PRO EXPERIMENTIS

Separation of Metal Ions on Inorganic Ion-Exchange Papers

Papers impregnated with synthetic inorganic ion-exchangers have been used recently for chromatography of metal ions[1–5]. These papers are highly selective for metal ions. Fast and clean separations are achieved on these papers due to combined effect of ion-exchange and partition. Titanic tungstate, a cation exchanger, was synthesized in these laboratories[6] and the chromatographic behaviour of several cations in some solvent systems on titanic tungstate paper was reported earlier[5]. In the present communication, important separations in 9 new solvent systems are reported. In addition titanic molybdate papers have also been prepared and their behaviour towards metal ions in a large number of solvent systems has been studied. As a result some outstanding separations have been achieved.

Experimental. Apparatus. Chromatography was performed in 20 × 5 cm glass jars using the ascending method on 14.5 × 3 cm Whatman No. 1 paper strips. *Reagents.* Chemicals and solvents were either E. Merck (Darmstadt) or British Drug House Analytical reagents. 15% titanic chloride solution of B.D.H. (England) was used.

Preparation of ion-exchange papers. Paper strips were first passed through the 0.25 *M* titanic chloride solution for 3 sec. The excess of titanic chloride is removed by placing the strips on filter paper sheets. After 30 min the papers were dipped in 0.25 *M* solution of sodium tungstate or sodium molybdate (as the case may be) for 5 sec and the excess was drained off. The strips were dried at room temperature and then were washed 3 times with water and dried again.

Cation solutions. 0.1 *M* solution of chlorides, nitrates or sulphates of most of the cations were used. Their preparation, procedure for spotting and detection reagents were described previously[5].

Table I. Separation of one cation from numerous metal ions as predicted by Rf values

Metal ion	Solvent system	Ions which interfere	Time	Ion-exchange papers
In^{+3} (0.85–0.73) from 27 cations	Ethyl aceto-acetate + 20% Methylamine Hydrochloride + HBr (9:2:4)	Sn^{+4}, Ga^{+3}, Hg^{+2}, Pd^{+2}, Ag^{+}, Pb^{+2}, Hg_2^{+2}, Bi^{+3}, Cu^{+2}, Sb^{+3}, As^{+3}, Fe^{+2}, Fe^{+3}, Au^{+3}, Pt^{+4}, Zn^{+2}, Cd^{+2}, Te^{+4}, Ru^{+3}, Cr^{+3}, Se^{+4}, Sn^{+2}, Ce^{+4}	1 h	Titanic-tungstate paper
Ge^{+4} (0.45–0.27) from 27 cations	Ethyl methyl ketone + Acetone 50% HCl (7:3:1)	Ag^{+}, Pb^{+2}, Hg_2^{+2}, Bi^{+3}, Cu^{+2}, Pd^{+2}, UO_2^{+2}, Sb^{+3}, As^{+3}, Fe^{+3}, Fe^{+2}, Au^{+3}, Pt^{+4}, Mo^{+6}, Zn^{+2}, Cd^{+2}, Te^{+4}, Ru^{+3}, Ce^{+4}, Th^{+4}, In^{+3}, Sn^{+2}, Sn^{+4}, Nb^{+5}	25 min	Titanic-tungstate paper
Sr^{+2} (0.72–0.44) from 25 cations	1 *M* Ammonium formate	Ni^{+2}, Co^{+2}, Cd^{+2}, K^{+}, Rb^{+}, Cs^{+}, Cu^{+2}, Pd^{+2}, Fe^{+2}, Au^{+3}, Ir^{+4}, Mn^{+2}, Zn^{+2}, Al^{+3}, Be^{+2}, Ga^{+3}, Ba^{+2}, Mg^{+2}, Ru^{+3}, Ce^{+4}, In^{+3}, Ca^{+2}, Nb^{+5}, V^{+4}, Se^{+4}, Ge^{+4}, Sn^{+4}	20 min	Titanic-tungstate paper
Be^{+2} (0.41–0.30) from 41 cations	HCl + *n*-butanol (3:7)	Co^{+2}, Cu^{+2}, Bi^{+3}, Sn^{+2}, As^{+3}, Ce^{+4}	4 h	Titanic-molybdate papers
Zr^{+4} (0.00) from 35 cations	Saturated KCl + 0.5 *M* HCl (1:1)	Ag^{+}, Tl^{+}, Hf^{+4}, Y^{+3}, W^{+6}, Pt^{+4}, Ir^{+4}, Se^{+4}, Te^{+4}, Nb^{+5}	30 min	Titanic-molybdate papers

Table II. Separations achieved on titanic tungstate and molybdate papers

Solvent system	Separations achieved						Time	Ion-exchange paper
n-butanol +	Mo^{+6} (0.00–0.26)	–	V^{+4} (0.39–0.59)	–	UO_2^{+2} (0.83–1.00)		2 h	Titanic-tungstate
dioxan + 50% HNO_3	Pb^{+2} (0.23–0.34)	–	Sn^{+4} (0.70–0.99)				2 h	Titanic-tungstate
(3:2:3)	Te^{+4} (0.00–0.06)	–	Pt^{+4} (0.47–0.77)				2 h	Titanic-tungstate
Formic acid + methyl	Th^{+4} (0.00–0.31)	–	UO_2^{+2} (0.73–0.87)				1.15 h	Titanic-tungstate
alcohol + HCl (1:3:1)	Ni^{+2} (0.49–0.74)	–	Zn^{+2} (0.90–1.00)				1.15 h	Titanic-tungstate
Ethyl methyl	Mn^{+2} (0.07–0.17)	–	Zn^{+2} (0.46–0.61)				25 min	Titanic-tungstate
ketone + acetone +	Tl^{+} (0.00–0.00)	–	Bi^{+3} (0.37–0.64)				25 min	Titanic-tungstate
50% HCl (7:3:1)	Mn^{+2} (0.07–0.17)	–	Fe^{+2} (0.47–0.77)				25 min	Titanic-tungstate
Acetone + acetic acid +	Pb^{+2} (0.00–0.14)	–	Bi^{+3} (0.50–0.68)				1.45 h	Titanic-tungstate
4 *M* HNO_3 + *n*-butanol	Ru^{+3} (0.00–0.04)	–	Pd^{+2} (0.40–0.70)				1.45 h	Titanic-tungstate
(1:1:1:1)	Cd^{+2} (0.17–0.34)	–	Sb^{+3} (0.48–0.75)				1.45 h	Titanic-tungstate
0.1 *M* Anthranilic acid	Pb^{+2} (0.00–0.00)	–	Ge^{+4} (0.22–0.49)	–	Hg^{+2} (0.72–0.90)		1.20 h	Titanic-tungstate
in 50% ethylalcohol	Pb^{+2} (0.00–0.00)	–	Cd^{+2} (0.17–0.49)	–	Hg^{+2} (0.69–0.86)		1.20 h	Titanic-tungstate
	Ag^{+} (0.00–0.00)	–	Co^{+2} (0.17–0.44)	–	Pt^{+4} (0.73–0.90)		1.20 h	Titanic-tungstate
	Ir^{+4} (0.00–0.30)	–	Pt^{+4} (0.60–0.85)				1.20 h	Titanic-tungstate
Acetone + acetic acid +	Fe^{+3} (0.65–0.62)	–	Al^{+3} (0.25–0.12)				1.30 h	Titanic-molybdate
n-butanol + 4 *M* HCl	Tl^{+} (0.17–0.00)	–	Ga^{+3} (0.76–0.67)				1.30 h	Titanic-molybdate
(1:1:1:1)	As^{+3} (0.08–0.22)	–	Sb^{+3} (0.61–0.64)				1.30 h	Titanic-molybdate
	Ba^{+2} (0.04–0.14)	–	Mg^{+2} (0.50–0.63)				1.30 h	Titanic-molybdate
HCl + *n*-butanol	Se^{+4} (0.04–0.13)	–	Te^{+4} (0.64–0.82)				4 h	Titanic-molybdate
(3:7)	Ni^{+2} (0.06–0.23)	–	Co^{+2} (0.39–0.48)	–	Zn^{+2} (0.86–0.94)		4 h	Titanic-molybdate
Saturated KCl +	Ag^{+} (0.00–0.00)	–	Au^{+3} (0.37–0.50)	–	Pd^{+2} (0.73–0.93)		30 min	Titanic-molybdate
0.5 *M* HCl (1:1)	Zr^{+4} (0.00–0.00)	–	Th^{+4} (0.93–0.91)				30 min	Titanic-molybdate

Results. In many cases it was possible to separate 1 cation from numerous metal ions easily and rapidly. Such results are summarized in Table I. Many important and difficult separations have been achieved practically and are given in Table II. Instead of simply giving Rf values of the cation the R_T (rear limit) and R_L (front limit) are given to have clear picture of the spot.

Discussion. It is clear from the results summarized in Tables I and II that titanic tungstate and titanic molybdate are good ion-exchangers. Papers impregnated with these ion-exchangers achieve fast, selective and specific separations of metal ions. Difficult separations: to mention a few Mo^{+6}-V^{+4}-UO_2^{+2}, Pb^{+2}-Sn^{+4}, Mn^{+2}-Zn^{+2}, and Zr^{+4}-Th^{+4} etc. have been achieved clearly and rapidly.

Selective separation of 1 metal ion from numerous metal ions has also been achieved with ease. Very few direct methods are available which separate beryllium from the majority of elements in a single step. Be^{+2} can be easily separated from 41 cations including Ag^+, Al^{+3}, Au^{+3} and Ga^{+3} (which interfere in beryllium determination) on titanic molybdate papers using HCl + *n*-butanol (3:7) as developer. Fast separation of zirconium can also be achieved on these papers from 35 cations (Table I) including Fe^{+3}, Th^{+4}, Sb^{+3}, Mo^{+6}, Ge^{+4}, Cr^{+3} and Ga^{+3}. These are the cations that interfere most in zirconium determination. This is probably the best separation of Zr^{+4} from numerous metal ions yet reported[7].

Zusammenfassung. Mit anorganischen Ionenaustauchern Titanwolframat und -molybdat imprägnierte Papiere wurden zur Chromatographie mehrerer Metallionen in verschiedenen wässrigen, nichtwässrigen und gemischten Lösungsmitteln verwendet. Trennungen einer Anzahl von ternären und binären Gemischen wurden damit erzielt.

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Quantitative Determination of Phospholipids

The quantitative determination of tissue phospholipids after their separation by thin layer chromatography (TLC) has been reported from several laboratories[1-3]. The major differences and similarities of these methods are summarized in Table I. It may be noted that in the methods reported the sensitivity range of phospholipid phosphorus determinations were comparable. There were differences in the choice of absorbent, solvent systems, and detection reagents. The greatest variation is in the time required for digestion of sample, for instance, digested for 20 min by ROUSER et al.[6] as compared with 4 h by PARKER and PETERSON[5].

The existing methods for tissue phospholipids determinations were found to be tedious where a large number of samples had to be determined. This paper describes a simple procedure which allows determination of several samples while still retaining a high degree of sensitivity and accuracy.

Methods. Glass plates (20 × 20 cm) were coated with a 0.3 mm layer of Silica Gel G (Merck) using the apparatus and methods described by CHAHL and KRATZING[9]. Liver lipid solutions usually containing up to 30 µg of phospholipid phosphorus were applied onto each lane by means of the multisample applicator of CHAHL and KRATZING[10]. They were then immediately placed in a light-proof tank

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Table I. Comparisons of methods and conditions for separation and quantitative determination of phospholipids using TLC techniques

Tissue	Silica Gel	Dimension	Detection reagent	Treatment of sample[a]	Digestion time	P in sample (µg)	Reference
Human CSF	G	1	H_2SO_4	D	3 h	0.5–5.0	1
Human serum (same procedure as 1)							2
Rat thymus	G	2	Iodine vapour	Ex	15 min	3.1–6.2	3
Rat liver	H	1	Iodine vapour	E	3 h	0.2–5.0	4
Rat liver	H[b]	1	Iodine vapour	E	4 h	1.85–7.17	5
Beef brain	H	2 × 2	Iodine vapour	D	20 min	0.07–2.40	6

[a] D P/L determined in presence of adsorbent Ex P/L extracted before P determination E P/L eluted before P determination. [b] Adsorbent washed before use.