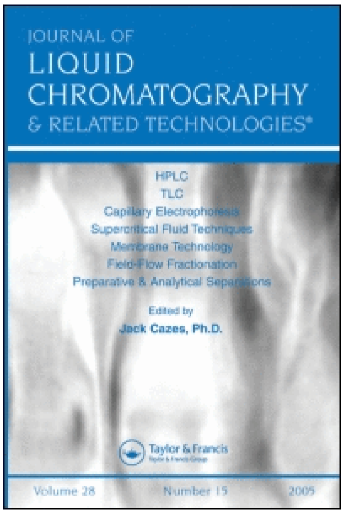

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Qureshi, M. , Sethi, B. M. and Sharma, S. D.(1983) 'Chromatographic Behaviour of 48 Metal Ions on TBP Impregnated Silica Gel-G Layers', Journal of Liquid Chromatography & Related Technologies, 6: 1, 165 — 177

To link to this Article: DOI: 10.1080/01483918308066880

URL: http://dx.doi.org/10.1080/01483918308066880

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(1), 165-177 (1983)

CHROMATOGRAPHIC BEHAVIOUR OF 48 METAL IONS ON TBP IMPREGNATED SILICA GEL - G LAYERS

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ABSTRACT

The separation potential of TBP impregnated silica gel-G for 48 metal ions has been explored in a number of solvent systems. The effect of the degree of impregnation of TBP has been studied and some important binary and ternary separations were achieved.

INTRODUCTION

In 1958, Winchester(1) first combined the favourable features of high molecular weight extractants with a chromatographic technique and reported the use of di(2⁻ethyl hexyl) phosphoric acid loaded on Al_2O_3 for separating a number of rare earths. Dilute HCl was used as a mobile phase. Since then reversed-phase chromatography has become very popular and hundreds of papers have been published using high molecular weight amines, substituted quaternary ammonium salts, heterocyclic amines(2) and tetra substituted pyrazole(3) as stationary phases. In this paper, we described the study of the effect of tri n⁻ butyl phosphate concentration on plates loaded with silica gel-G. HCl and HNO_3 have been used as eluants.

We have tried to improve the separations by using some complexing acids such as tartaric acid, citric acid and oxalic acid.

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MATERIALS AND METHODS

Apparatus

TLC apparatus (Toshniwal, India) was used to prepare thin layers on glass plates (20x3 cm). The plates were developed in glass jars (20x6 cm).

Reagents

Silica gel-G, tri n-butyl phosphate and benzene were all of analytical grade from B.D.H. England. Other chemicals were of AnalaR grade.

Test solutions and Detectors

Test solutions, 0.1M of chlorides, nitrates or sulphates of cations were prepared in a little amount of the corresponding acids. Conventional spot test reagents were used for detection perposes(4).

Preparation of TBP impregnated thin layers

The slurry was prepared by mixing silica gel-G with conductivity water in the ratio of 1:3 with constant shaking for about 5 min. This slurry was immediately coated on the clean glass plates with the help of an applicator and uniform thin layers (~ 0.15 mm thick) were obtained. The plates were first dried at room temperature and then in an electric oven for 2 hrs. at 100 ± 5°C. These plates were stored in an oven at room temperature. Silica gel-G layers were then impregnated with tri n- butyl phosphate in benzene. Benzene was evaporated by heating the plates in an electric oven at 90 ± 5°C for 1 hr. The plates were then stored in an oven at room temperature and used as such for chromatography.

Procedure

The sample solution was loaded (1 or 2 Spots) on TBP impregnated silica gel-G plates with the help of glass capillaries and the spots were allowed to dry at room temperature. The solvent ascent was always 11 cm. The R_L and R_T were measured after detection.

Solvent systems

The following solvents were used:

S_1	1N HCl
S_2	1N HNO_3
S_3	1N H_2SO_4
S_4	0.1M Oxalic Acid
S_5	0.1M Tartaric Acid
S_6	0.1M Citric Acid

RESULTS

The R_f values for only those cations which give compact spots were taken for plotting the figures. Interestingly, most of the

TABLE 1

Binary Separations Achieved Experimentally

Solvent	% TBP Impregnation	Separations Achieved Metal ion (R_T-R_L)	Time
S_1	20	Tl^{3+}(0.00-0.00) - Ga^{3+}(0.50-0.60)	1h.30m.
		In^{3+}(0.00-0.10) - La^{3+}(0.55-0.85)	
		Mo^{6+}(0.10-0.25) - Te^{4+}(0.70-0.95)	
		Mo^{6+}(0.00-0.20) - UO_2^{2+}(0.30-0.62)	
		Cs^{+}(o.10 -0.35) - K^{+} (0.90-1.00)	
		W^{6+} (0.00-0.00) - UO_2^{2+}(0.20-0.40)	
		W^{6+} (0.00-).00) - Cr^{3+}(0.36-0.64)	
		Ti^{4+}(0.00-0.06) - Ce^{3+}(0.35-0.65)	
S_1	40	W^{6+} (0.00-0.00) - Se^{4+}(0.80-1.00)	1h.40m.
		Mo^{6+}(0.00-0.20) - Se^{4+}(0.80-1.00)	
		Th^{4+}(0.85-1.00) - UO_2^{2+}(0.00-0.10)	
		Fe^{3+}(0.08-0.30) - VO^{2+}(0.45-0.55)	
S_2	20	Zr^{4+}(0.00-0.08) - La^{3+}(0.50-0.90)	1h.40m.
		Ti^{4+}(0.00-0.28) - La^{3+}(0.58-0.88)	
		Y^{3+} (0.21-0.47) - La^{3+}(0.58-0.88)	
S_2	Zero	Zr^{4+}(0.00-0.20) - Th^{4+}(0.50-0.55)	40m.
		Zr^{4+}(0.00-0.05) - Pr^{3+}(0.60-0.90)	
S_3	20	Th^{4+}(0.00-0.35) - Y^{3+} (0.85-0.95)	2h.
		Pb^{2+}(0.00-0.00) - Fe^{3+}(0.90-1.00)	
		Ti^{4+}(0.00-0.30) - Mn^{2+}(0.70-1.00)	
		Nb^{5+}(0.00-0.10) - VO^{2+}(0.80-1.00)	
S_4	20	Mo^{6+}(0.00-0.10) - Fe^{3+}(0.60-0.80)	1h.50m.
		Ti^{4+}(0.00-0.05) - Zr^{4+}(0.22-0.36)	
		Pr^{3+}(0.15-0.50) - Ce^{3+}(0.62-0.85)	
S_5	20	Au^{3+}(0.00-0.00) - Pt^{4+}(0.90-1.00)	1h.50m.
		Sn^{4+}(0.00-0.35) - Sn^{2+}(0.50-0.80)	
S_6	20	UO_2^{2+} (0.00-0.30) - Fe^{3+}(0.75-1.00)	1h.50m.
		Hg^{2+}(0.00-0.15) - Cd^{2+}(0.70-1.00)	
		Hg^{2+}(0.00-0.10) - Zn^{2+}(0.72-1.00)	

TABLE 2

Ternary Separations Achieved Experimentally

Solvent	% TBP Impregnation	Separations Achieved Metal ion (R_T-R_L)	Time
S_1	20	Bi^{3+}(0.10-0.20) - Ir^{3+}(0.35-0.55) - Pd^{2+}(0.85-1.00)	1h.30m.
S_2	20	Pb^{2+}(0.00-0.00) - Fe^{3+}(0.40-0.60) - Pd^{2+}(0.70-0.90)	1h.40m.
S_2	Zero	Zr^{4+}(0.00-0.00) - UO_2^{2+}(0.52-0.72) - Pd^{2+}(0.94-1.00)	40m.
S_4	20	Sn^{4+}(0.00-0.15) - Fe^{3+}(0.30-0.60) - Cd^{2+}(0.80-0.90) Sn^{4+}(0.00-0.15) - Fe^{3+}(0.50-0.70) - Pd^{2+}(0.80-1.00)	1h.50m.
S_6	20	Pb^{2+}(0.00-0.00) - Ti^{4+}(0.40-0.70) - VO^{2+}(0.80-1.00)	1h.50m.

separations were achieved on 20% TBP inpregnated silica gel-G layers. The important binary and ternary separations are summarized in Table 1 and 2.

DISCUSSION

Figs. 1a and 1b show the effect of impregnation on the R_f values of the metal ions in 1MHCl and 1M HNO_3. It is apparant that as we increase the impregnation, the R_f value generally decreases. However, in the case of Ag^+, Pb^{2+}, Sn^{2+} and Zr^{4+}, the R_f values are uniformly low in both the solvents at different degrees of impregnation. This shows a definite interaction of silica gel-G with the cations in question.

Figs. 2 and 3 refer to the R_f values of different metal ions in 1M HNO_3 and 0.1M citric acid. Even at the low concentration of 0.1M, the complexing properties of citric acid are apparant and very few metal ions show an R_f value of less than 0.1.

Figs. 4a, b and c explain the effect of pK_1 of the acids used as solvents, on the R_f values of metal ions. In almost all cases, the curve passes through a maximum or a minimum. This is because of the two factors which are affecting the R_f values i.e., the pH and the complex formation.

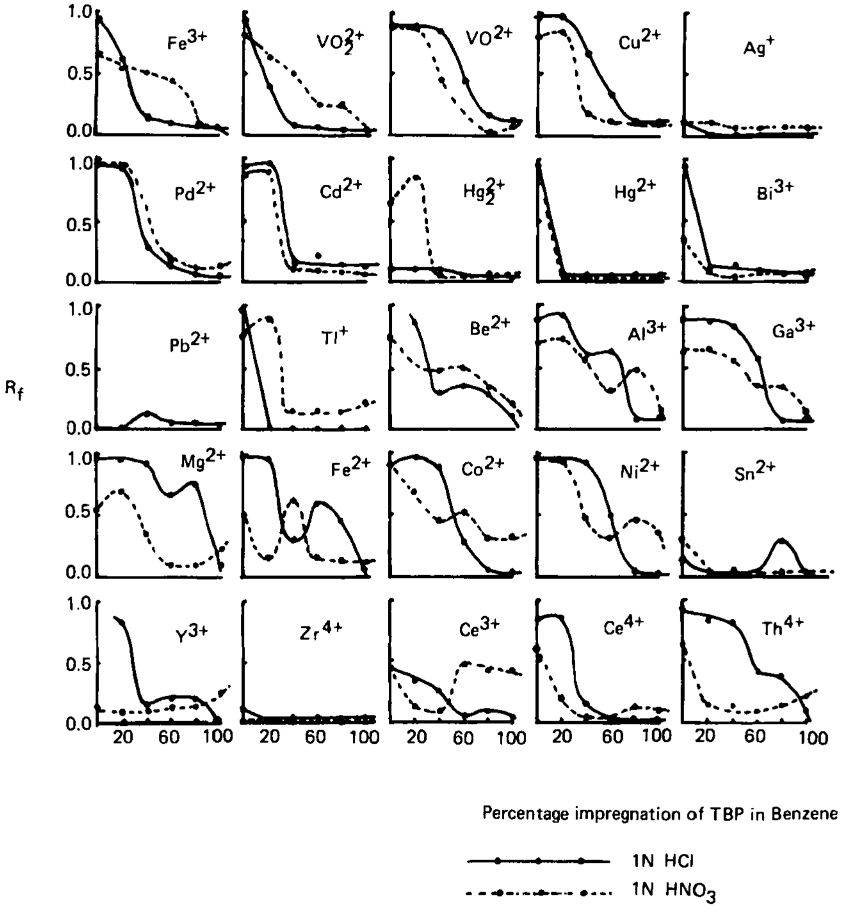

FIGURE 1a. Plot of R_f Vs. percentage impregnation of TBP.

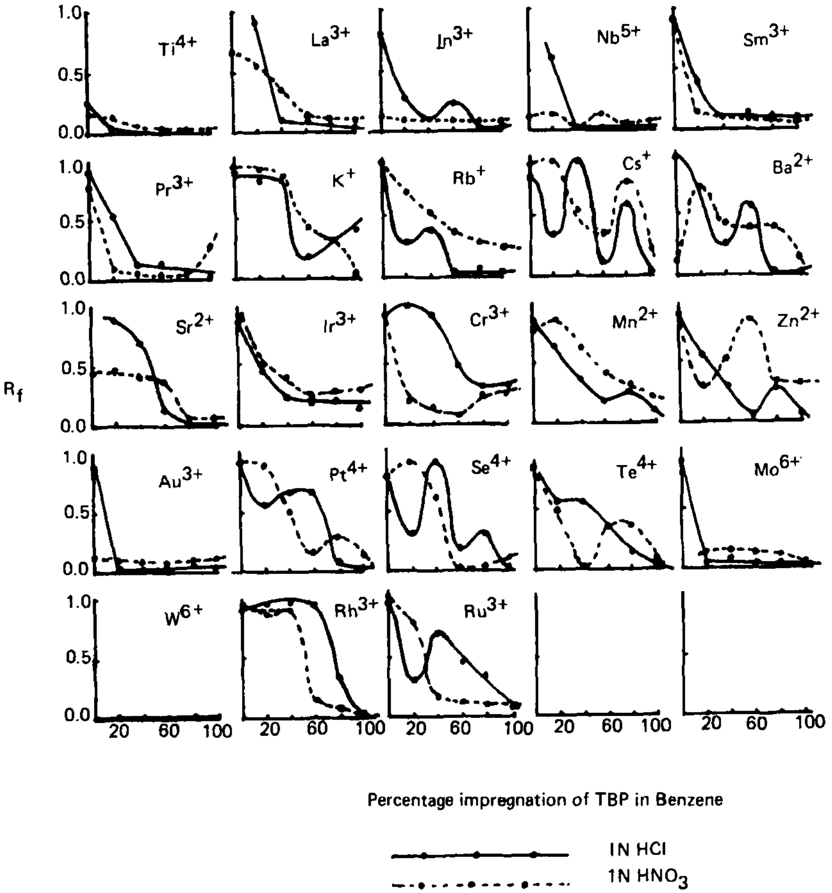

FIGURE 1b. Plot of R_f Vs. percentage impregnation of TBP.

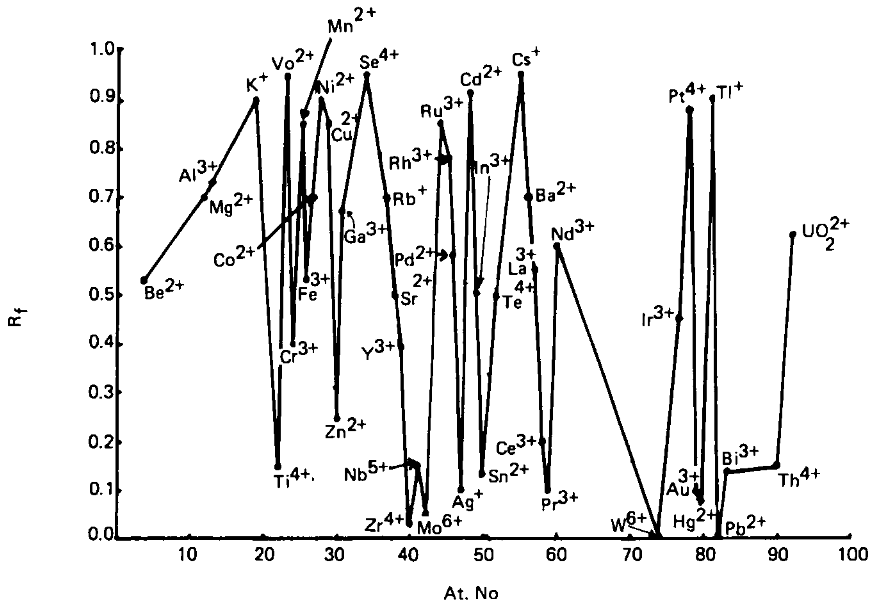

FIGURE 2. Plot of R_f Vs. atomic number in 1N HNO_3 (20% impregnation of TBP).

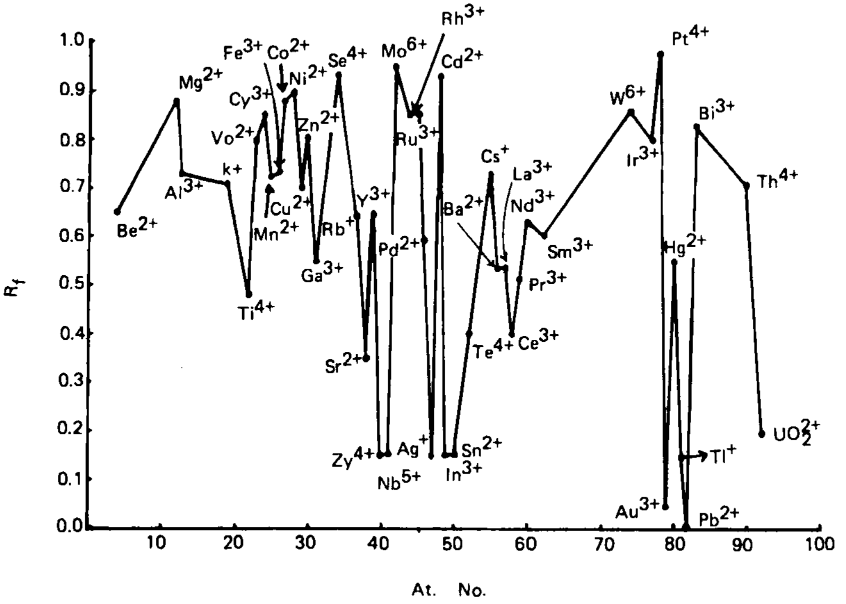

FIGURE 3. Plot of R_f Vs. atomic number in 0.1M citric acid (20% impregnation of TBP).

TABLE 3

Precipitation of Cations in the Solvents Used

Solvent	Cations which precipitate	Cations which do not precipitate
S_1	Hg_2^{2+}, W^{6+}, Ag^+, Tl^+	Pb^{2+}, Ti^{4+}, K^+, Ce^{3+}, La^{3+}, Mn^{2+}, VO^{2+}, Fe^{3+}, Nb^{5+}, Be^{2+}, Cs^+, Rb^+, Cd^{2+}, Ba^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Sn^{4+}, Ni^{2+}, Sr^{2+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Cu^{2+}, Ru^{3+}, Ce^{4+}, Mo^{6+}, Th^{4+}, Pd^{2+}, Y^{3+}, Zr^{4+}, Mg^{2+}, Te^{4+}, Bi^{3+}, Co^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+}, Nd^{3+}, Ir^{3+}
S_2	W^{6+}, Mo^{6+}	Pb^{2+}, Ti^{4+}, K^+, Ce^{3+}, La^{3+}, Hg_2^{2+}, Mn^{2+}, VO^{2+}, Fe^{3+}, Nb^{5+}, Be^{2+}, Cs^+, Rb^+, Cd^{2+}, Ba^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Sn^{4+}, Ni^{2+}, Sr^{2+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Cu^{2+}, Ru^{3+}, Ce^{4+}, Th^{4+}, Zr^{4+}, Mg^{2+}, Te^{4+}, Ag^+, Bi^{3+}, Co^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+}, Tl^+, Nd^{3+}, Ir^{3+}, Pd^{2+}, Y^{3+}
S_3	Pb^{2+}, Ba^{2+}, Sn^{4+}, W^{6+}, Sr^{2+}	Ti^{4+}, K^+, Ce^{3+}, La^{3+}, Hg_2^{2+}, Mn^{2+}, VO^{2+}, Fe^{3+}, Nb^{5+}, Be^{2+}, Cs^+, Rb^+, Cd^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Ni^{2+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Cu^{2+}, Ru^{3+}, Ce^{4+}, Mo^{6+}, Th^{4+}, Zr^{4+}, Mg^{2+}, Te^{4+}, Ag^+, Bi^{3+}, Co^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+}, Tl^+, Nd^{3+}, Ir^{3+}, Pd^{2+}, Y^{3+}

S_4	Pb^{2+}, Ce^{3+}, La^{3+}, Y^{3+}, Cd^{2+}, Sn^{4+}, Sr^{2+}, Cu^{2+}, Ce^{4+}, Th^{4+}, Te^{4+}, Ag^{+}, $\mathbf{Bi}^{3+}$, Co^{2+}, Nd^{3+}, Pd^{2+}, Hg_2^{2+}	Ti^{4+}, K^{+}, Mn^{2+}, VO^{2+}, Fe^{3+}, $\mathbf{Nb}^{5+}$, Fe^{2+}, Cs^{+}, Rb^{+}, Ba^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Ni^{2+}, W^{6+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Ru^{3+}, Mo^{6+}, Zr^{4+}, Mg^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+}, Tl^{+}, Ir^{3+}
S_5	Th^{4+}, Te^{4+}, Bi^{3+}	Pb^{2+}, Ti^{4+}, K^{+}, Ce^{3+}, La^{3+}, Mn^{2+}, VO^{2+}, Fe^{3+}, Nb^{5+}, Be^{2+}, Cs^{+}, Rb^{+}, Cd^{2+}, Ba^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Sn^{4+}, Ni^{2+}, W^{6+}, Sr^{2+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Cu^{2+}, Ru^{3+}, Ce^{4+}, Mo^{6+}, Zr^{4+}, Mg^{2+}, Ag^{+}, Co^{2+}, Ga^{3+}, Sn^{2+}, Tl^{+}, Nd^{3+}, Ir^{3+}, Pd^{2+}, Y^{3+}, UO_2^{2+}, Hg_2^{2+}
S_6	$\mathbf{Th}^{4+}$	Pb^{2+}, $\mathbf{Ti}^{4+}$, K^{+}, Ce^{3+}, La^{3+}, Mn^{2+}, VO^{2+}, Fe^{3+}, Nb^{5+}, Be^{2+}, Cs^{+}, Rb^{+}, Cd^{2+}, Ba^{2+}, Cr^{3+}, Au^{3+}, Al^{3+}, Sn^{4+}, Ni^{2+}, W^{6+}, Sr^{2+}, Rh^{3+}, Hg^{2+}, Se^{4+}, Cu^{2+}, Ru^{3+}, Ce^{4+}, Mo^{6+}, Zr^{4+}, Mg^{2+}, Te^{4+}, Ag^{+}, Bi^{3+}, Co^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+}, Tl^{+}, Nd^{3+}, Y^{3+}, Ir^{3+}, Pd^{2+}, Hg_2^{2+}

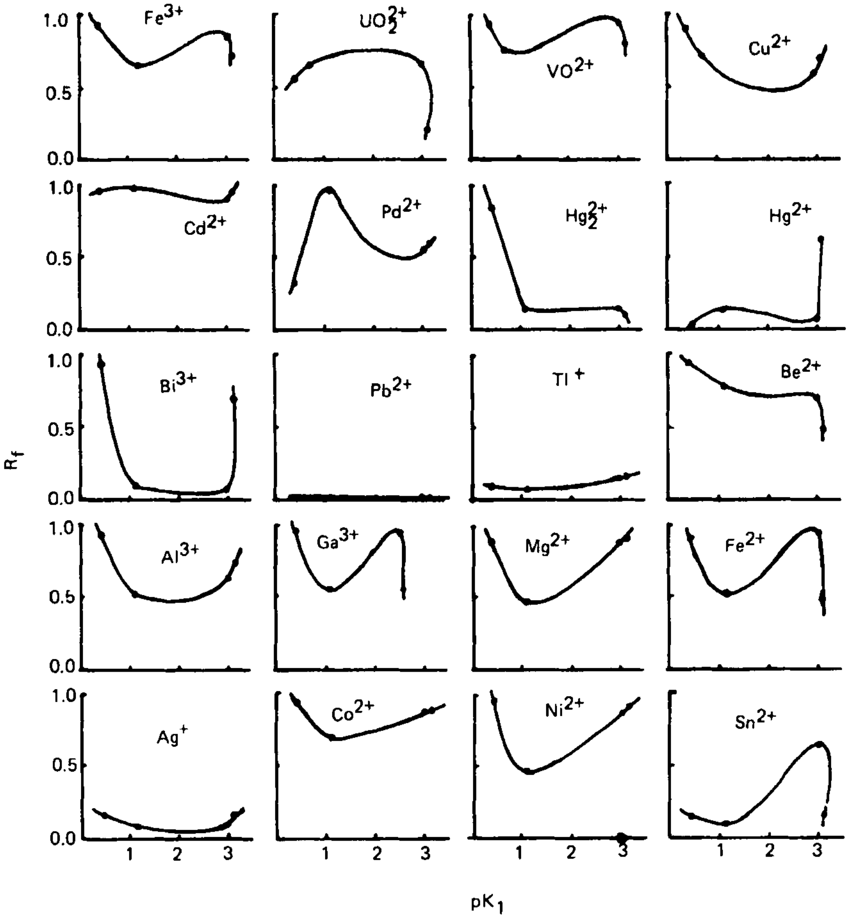
Fe3+
UO22+
VO2+
Cu2+
Cd2+
Pd2+
Hg22+
Hg2+
Bi3+
Pb2+
Tl+
Be2+
Al3+
Ga3+
Mg2+
Fe2+
Ag+
Co2+
Ni2+
Sn2+
1.0
0.5
0.0
Rf
1
2
3
pK1

FIGURE 4a.

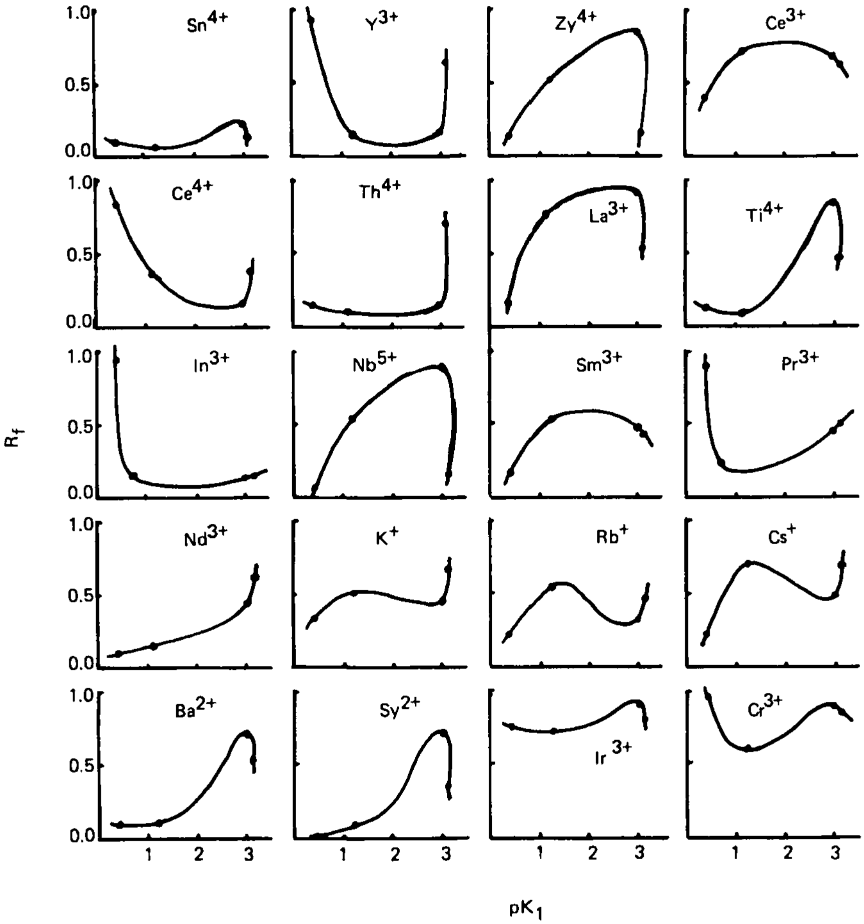
1.0
0.5
0.0
Sn4+
Y3+
Zy4+
Ce3+
Ce4+
Th4+
La3+
Ti4+
In3+
Nb5+
Sm3+
Pr3+
Nd3+
K+
Rb+
Cs+
Ba2+
Sy2+
Ir 3+
Cr3+
Rf
1
2
3
pK1

FIGURE 4b.

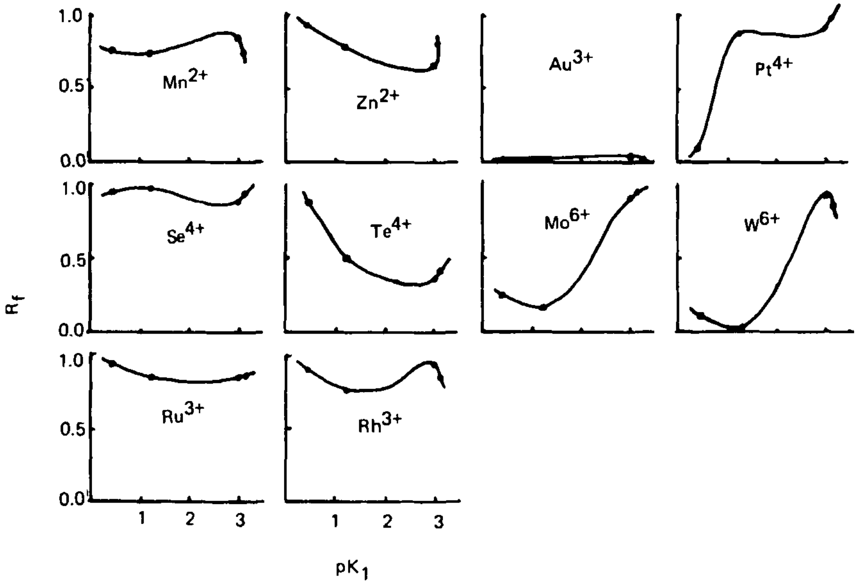

FIGURE 4c.
Plot of R_f Vs. pk_1.

A plot of R_f Vs. atomic number in 1M HNO_3 on 20% TBP impregnated layers (Fig. 5) shows some interesting results. Almost all the transitional metals fall on a straight line. This indicates that in case of transitional metals, the R_f is proportional to the atomic number which may be attributed to their similar chemical nature.

Table 1 summarizes the separations achieved. Thus the separations of Cs^+-K^+, Fe^{3+}-VO^{2+}, Y^{3+}-La^{3+}, Zr^{4+}-Th^{4+} and Ti^{4+}-Zr^{4+} with the help of simple eluants are interesting and show the advantage of reversed phase chromatography. This is confirmed by the ternary separations described in Table 2.

Table 3 shows that most of the cations which have low R_f values prcipitate in the solvent system concerned. There are, however, a few exceptions e.g., Ce^{3+}, La^{3+} and Pd^{2+} in solvent S_4 amd Th^{4+} in solvent S_6. These ions precipitate in the solvent systems but show a high R_f on TBP impregnated silica gel-G layers. This is probably due to the fact that the TBP impregnated silica gel-G immobilizes

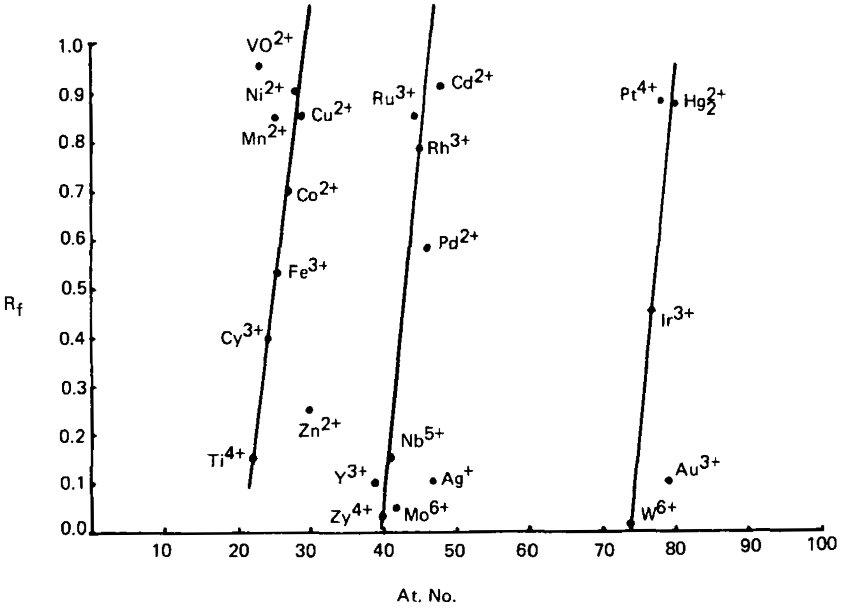

FIGURE 5. Plot of R_f Vs. atomic number of transitional metal ions in 1N HNO_3 (20% impregnation of TLP).

the precipitating oxalate, tartarate and citrate ions and hence increases the R_f value of the metal ions.

ACKNOWLEDGEMENT

The authors thank the University Grants Commission, New Delhi (India) for financial assistance to B.M.S.

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