. V. Lan, and G. Werner, *J. Chromatogr.*, *20*, 580 (1965).
23. H. Holzapfel, L. V. Lan, and G. Werner, *Ibid.*, *24*, 153 (1966).
24. M. P. Volynets and L. I. Guseva, *Zh. Anal. Khim.*, *23*, 947 (1968).
25. H. Starter Mendes, *C. R. Hebd. Seances Acad. Sci., Ser. C*, *273*, 342 (1971).
26. J. Stolkowski and B. Lubochinsky, *Ibid., Ser. D*, *264*, 2059 (1967).
27. U. A. Th. Brinkman and G. De Vries, *J. Chromatogr.*, *18*, 142 (1965).
28. U. A. Th. Brinkman, G. De Vries, and E. Van Delen, *Ibid.*, *22*, 407 (1966).
29. U. A. Th. Brinkman and G. De Vries, *Ibid.*, *23*, 287 (1966).
30. T. Deguchi, *Bunseki Kagaku*, *15*, 352 (1966).
31. R. J. T. Graham and A. Carr, *J. Chromatogr.*, *46*, 301 (1970).

Downloaded At: 11:59 25 January 2011

32. T. B. Pierce and R. F. Flint, *Ibid.*, *24*, 141 (1966).
33. L. S. Bark, G. Duncan, and R. J. T. Graham, *Analyst (London)*, *92*, 31 (1967).
34. G. Bottura, A. Breccia, and F. Marchetti, *Ric. Sci.*, *34*, 373 (1964).
35. U. A. Th. Brinkman and H. Veltkamp. *J. Chromatogr.*, *24*, 489 (1966).
36. U. A. Th. Brinkman and G. De Vries, *Ibid.*, *56*, 103 (1971).
37. U. A. Th. Brinkman, G. De Vries, and E. Van Dalen, *Ibid.*, *25*, 447 (1966).
38. U. A. Th. Brinkman, G. De Vries, and H. R. Leene, *Ibid.*, *69*, 181 (1972).
39. H. R. Leene, G. De Vries, and U. A. Th. Brinkman, *Ibid.*, *57*, 173 (1971).
40. A. Muchova and V. Jokl, *Chem. Zvesti*, *25*, 280 (1971).
41. A. Muchova and V. Jokl, *Ibid.*, *26*, 289 (1972).
42. W. S. Sijperda and G. De Vries, *Geol. Mijnbouw*, *45*, 315 (1966).
43. W. S. Sijperda and G. De Vries, *Ibid.*, *47*, 197 (1968).
44. M. Muto, *Nippon Kagaku Zasshi*, *85*, 147, 782 (1964).
45. S. P. Srivastava and V. K. Dua, *Fresenius Z. Anal. Chem.*, *282*, 137 (1976).
46. S. P. Srivastava, V. K. Dua, and K. Gupta, *J. Indian Chem. Soc.*, *56*, 529 (1979).
47. S. P. Srivastava, V. K. Dua, and K. Gupta, *Fresenius Z. Anal. Chem.*, *292*, 415 (1978).
48. S. Kh. Babayan and G. M. Varshal, *Zh. Anal. Khim.*, *27*, 921 (1973).
49. A. Muchova and V. Jokl, *Chem. Zvesti*, *26*, 303 (1972).
50. C. T. Hu and C. L. Lia, *Sci. Sin.*, *14*, 1235 (1965); *K'o Hsueh T'ung Pao*, p. 1103 (1964).
51. S. P. Srivastava, V. K. Dua, and V. K. Gupta, *Anal. Lett.*, *A11*(8), 613 (1978).
52. S. P. Srivastava, V. K. Dua, and K. Gupta, *Chromatographia*, *11*, 538 (1978).
53. S. P. Srivastava, V. K. Gupta, and Kamlesh, *J. Liq. Chromatogr.*, *6*, 245 (1983).
54. S. P. Srivastava, R. Bhushan, and R. S. Chauhan, *Ibid.*, *7*, 1341 (1984).
55. N. Fatima and A. Mohammad, *Sep. Sci. Technol.*, *19*, 429 (1984).
56. M. Qureshi, A. Mohammad, and N. Fatima, *J. Liq. Chromatogr.*, *8*, 1279 (1985).
57. S. P. Srivastava, R. Bhushan, and R. S. Chauhan, *Ibid.*, *8*, 571 (1985).
58. M. Ajmal, A. Mohammad, and N. Fatima, *Ibid.*, *9*, 1877 (1986).
59. M. Ajmal, A. Mohammad, N. Fatima, and J. Ahmad, *J. Planar Chromatogr.*, *1*, 329 (1988).
60. N. Suzuki, K. Saitoh, and Y. Shibata, *J. Chromatogr.*, *504*(1), 179 (1990).
61. B. Galli, F. Gasparrini, D. Mistri, G. Natile, and G. Palmieri, *Ibid.*, *409*, 377 (1987).
62. O. Hadzija, M. Tonkovic, and S. Iskric, *J. Liq. Chromatogr.*, *10*(16), 3673 (1987).
63. H. Luo and J. Mo, *Fenxi Huaxue*, *16*(9), 821 (1988).
64. H. Luo and J. Mo, *Fenxi Shiyanshi*, *7*(4), 27 (1988).
65. M. P. Volynets and M. S. Miukova, *Radio Khim.*, *13*, 72 (1971).
66. Z. Hsu, X. Jia, and C. Hu, *Talanta*, *33*, 455 (1986).
67. M. Ajmal, A. Mohammad, N. Fatima, and A. H. Khan, *Microchem. J.*, *39*, 361 (1989).
68. S. Shrey, K. Bansal, and R. S. Sindhu, *Orient. J. Chem.*, *8*, 71 (1992).
69. A. Asalkar, A. Kumar, P. Pandey, and R. Bhardwaj, *J. Liq. Chromatogr.*, *15*, 1689 (1992).
70. A. Orinak, K. Gyoryova, and S. Lancaricova, *J. Planar Chromatogr.*, *6*, 153 (1993).
71. Q. S. Wang and D. P. Fan, *J. Chromatogr.*, *567*, 359 (1991).
72. A. Mohammad and S. Tiwari, *Microchem. J.*, *44*, 39 (1991).
73. D. Sherma and S. Misra, *J. Liq. Chromatogr.*, *14*, 3301 (1991).
74. A. Jain, O. V. Singh, and S. N. Tondon, *Indian J. Chem.*, *30A*, 196 (1991).
75. M. Ajmal, A. Mohammad, N. Fatima, and J. Ahmad, *J. Liq. Chromatogr.*, *12*, 3163 (1989).
76. R. Sharma, N. K. Jha, and H. M. Chawla, *Chim. Acta Turc.*, *18*, 105 (1990).

Downloaded At: 11:59 25 January 2011

77. I. Skvorc, N. Zambeli, S. Iskric, and O. Hadjija, *J. Chromatogr.*, *498*, 428 (1990).
78. A. Mohammad and S. Tiwari, *Chromatographia*, *30*, 405 (1990).
79. K. S. Panesar, O. V. Singh, and S. N. Tondon, *Anal. Lett.*, *23*, 125 (1990).
80. A. Jain, O. V. Singh, and S. N. Tondon, *J. Planar Chromatogr.*, *3*, 79 (1990).
81. M. Ajmal, A. Mohammad, N. Fatima, and A. H. Khan, *Ibid.*, *1*, 128 (1988).
82. I. N. Brezgunova, V. V. Smodyaninov, and N. I. Kharlamova, *Zh. Fiz. Khim.*, *45*, 1785 (1971).
83. V. V. Smolyaninov, *J. Chromatogr.*, *53*, 337 (1970).
84. W. Werner, *Fresenius Z. Anal. Chem.*, *321*, 374 (1985).
85. K. S. Panesar, O. V. Singh, and S. N. Tondon, *J. Planar Chromatogr.*, *5*, 289 (1992).
86. M. Ajmal, A. Mohammad, N. Fatima, and J. Ahmad, *Ibid.*, *3*, 181 (1990).
87. J. M. Tanzer, M. I. Krichevsky, and B. Chassy, *J. Chromatogr.*, *38*, 526 (1968).
88. K. Ishida and T. Saito, *Ibid.*, *152*, 191 (1978).
89. T. Shimizu, H. Kashima, and K. Watanabe, *Chromatographia*, *11*, 517 (1978).
90. T. Shimizu, T. Shimojo, and A. Nakamura, *Ibid.*, *12*, 135 (1979).
91. T. Shimizu, A. Miyazki, and I. Saitoh, *Ibid.*, *13*, 119 (1980).
92. T. Shimizu, H. Tanaka, and T. Ohsawa, *Ibid.*, *15*, 177 (1982).
93. T. Shimizu, K. Tadokoro, A. Suganuma, and M. Hirose, *Ibid.*, *18*, 692 (1984).
94. T. Shimizu, T. Kurosaki, and H. Suwa, *Ibid.*, *20*, 364 (1985).
95. R. Bhushan, S. P. Srivastava, and R. S. Chauhan, *Anal. Lett.*, *18*(A12), 1549 (1985).
96. T. Shimizu and S. Abe, *Chromatographia*, *21*, 708 (1986).
97. T. Shimizu, E. Uehara, and M. Ohtani, *Ibid.*, *21*, 175 (1986).
98. G. V. Myasoedova, M. P. Volynets, T. G. Akimova, L. I. Bolshakova, T. V. Dubrova, S. B. Savvin, and A. N. Eramakov, *Zh. Anal., Khim.*, *41*, 662 (1986).
99. T. Shimizu, Y. Suzuki, and C. Inose, *Chromatographia*, *23*, 648 (1987).
100. *Sci. Rep. Fac. Educ., Gunma Univ., Jpn.*, *47*, 15 (1989).
101. T. Shimizu, H. Hirata, and K. Nakajima, *Chromatographia*, *28*, 620 (1989).
102. T. Shimizu, K. Nonaka, and N. Arikawa, *J. Planar Chromatogr.*, *2*, 393 (1989).
103. T. Shimizu, F. Nishimura, T. Imai, and S. Jindo, *Chem. Environ. Res.*, *1*, 73 (1992).
104. T. Hamada, T. Morita, M. Matzuzuka, and K. Ishida, *Fresenius J. Anal. Chem.*, *338*(1), 54 (1990).
105. T. Shimizu, T. Ohtomo, and T. Shimizu, *J. Planar Chromatogr.*, *3*(1-2), 88 (1990).
106. N. U. Perisic, S. M. Petrovic, and S. Podunavac, *Chromatographia*, *31*, 281 (1991).
107. T. Shimizu, K. Hashimoto, and K. Tsunoda, *Ibid.*, *31*, 60 (1991).
108. T. Shimizu, S. Jindo, and D. Kanoh, *J. Planar Chromatogr.*, *4*, 261 (1991).
109. T. Shimizu, N. Arikawa, T. Miyakazi, and K. Nonaka, *Ibid.*, *2*, 90 (1989).
110. T. Shimizu, R. Igarashi, Y. Hayashi, and S. Jindo, *Ibid.*, *4*, 487 (1991).

Received by editor October 11, 1994

Downloaded At: 11:59 25 January 2011