

# Quantitative separation of $\text{Cr}^{3+}$ from $\text{Mo}^{6+}$ , $\text{W}^{6+}$ , $\text{Hg}_2^{2+}$ , $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$

## Chromatographic behaviour of 51 cations on papers impregnated with Sn(IV)-based inorganic ion exchangers in complex-forming acid systems

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(First received July 19th, 1991; revised manuscript received November 6th, 1991)

### ABSTRACT

The chromatographic behaviour of 51 metal ions was studied on tin(IV) arsenate-, tin(IV) phosphate-, tin(IV) tungstate-, tin(IV) molybdate- and tin(IV) selenite-impregnated papers in 0.5 M oxalic, citric and tartaric acid media. The composition and ion-exchange capacity of these papers were determined. The concentration of the anion in the exchanger deposited was found to vary directly with the  $pK_a$  of the corresponding anionic acids. The selectivity of the papers for different cations is discussed. The mechanism of migration is explained in terms of ion exchange, precipitation and adsorption. A published view on the prediction of elution sequence from  $R_F$  values was also checked. A number of binary and ternary separations were achieved.  $\text{Cr}^{3+}$  was quantitatively separated from binary mixtures and from synthetic mixtures containing common interfering metals.

### INTRODUCTION

Chromatography of metal ions on papers impregnated with tin(IV)-based inorganic ion exchangers offers interesting separation possibilities [1–10]. These papers are highly selective and give rapid separations with simple aqueous systems. Recently, ion-exchange chromatographic separations of some anions on hydrated tin(IV) oxide-impregnated papers were also reported [11]. However, the methods of preparation of these papers by different workers during the last two decades have not always been the same and the chemical composition of the material loaded on the strips was not determined. It is important that the various ion-exchange papers should be prepared again under similar experimental conditions, their compositions de-

termined and their selectivities for metal ions studied.

Another limitation in the earlier studies was the selection of solvents. In most instances, the non-complexing substance was used as a developer. To enhance the separation potential of these papers, it is therefore desirable to combine complexation with ion exchange. In this paper we show that the combination of these processes leads to excellent separation possibilities.

The exchangers based on tin(IV) were used to impregnate the papers owing to their high chemical stability and good ion-exchange capacity [12–16]. As these exchangers show high selectivity at low pH and decompose at high pH, weak acids were chosen as solvents so as to prevent the hydrolysis of the exchange materials. The complexing acids chosen

were oxalic, citric and tartaric acid. As a result, some analytically important separations were achieved, e.g.,  $\text{Cr}^{3+}$  was quantitatively separated from  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$  and other metal ions.

## EXPERIMENTAL

### Apparatus

Chromatography was performed on  $15 \times 3.5$  cm Whatman No. 1 paper strips in  $20 \times 5$  cm glass jars. A Bausch and Lomb Spectronic-20 instrument was used for colorimetry.

### Reagents

Tin(IV) chloride pentahydrate was used. All other chemicals and solvents used were of analytical-reagent grade from BDH.

### Preparation of ion-exchange papers

Papers impregnated with tin(IV)-based inorganic ion exchangers were prepared in the same manner as the tin(IV) arsenate-impregnated papers reported previously [6].

### Test solutions and detectors

The test solutions were generally 0.1 *M* in the metal nitrate or chloride and were prepared as described previously [5]. Conventional spot test reagents were used for detection purposes.

### Procedure

**Chromatography.** Chromatography was performed as described previously [5].

**Composition of paper.** Impregnated paper strips for each exchanger were separately dissolved in

$\text{HClO}_4\text{--HNO}_3\text{--H}_2\text{SO}_4$  (3:1:4) and the solution was evaporated to dryness. The residue was dissolved in 4 *M* hydrochloric acid and the solution was diluted to 50 ml in each instance. The tin and the anion present were determined by methods reported previously [12–16].

**Quantitative work.** A  $5 \cdot 10^4$   $\mu\text{g/ml}$  stock solution of chromium chloride was prepared, then diluted 200-fold. A 20- $\mu\text{l}$  volume of the solution containing 5  $\mu\text{g}$  of  $\text{Cr}^{3+}$  was then applied on to tin(IV) phosphate papers with the help of a lambda pipette. The other cations to be separated were also applied in the amounts shown in Table V. The strips were dried in air and saturated for 10 min with the developer and were then developed in 0.5 *M* oxalic acid until the solvent had ascended 11 cm. A pilot paper for each separation was run simultaneously in order to locate the exact position of the  $\text{Cr}^{3+}$  spot with the help of a colour agent. The area on the working strip was cut into small pieces and chromium was eluted with 0.25 *M*  $\text{H}_2\text{SO}_4$  at room temperature. The volume of solution was reduced by heating on a hot-plate. The paper pulp was oxidized with  $\text{HNO}_3\text{--HClO}_4\text{--H}_2\text{SO}_4$  (1:3:2). The solution was then evaporated to 10 ml, cooled and 0.5 ml of 0.1 *M*  $\text{KMnO}_4$  was added to oxidize [17]  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ . Five drops of 5% sodium azide solution were added to decolorize the brownish tint. The solution was transferred to a 25-ml volumetric flask and 1 ml of diphenyl carbazide solution was added followed by 2 ml of  $\text{NaH}_2\text{PO}_4$  solution. The blank was run in a similar way by following the entire procedure for an unspotted paper strip. The absorbance of this colour was measured at 540 nm and the amount of  $\text{Cr}^{3+}$  was obtained from a calibration graph [18].

TABLE I

COMPOSITION AND ION-EXCHANGE CAPACITY OF TIN(IV)-BASED ION-EXCHANGE PAPERS

Paper impregnated with	Concentration of reagents ( <i>M</i> )		Anion:Sn ratio	Ion-exchange capacity of impregnated papers (mequiv./g)
	Tin(IV) chloride pentahydrate	Sodium salt of anion		
Tin(IV) arsenate	0.10	0.25	2.15:1	0.38
Tin(IV) molybdate	0.10	0.25	2.75:1	0.40
Tin(IV) phosphate	0.10	0.10	1.44:1	0.34
Tin(IV) tungstate	0.10	0.20	4.8:1	0.30
Tin(IV) selenite	0.10	0.20	2.2:1	0.32

TABLE II

 $R_F$  VALUES OF CATIONS ON TIN(IV)-BASED ION-EXCHANGE PAPERS IN COMPLEX-FORMING ACID SYSTEMS

Cation	Tin(IV) arsenate			Tin(IV) phosphate			Tin(IV) molybdate			Tin(IV) tungstate			Tin(IV) selenite			Whatman No.1		
	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>
Ag <sup>+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb <sup>2+</sup>	0.00	0.05	0.11	0.03	0.14	0.14	0.81	0.02	0.30	0.04	0.04	0.11	0.05	0.02	0.30	0.06	0.90	0.95
Hg <sub>2</sub> <sup>2+</sup>	0.68	0.66	0.76	0.03	0.71	0.78	0.80	0.84	0.87	0.06	0.00	0.00	0.15	0.90	0.80	0.00	0.72	0.00
Hg <sub>2</sub> <sup>2+</sup>	0.95	0.65	0.80	0.85	0.75	0.76	0.87	0.76	0.81	0.82	0.82	0.86	0.72	0.74	0.75	0.00	0.00	0.00
Bi <sup>3+</sup>	0.50	0.30	0.07	0.11	0.75	0.12	0.90	0.37	0.17	0.77	0.07	0.94	0.25	0.34	0.32	0.07	0.95	0.95
Sb <sup>3+</sup>	N.D. <sup>a</sup>	0.78	N.D.	N.D.	N.D.	0.00	0.04	0.92	0.93	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.00	0.00
Pd <sup>2+</sup>	0.91	0.75	0.82	0.86	0.93	0.90	0.84	0.87	0.92	0.82	0.86	0.87	0.87	0.85	0.90	0.90	0.90	0.95
Pd <sup>4+</sup>	0.77	0.81	0.80	0.10	0.41	0.80	0.83	0.87	0.94	0.86	0.95	0.81	0.82	0.85	0.85	0.84	0.04	0.00
Ti <sup>+</sup>	0.54	0.72	0.52	0.69	0.42	0.37	0.73	0.54	0.56	0.04	0.17	0.06	0.74	0.74	0.72	0.91	0.82	0.90
Cd <sup>2+</sup>	0.94	0.86	0.57	0.89	0.74	0.61	0.87	0.90	0.84	0.94	0.91	0.96	0.85	0.85	0.90	0.96	0.95	0.97
Fe <sup>2+</sup>	0.77	0.94	0.44	0.81	0.65	0.85	0.83	0.93	0.86	0.68	0.82	0.72	0.98	0.85	0.77	0.00	0.94	0.96
Fe <sup>3+</sup>	0.75	0.06	0.13	0.85	T <sup>b</sup>	T	0.83	0.92	0.77	0.70	0.12	0.10	0.98	0.74	0.61	1.00	0.92	0.98
UO <sub>2</sub> <sup>2+</sup>	0.84	0.29	0.15	0.82	T	T	0.92	0.90	0.81	0.73	0.46	0.24	0.95	0.45	0.32	1.00	0.95	0.98
VO <sub>2</sub> <sup>2+</sup>	0.80	0.89	0.84	0.86	0.79	0.82	0.90	0.83	0.90	0.91	0.82	0.89	0.95	0.92	0.93	1.00	0.95	0.98
Ir <sup>3+</sup>	0.91	0.96	0.98	0.93	0.98	0.84	0.75	0.93	0.95	0.69	0.95	0.86	0.95	0.95	0.92	1.00	0.98	0.98
Zn <sup>2+</sup>	0.86	0.81	0.69	0.95	0.80	0.88	0.80	0.90	0.86	0.70	0.95	0.87	0.97	0.95	0.93	1.00	0.98	0.98
Mn <sup>2+</sup>	0.72	0.78	0.98	0.95	0.82	0.83	0.85	0.88	0.75	0.91	0.92	0.93	0.95	0.95	0.92	1.00	0.98	0.98
Cr <sup>3+</sup>	0.90	0.94	0.66	0.90	0.83	0.87	0.77	0.91	0.85	0.80	0.97	0.89	0.97	0.90	0.92	1.00	0.98	0.98
La <sup>3+</sup>	0.91	0.96	0.94	0.93	0.78	T	0.84	0.84	0.92	0.93	0.80	0.20	0.94	0.85	0.81	0.97	0.95	0.97
Y <sup>3+</sup>	0.86	0.71	0.95	0.88	0.04	0.07	0.75	0.95	0.68	0.95	0.50	0.19	0.97	0.95	0.92	0.97	0.95	0.95
Pr <sup>3+</sup>	0.95	0.88	0.70	0.10	0.32	0.34	0.82	0.85	0.89	0.98	0.57	0.21	0.10	0.64	0.87	0.00	0.96	0.97
Nb <sup>5+</sup>	0.88	0.98	0.87	0.89	0.86	0.84	0.80	0.92	0.83	0.95	0.81	0.91	0.92	0.85	0.85	0.97	0.95	0.95
Ce <sup>3+</sup>	0.95	0.50	0.92	0.06	0.20	0.25	0.86	0.93	0.80	0.91	0.25	0.09	0.95	0.92	0.94	0.00	0.95	0.95
Ce <sup>4+</sup>	0.84	0.45	0.93	0.96	0.15	0.17	0.81	0.63	0.85	0.95	0.28	0.24	0.00	N.D.	N.D.	0.00	0.95	0.95
Zr <sup>4+</sup>	0.92	0.96	0.79	T	T	0.00	0.54	0.90	0.82	0.97	0.75	0.10	0.45	N.D.	N.D.	0.00	0.94	0.95
Rh <sup>3+</sup>	0.95	N.D.	0.93	0.77	N.D.	0.43	0.86	0.92	0.92	0.87	0.88	0.83	0.90	0.87	0.97	0.97	0.95	0.97
Ta <sup>5+</sup>	0.92	0.83	0.87	0.92	0.95	0.96	0.75	0.94	0.86	0.95	0.83	0.86	0.98	0.92	0.92	0.97	0.95	0.95
Cu <sup>2+</sup>	0.95	0.69	0.77	0.02	0.55	0.73	0.76	0.87	0.95	0.02	0.70	0.87	0.70	0.85	0.83	0.05	0.95	0.98
Gd <sup>3+</sup>	N.D.	N.D.	N.D.	N.D.	0.15	0.15	0.30	0.83	0.77	0.00	0.39	0.12	0.10	0.85	0.79	0.97	0.96	0.95
In <sup>3+</sup>	0.92	0.94	0.95	0.87	0.07	0.09	0.86	0.92	0.92	0.87	0.80	0.86	0.75	0.85	0.85	0.97	0.95	0.95
Ru <sup>3+</sup>	0.88	0.87	0.87	0.90	0.80	0.72	0.89	0.76	0.88	0.79	0.91	0.81	0.95	0.95	0.95	0.97	0.95	0.97
Th <sup>4+</sup>	0.94	0.80	0.84	0.17	T	0.20	0.11	0.74	0.58	0.10	0.27	0.18	0.60	0.75	0.77	0.20	0.95	0.95
Ti <sup>4+</sup>	0.33	0.93	0.27	N.D.	0.75	0.12	N.D.	0.92	0.91	0.88	0.51	0.97	N.D.	0.20	0.20	T	0.02	0.97
Au <sup>3+</sup>	0.60	0.31	0.63	0.51	0.70	0.61	0.61	0.55	0.61	0.54	0.66	0.70	0.30	0.45	0.70	0.20	0.00	0.50
Pt <sup>4+</sup>	0.98	0.82	0.95	0.87	0.98	0.92	0.00	0.75	0.82	0.73	0.91	0.84	N.D.	N.D.	0.88	0.93	0.98	0.95
W <sup>6+</sup>	0.98	0.98	0.98	0.00	0.98	0.98	N.D.	0.87	0.88	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.98	0.95
Mo <sup>6+</sup>	0.92	0.98	0.95	0.00	0.00	0.00	N.D.	N.D.	N.D.	0.73	0.81	0.90	N.D.	N.D.	N.D.	0.05	0.98	0.95
Se <sup>4+</sup>	0.85	0.78	0.80	0.93	0.79	0.67	N.D.	0.32	0.37	0.61	0.13	0.52	N.D.	N.D.	N.D.	0.93	0.98	0.95
Te <sup>4+</sup>	0.95	0.33	0.81	0.15	0.07	0.12	0.40	0.08	0.06	0.05	0.00	0.05	N.D.	N.D.	N.D.	0.95	0.90	0.92
Mg <sup>2+</sup>	0.75	0.80	0.79	0.85	0.87	0.63	0.65	0.83	0.90	0.67	0.78	0.64	0.77	0.85	0.80	0.80	0.93	0.93
Be <sup>2+</sup>	0.90	0.64	0.23	0.61	0.10	0.10	0.90	0.86	0.90	0.89	0.98	0.91	0.98	0.94	0.93	1.00	0.96	0.97
Al <sup>3+</sup>	0.97	0.22	0.10	0.55	0.16	0.16	0.91	0.88	0.79	0.95	0.98	0.94	0.94	0.95	0.85	1.00	0.95	0.96
Ga <sup>3+</sup>	0.94	0.82	0.77	0.19	0.82	0.32	0.92	0.92	0.93	0.92	0.98	0.70	0.98	0.95	0.85	1.00	0.95	0.97
K <sup>+</sup>	0.92	0.72	0.80	0.92	0.83	0.85	0.79	0.83	0.92	0.75	0.86	0.72	0.95	0.95	0.84	0.95	0.98	0.98
Rb <sup>+</sup>	0.95	0.93	0.51	0.81	0.80	0.86	0.66	0.90	0.81	0.71	0.75	0.75	0.93	0.95	0.82	0.95	0.98	0.98
Cs <sup>+</sup>	0.95	0.92	0.73	0.87	0.74	0.78	0.69	0.90	0.92	0.42	0.50	0.40	0.95	0.95	0.84	0.95	0.98	0.98
Ba <sup>2+</sup>	0.44	0.43	0.86	T	0.72	0.61	0.44	N.D.	N.D.	0.44	0.65	0.26	0.83	0.94	0.83	1.00	0.96	0.95
Sr <sup>2+</sup>	0.95	0.92	0.93	0.08	0.82	0.87	N.D.	N.D.	N.D.	0.89	0.91	0.98	0.93	0.90	0.90	1.00	0.95	0.95
Ni <sup>2+</sup>	0.98	0.94	0.84	0.77	0.98	0.95	0.91	0.97	N.D.	0.83	0.82	0.66	0.78	0.75	0.72	1.00	0.95	0.95
Co <sup>2+</sup>	0.98	0.92	0.73	0.92	0.95	0.82	0.83	0.82	0.89	0.79	0.85	0.87	0.95	0.92	0.89	1.00	0.95	0.97
Ca <sup>2+</sup>	0.92	0.95	0.89	0.92	0.92	0.90	0.84	0.91	0.90	0.88	0.90	0.80	N.D.	N.D.	N.D.	1.00	0.95	0.95

<sup>a</sup> N.D. = Not detected.<sup>b</sup> T = Tailing.

TABLE III  
PRECIPITATION OF CATIONS IN MIXTURES OF SOLVENT AND IMPREGNATING MATERIAL

Solvent	Cations + solvent	Cations + sodium arsenate + solvent		Cations + sodium molybdate + solvent		Cations + sodium phosphate + solvent		Cations + sodium tungstate + solvent		Cations + sodium selenite + solvent	
		P	NP	P	NP	P	NP	P	NP	P	NP
0.5 M citric acid	None	$\text{Hg}^{2+}, \text{Ti}^{4+}, \text{Pd}^{4+}, \text{Ag}^+, \text{Sb}^{3+}$	None	$\text{Ag}^+, \text{Pb}^{2+}$	$\text{Ag}^+$	NIL	$\text{Ag}^+, \text{Mo}^{6+}$	$\text{Pb}^{2+}$	$\text{Ag}^+, \text{Hg}_2^{2+}, \text{Te}^{4+}$	$\text{Ag}^+$	None
0.5 M tartaric acid	None	$\text{Ag}^+, \text{Sb}^{3+}, \text{Hg}_2^{2+}$	None	None	$\text{Ag}^+, \text{Te}^{4+}$	$\text{Zr}^{4+}$	$\text{Ag}^+, \text{Mo}^{6+}$	None	$\text{Ag}^+, \text{Hg}_2^{2+}$	$\text{Ag}^+$	None
0.5 M oxalic acid	$\text{Cu}^{2+}, \text{Hg}_2^{2+}, \text{Hg}^{2+}, \text{Pb}^{2+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Ce}^{4+}, \text{Th}^{4+}$	$\text{Ag}^+, \text{Fe}^{2+}, \text{Zr}^{4+}$	None	None	$\text{Ag}^+, \text{Sb}^{3+}, \text{Pt}^{4+}$	$\text{Ag}^+, \text{Pb}^{2+}, \text{Zr}^{4+}, \text{W}^{6+}$	$\text{Mo}^{6+}$	$\text{Pb}^{2+}, \text{Cu}^{2+}, \text{Pt}^{4+}$	$\text{Ag}^+$	$\text{Ag}^+, \text{Ce}^{4+}$	None

<sup>a</sup> P = Cations that precipitate.

<sup>b</sup> NP = Cations that do not precipitate.

## RESULTS AND DISCUSSION

The anion:Sn ratios of the exchangers deposited on paper and the ion-exchange capacity of the treated papers are given in Table I. Chromatography was performed on tin (IV) arsenate-, tin (IV) molybdate-, tin (IV) phosphate-, tin (IV) tungstate- and tin (IV) selenite-impregnated papers in the following solvents:  $S_1$ , 0.5 *M* oxalic acid;  $S_2$ , 0.5 *M* citric acid; and  $S_3$ , 0.5 *M* tartaric acid. The same solvents were used for Whatman No.1 papers for comparison.

In many instances it was found possible to separate one cation from numerous metal ions. The  $R_F$  values are summarized in Table II. Some useful separations were also achieved on plain papers.

Table I summarizes the composition studies on impregnated papers. A plot of anion:Sn ratio *versus*  $pK_a$  of anionic acids for all the impregnated papers reveals that the concentration of the anion in the exchanger deposited varies directly with the  $pK_a$  of the corresponding anionic acids (Fig. 1).

In order to study the effect of impregnation, the value of  $R_i$  ( $= R_F$  on Whatman No.1 papers  $- R_F$  on impregnated papers) for all cations were calculated. For the cations having  $R_i > 0.4$ , the following conclusions can be drawn.

(1) Tin(IV) arsenate-impregnated papers in 0.5 *M* tartaric acid media are selective for  $Rb^+$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $UO_2^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Be^{2+}$  and  $Al^{3+}$  owing to the higher adsorption on these papers.

(2) With tin(IV) phosphate-impregnated papers,

$Be^{2+}$ ,  $Y^{3+}$ ,  $Rh^{3+}$  and  $Ti^{4+}$  in 0.5 *M* tartaric acid,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$  and  $Ga^{3+}$  in 0.5 *M* oxalic acid and  $In^{3+}$ ,  $Zr^{4+}$  and  $Th^{4+}$  in 0.5 *M* citric acid media are selectively adsorbed.

(3) On tin(IV) tungstate-impregnated papers,  $Cs^+$ ,  $Pb^{2+}$ ,  $Tl^+$ ,  $La^{3+}$  and  $Zr^{4+}$  in 0.5 *M* tartaric acid,  $Se^{4+}$  and  $Te^{4+}$  in 0.5 *M* citric acid and  $Gd^{3+}$  in 0.5 *M* oxalic acid media show a high degree of adsorption.

(4) In 0.5 *M* oxalic acid media, tin(IV) selenite-impregnated papers are highly selective for  $Pr^{3+}$  whereas tin(IV) molybdate-impregnated papers selectively adsorb  $Pt^{4+}$ .

The zero  $R_F$  for a number of cations on impregnated papers may be due to precipitation, ion exchange and strong adsorption owing to the high charge. On mixing solutions of the cations with oxalic acid, it was found that with  $Cu^{2+}$ ,  $Hg_2^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Pr^{3+}$ ,  $Ce^{3+}$ ,  $Ce^{4+}$  and  $Th^{4+}$  a precipitate was obtained. In such instances, the zero  $R_F$  on plain papers is therefore due to the precipitation mechanism. On mixing with citric and tartaric acid, no ion was precipitated. The zero  $R_F$  on plain papers in these solvents may be due to interaction with the paper matrix, as in the case of  $Ag^+$  and  $Sb^{3+}$ . For  $Zr^{4+}$ ,  $Ti^{4+}$  and  $Pd^{4+}$ , the zero  $R_F$  may be due to the strong adsorption owing to the high charge. In order to simulate conditions on impregnated papers, the sodium salt of the anion was added to the cation solution followed by the solvent. A number of ions precipitated under these conditions (see Table III). In these instances also the precipitation mechanism holds good.

The chromatographic behaviour of metal ions on ion-exchange columns and on impregnated papers using the same exchangers is interesting. The  $R_F$  values of metal ions are related to their distribution coefficients on tin(IV)-based exchangers. For higher distribution coefficients, we observe lower  $R_F$  values. This behaviour is expected because when the  $K_d$  is higher, the ion is more strongly held by the ion exchanger and is less easily allowed to move further, giving a lower  $R_F$  value. This trend was confirmed by determining the  $R_F$  values of some common metal ions on all the impregnated papers in demineralized water. The  $K_d$  values for these ions are given for comparison in Table IV, which shows that for most of the cations studied, the sequence of  $K_d$  values is the same as that predicted from  $R_F$  values. If

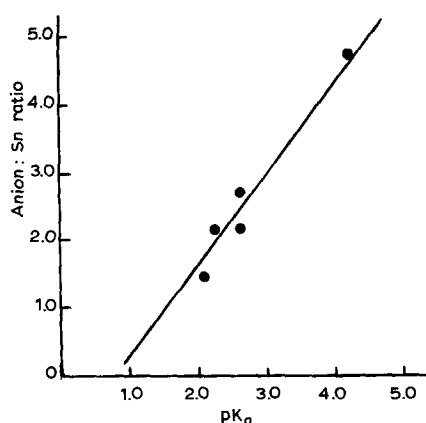


Fig. 1. Plot of anion:Sn ratio *versus*  $pK_a$  for anionic acids.

TABLE IV

COMPARISON OF  $K_d$  VALUES AND  $R_F$  VALUES OF SOME IONS ON TIN(IV)-BASED EXCHANGERS

Demineralized water as medium.

Exchanger	$K_d$ [12-16, 19]	$R_F$
Tin(IV) arsenate	$\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+}$ $\text{Zn}^{2+} > \text{Cd}^{2+}$ $\text{In}^{3+} > \text{Y}^{3+} > \text{Al}^{3+} > \text{La}^{3+} > \text{Ga}^{3+}$ $\text{Ni}^{2+} > \text{Fe}^{3+} > \text{Co}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$ $\text{Th}^{4+} > \text{Zr}^{4+}$	$\text{Mg}^{2+} > \text{Ba}^{2+} = \text{Sr}^{2+} > \text{Ca}^{2+}$ $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ $\text{La}^{3+} > \text{Y}^{3+} > \text{In}^{3+} > \text{Al}^{3+} > \text{Ga}^{3+}$ $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Fe}^{3+} > \text{Mn}^{2+}$ $\text{Th}^{4+} > \text{Zr}^{4+}$
Tin(IV) molybdate	$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$ $\text{Y}^{3+} > \text{Al}^{3+}$	$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$ $\text{Al}^{3+} > \text{Y}^{3+}$
Tin(IV) tungstate	$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$ $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$	$\text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$
Tin(IV) phosphate	$\text{Cu}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$	$\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$
Tin(IV) selenite	$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ $\text{Cd}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+}$ $\text{La}^{3+} > \text{Y}^{3+} > \text{In}^{3+} > \text{Ga}^{3+} > \text{Al}^{3+}$ $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Fe}^{3+}$ $\text{Zr}^{4+} > \text{Th}^{4+}$	$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+}$ $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$ $\text{Al}^{3+} > \text{In}^{3+} > \text{Ga}^{3+} > \text{Y}^{3+} > \text{La}^{3+}$ $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+} > \text{Pb}^{2+}$ $\text{Th}^{4+} > \text{Zr}^{4+}$

it is considered that the elution sequence can be predicted from  $K_d$  values, it follows that the  $R_F$  values are not reliable for such prediction for the following reasons: in paper chromatography the solvent ascent is too fast to achieve equilibrium; some of the ions definitely interact in a different manner with the paper than with the ion exchanger; and the material obtained by precipitation from solution and that deposited on paper have different compositions. As the  $K_d$  values depend on the composition of the material, they are found to be different.

Owing to above facts, the Alberti and Torracca's view [20] that the elution sequence can be predicted from  $R_F$  values is not very convincing. At best the  $R_F$  values are a rough guide especially when they differ from one another considerably.

On the basis of  $R_F$  values, a large number of binary and ternary separations are possible. Some of the important ones actually achieved are as follows:

(a)  $\text{Cr}^{3+}$ – $\text{Mo}^{6+}$  or  $\text{W}^{6+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Sr}^{2+}$  [on tin(IV) phosphate paper in 0.5 *M* oxalic acid];

(b)  $\text{Ba}^{2+}$ – $\text{Sr}^{2+}$  or  $\text{Ca}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pd}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  or  $\text{Cu}^{2+}$  [on tin(IV) tungstate paper in 0.5 *M* tartaric acid];

(c)  $\text{Zr}^{4+}$ – $\text{Th}^{4+}$  or  $\text{Gd}^{3+}$  or  $\text{Te}^{4+}$  [on tin(IV) tungstate paper in 0.5 *M* oxalic acid];

(d)  $\text{In}^{3+}$ – $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ti}^{4+}$  or  $\text{Be}^{2+}$  [on tin(IV) arsenate paper in 0.5 *M* tartaric acid];

(e)  $\text{Pb}^{2+}$ – $\text{UO}_2^{2+}$  or  $\text{Pd}^{4+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{VO}_2^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  or  $\text{Mg}^{2+}$  [on Whatman No.1 paper in 0.5 *M* oxalic acid];

(f)  $\text{Pb}^{2+}$ – $\text{Hg}_2^{2+}$ – $\text{Bi}^{3+}$  and  $\text{Ag}^+$ – $\text{Au}^{3+}$ – $\text{Pt}^{4+}$  [on tin(IV) arsenate paper in 0.5 *M* oxalic acid].

The main advantage of this work lies in the fact that  $\text{Cr}^{3+}$  was quantitatively separated from binary mixtures containing larger amounts of other metal ions such as  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  (Table V). In order to explore the possible application of the method in a wider field, two synthetic mixtures were prepared by taking  $\text{Cr}^{3+}$  together with all these metal ions.  $\text{Cr}^{3+}$  was successfully separated from these mixtures as indicated in Table V. The complex-forming acids were found to be very useful solvents for metal ion separations. Even on Whatman No.1 paper, such important separations such as  $\text{Cr}^{3+}$ – $\text{Mo}^{6+}$  (in 0.5 *M* oxalic acid),  $\text{Hg}_2^{2+}$ – $\text{Hg}_2^{2+}$  (in 0.5 *M* citric acid) and  $\text{Ti}^{4+}$ – $\text{Zr}^{4+}$  or  $\text{La}^{3+}$  (in 0.5 *M* citric acid) were achieved.

TABLE V

QUANTITATIVE SEPARATION OF  $\text{Cr}^{3+}$  IN BINARY AND SYNTHETIC MIXTURES

Sample No.	Amount of $\text{Cr}^{3+}$ loaded ( $\mu\text{g}$ )	Amount of other metal ion loaded ( $\mu\text{g}$ )	Amount of $\text{Cr}^{3+}$ found ( $\mu\text{g}$ )	Error (%)
1	5.00	$\text{Ag}^+$ (340)	5.00	0.00
2	5.00	$\text{Sr}^{2+}$ (423)	5.40	-8.00
3	5.00	$\text{Pb}^{2+}$ (662)	5.00	0.00
4	5.00	$\text{Ba}^{2+}$ (522)	5.30	-6.00
5	5.00	$\text{Hg}_2^{2+}$ (560)	5.35	-7.00
6	5.00	$\text{Cu}^{2+}$ (500)	5.40	-8.00
7	5.00	$\text{Mo}^{6+}$ (412)	5.00	0.00
8	5.00	$\text{W}^{6+}$ (660)	5.00	0.00
9	5.00	Mixture	5.60	-12.00
10	5.00	Mixture	5.50	-10.00

## ACKNOWLEDGEMENT

The authors are grateful to the University Grants Commission, New Delhi (India), for financial assistance.

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