

Complexation Ion-exchange Chromatography of Some Metal Ions on Papers Impregnated with Ti(IV)-Based Inorganic Ion Exchangers

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Abstract

The chromatographic behavior of 40 metal ions is studied on titanium (IV) arsenate, titanium(IV) phosphate-, titanium (IV) molybdate-, titanium(IV) tungstate-, and titanium(IV) selenite-impregnated papers in 0.1M oxalic, citric, and tartaric acid as mobile phases. Similar studies are carried out on Whatman No. 1 papers for comparison. The ion-exchange capacity of these papers is determined, and their selectivity for different cations is discussed. The mechanism of migration is explained in terms of ion-exchange, precipitation, and adsorption. The prediction of elution sequence from R_f values is also checked. The average R_i is found to be almost linearly dependent on the charge of the metal ions. The effect of the pK_a of complexing acids on average R_f values of 3d series metal ions is explained. A number of binary and ternary separations are achieved.

Introduction

Titanium(IV) based inorganic ion-exchangers have been found to possess promising thermal and chemical stability and have been used in the column chromatography (1,2), thin-layer chromatography (3,4), and paper chromatography (5–13) of metal ions. Papers impregnated with these materials are highly selective for metal ions, and a number of metal ion separations can be achieved. However, the methods of preparation of these papers have not always been the same in the last 25 years, and their ion-exchange capacity was not determined. It is therefore important that papers impregnated with various titanium(IV)-based exchangers should be prepared again, their ion-exchange capacity determined, and selectivities for metal ions studied.

In earlier studies, noncomplexing substances were generally used as a mobile phase, and in only one case was a complexing acid eluent used (14). In order to enhance the separation potential of these papers, therefore, it is desirable to combine complexation with ion-exchange. It is observed that the combined effect of these two separation mechanisms leads to much better separation possibilities.

The titanium(IV)-based exchangers show high selectivity at low pH and decompose at high pH. As such, weak acids were chosen as mobile phases in order to prevent the hydrolysis of the exchange material. Appropriate complexing acids chosen for evaluation included oxalic, citric, and tartaric acid.

Experimental

Apparatus

Chromatography was performed on 15- × 3.5-cm Whatman (Clifton, NJ) No. 1 paper strips in 20- × 5-cm glass jars.

Reagents

Titanium(IV) chloride (Reidal, Germany) was used. All other chemicals and solvents used were of analytical reagent grade from B.D.H. (British Drug House, London, England).

Preparation of ion-exchange papers

Papers impregnated with titanium(IV)-based inorganic ion-exchangers were prepared in the same manner as the titanium(IV) arsenate-impregnated papers reported earlier (13). In the case of titanium(IV) phosphate-impregnated papers, the ones prepared using sodium dihydrogen phosphate (NaH_2PO_4) were chosen for chromatography.

Ion exchange capacity

All impregnated papers were found to possess considerable ion-exchange capacity. For Na^+ ions ($\text{Na}^+ - \text{H}^+$ exchange), the ion-exchange capacity in mequiv-per-gram of treated papers was determined by column experiments (saturation method) (15).

Test solutions

The test solutions were generally 0.1M in metal nitrate or chloride and were prepared as described previously (16).

Detectors

Conventional spot test reagents were used for detection purposes.

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Results and Discussion

The conditions of preparation and the ionexchange capacity of the treated papers are given in Table I. Chromatography was performed on titanium(IV) phosphate (TiP), titanium(IV) tungstate (TiW), titanium(IV) molybdate (TiMo), titanium(IV) selenite (TiSe), and titanium(IV) arsenate (TiAs) papers in the following mobile phases: M₁, 0.1M oxalic acid; M₂, 0.1M citric acid; and M₃, 0.1M tartaric acid. The same mobile phases were used for Whatman No. 1 papers for comparison. In the case of different sets of papers impregnated with TiP and TiSe, the papers having higher ion-exchange capacity were chosen for studies. The R_F values of metal ions are summarized in Table II. In many instances, it is possible to separate metal ions. Some useful separations were actually achieved on impregnated and Whatman No. 1 papers. The salient features of this study are described in the following sections.

Table I. Composition and Ion-Exchange Capacity of Titanium(IV)-Based Ion-Exchange Papers

Paper impregnated with	Concentration of reagents (M)		Ion-exchange capacity of impregnated papers (mequiv/g)
	Titanium(IV) chloride	Sodium salt of anion	
1. Titanium(IV) molybdate	0.25	0.25	0.33
2a. Titanium(IV) phosphate*	0.50	0.50	0.34
2b. Titanium(IV) phosphate [†]	0.50	0.50	0.10
3. Titanium(IV) arsenate	0.25	0.25	0.30
4. Titanium(IV) tungstate	0.25	0.25	0.35
5a. Titanium(IV) selenite	0.10	0.20	0.10
5b. Titanium(IV) selenite	0.05	0.05	0.05
5c. Titanium(IV) selenite	0.50	0.50	0.38

* Using NaH₂PO₄.
[†] Using Na₃PO₄.

Effect of impregnation

In order to study the effect of impregnation, R_i values (R_F on Whatman No. 1 paper – R_F

on impregnated paper) for all metal ions were calculated. For metals with $R_i > 0.6$, the following conclusions can be drawn.

First, on TiW-impregnated papers, Cu²⁺, Ba²⁺, and Rb⁺ in 0.1M oxalic acid; Bi³⁺, UO₂²⁺, VO₂⁺, Zn²⁺, La³⁺, Pr³⁺, and Al³⁺ in 0.1M citric acid; and K⁺, Ni²⁺, and Se⁴⁺ in 0.1M tartaric acid media show a higher degree of adsorption.

Second, with TiAs-impregnated papers, Fe³⁺, UO₂²⁺, VO₂⁺, and Co²⁺ in 0.1M tartaric acid; Bi³⁺ and Al³⁺ in 0.1M citric acid; and Pd²⁺, Tl²⁺, Zn²⁺, and Mo⁶⁺ in 0.1M oxalic acid media are selectively adsorbed.

Third, Sm³⁺, Cu²⁺, and Nd³⁺ in 0.1M oxalic acid; Sb³⁺, Bi³⁺, Cd²⁺, and Sn⁴⁺ in 0.1M citric acid; and Fe³⁺, UO₂²⁺, VO₂⁺, Fe²⁺, and Cr³⁺ in 0.1M tartaric acid media are selectively adsorbed on TiMo-impregnated papers.

Fourth, TiP-impregnated papers in 0.1M citric acid are highly selective for Co²⁺ and Mo⁶⁺. The same is true on TiSe-impregnated papers for Hg²⁺, Al³⁺, and Sr²⁺ due to higher adsorption on these papers.

Precipitation effect

The metal ions that have zero or very low R_F values are because of (a) precipitation, (b) strong adsorption due to high charge, and (c) complex formation.

Upon mixing a solution of metal ion with sodium tungstate solution followed by 0.1M citric acid, a precipitate was obtained for Hg²⁺, Ag⁺, Bi³⁺, UO₂²⁺, Zr⁴⁺, and La³⁺. For these metal ions, the zero or very low R_F values on TiW papers in 0.1M citric acid media are therefore due to a precipitation mechanism. In order to simulate conditions on other impregnated papers in different mobile phases, a solution of corresponding sodium salt of the anionic part of the exchanger was added to the

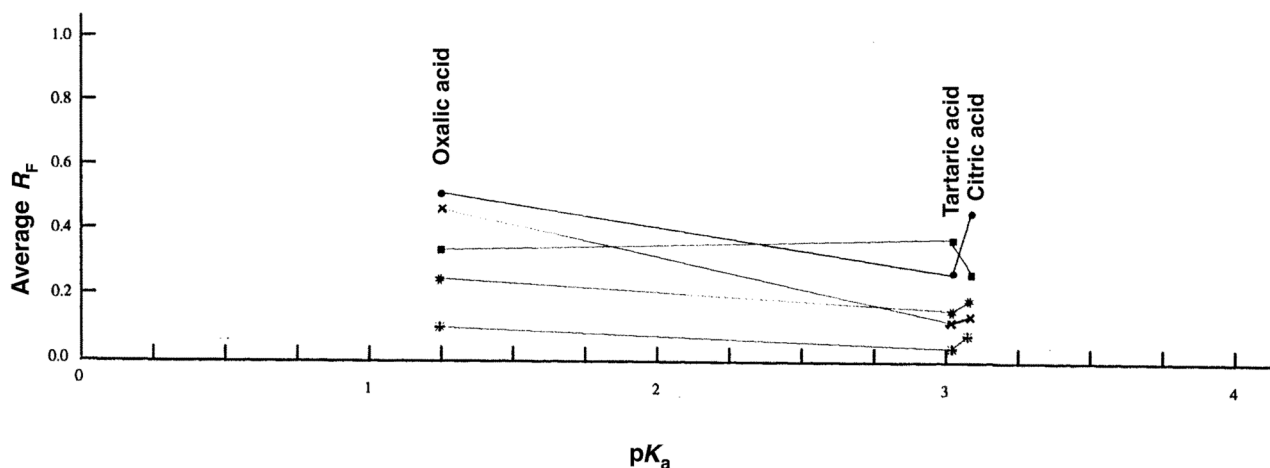


Figure 1. Plots of Average R_F versus pK_a : ●, titanium(IV) molybdate; x, titanium(IV) phosphate; ■, Titanium(IV) tungstate; x, titanium(IV) selenite; *, titanium(IV) arsenate.

metal ion solution followed by the addition of the mobile phase used. Various metal ions were precipitated under these conditions (Table III).

For all those metal ions, zero or very low R_F values are due to a precipitation mechanism. In contrast, for metal ions having zero or very low R_F values on Whatman No. 1 papers, no precipitate was obtained upon the addition of metal ion solution with the mobile phase used (Table III). Thus, the zero or very low R_F values of metal ions on Whatman No. 1 papers in these mobile phases is probably due to interaction with the paper matrix, as in the case of Ag^+ and Hg_2^{2+} .

Prediction of elution sequence

The chromatographic behavior of metal ions on ion-exchange columns and on impregnated papers using the same exchangers is quite interesting. The R_F values of metal ions are related to their distribution coefficients (K_d) on titanium(IV)-based exchangers. For higher distribution coefficients, lower R_F values were observed. This behavior is expected, because when K_d is higher, the ion is more strongly held by the ion-exchanger and 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 demineral-

Table II. R_F Values of Metal Ions on Titanium(IV)-Based Ion-Exchange Papers in Complex-Forming Acid Mobile Phases

Cation	Titanium(IV) arsenate			Titanium(IV) phosphate			Titanium(IV) molybdate			Titanium(IV) tungstate			Titanium(IV) selenite			Whatman No. 1		
	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3
Ag ⁺	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 ²⁺	0.10	0.04	0.09	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.05	0.09	0.00	0.00	0.00	0.00	0.88	0.95
Cu ²⁺	0.46	0.23	0.17	0.68	0.08	0.08	0.11	0.40	0.49	0.07	0.37	0.34	0.10	T [†]	0.06	0.95	0.95	0.93
Sb ³⁺	0.14	0.18	0.29	0.06	0.00	0.04	T	0.18	0.11	0.04	0.04	0.05	ND [†]	ND	ND	0.86	0.89	0.97
Bi ³⁺	0.13	0.08	0.03	0.08	0.00	0.00	0.38	0.11	0.00	0.15	0.00	0.04	0.00	0.04	0.00	0.06	0.80	T
Td ²⁺	0.38	0.80	0.74	0.70	0.00	0.00	T	0.62	0.35	0.48	0.29	0.70	0.09	0.07	0.07	0.89	0.90	0.90
Cd ²⁺	0.24	0.06	0.12	0.21	0.06	0.08	0.65	0.15	0.79	0.38	0.43	0.65	0.11	0.13	0.13	0.93	0.87	0.95
Hg ²⁺	0.79	0.76	0.76	0.76	0.74	0.70	0.43	0.75	0.64	0.73	0.38	0.67	0.35	0.73	0.68	0.84	0.79	0.75
Hg ₂ ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.16	0.00	0.00	0.00	0.00
Tl ⁺	0.32	0.71	0.67	0.78	0.02	0.00	0.87	0.69	0.48	0.30	0.39	0.57	0.12	T	0.09	0.90	0.85	0.87
Sn ⁴⁺	0.07	0.12	0.12	ND	0.21	0.22	T	0.06	0.37	ND	ND	ND	ND	ND	ND	0.77	0.77	0.79
Sn ²⁺	0.29	0.12	0.12	0.08	0.05	0.05	0.06	0.08	0.06	0.20	0.15	0.30	0.00	0.00	0.00	0.87	0.86	0.85
Fe ³⁺	0.14	0.05	0.00	0.65	0.00	0.00	0.67	0.70	0.00	0.41	0.06	0.10	0.30	0.00	0.00	0.92	0.95	0.95
UO ₂ ²⁺	ND	0.11	0.07	ND	0.00	0.00	0.43	0.38	0.00	ND	0.00	0.50	0.06	0.00	0.06	0.97	0.93	0.94
VO ²⁺	0.40	0.31	0.11	0.78	0.08	0.04	0.82	0.46	0.03	0.57	0.29	0.46	0.30	0.08	0.07	0.93	0.93	0.97
Fe ²⁺	0.28	0.10	0.13	0.27	0.00	0.00	0.56	0.70	0.16	0.16	0.10	0.14	0.16	0.06	0.06	0.93	0.93	0.97
Zn ²⁺	0.08	0.18	0.40	T	0.10	0.06	0.45	0.50	0.48	0.53	0.08	0.70	0.10	0.10	0.08	0.96	0.90	0.94
Cr ³⁺	0.16	0.07	0.05	T	0.08	0.10	0.36	0.50	0.15	0.04	0.10	0.87	0.06	0.03	0.00	0.98	0.87	0.90
Mn ²⁺	ND	0.30	0.26	0.74	0.74	0.69	0.45	0.30	0.55	0.40	0.59	0.68	0.22	0.17	0.07	0.85	0.95	0.90
Ca ²⁺	0.76	0.50	0.66	0.72	0.70	0.78	0.51	0.70	0.64	0.41	0.46	0.68	0.11	0.22	0.20	0.94	0.80	0.90
Zr ⁴⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.90	0.90	T
Th ⁴⁺	0.05	0.00	0.00	0.00	0.00	0.00	0.02	0.84	0.00	0.08	0.00	0.06	0.00	0.13	0.00	0.89	0.90	0.89
Ce ⁴⁺	0.00	0.00	0.00	0.81	0.00	0.00	0.75	0.02	0.08	0.48	0.11	0.06	0.00	0.00	0.00	0.89	0.90	0.95
Ce ³⁺	0.10	0.12	0.12	0.04	T	0.12	0.55	0.54	T	0.13	0.16	0.10	0.09	0.11	0.08	0.91	0.90	0.95
La ³⁺	0.40	0.10	0.12	0.00	0.10	0.05	0.00	0.00	0.08	0.34	0.00	0.15	0.05	0.09	0.10	0.97	0.94	0.95
Sm ³⁺	0.09	0.10	0.11	0.05	0.15	T	0.04	0.70	0.22	0.29	0.28	0.35	0.09	0.17	0.12	0.95	0.92	0.95
Pr ³⁺	0.13	0.12	0.12	0.02	0.12	0.11	0.30	0.80	0.34	0.30	0.24	0.83	0.07	0.08	0.09	0.92	0.90	0.93
Nd ³⁺	0.22	0.13	0.29	0.08	T	0.15	0.16	0.79	0.40	0.36	0.37	0.81	0.06	0.06	0.09	0.94	0.89	0.97
Al ³⁺	0.39	0.13	0.11	0.45	ND	ND	0.64	0.53	0.46	0.15	0.35	0.82	0.10	0.48	0.40	0.96	0.93	0.92
Ba ³⁺	0.68	0.17	0.13	0.10	0.10	0.04	0.19	0.08	0.00	0.05	0.28	0.40	0.04	0.08	0.07	0.92	0.90	0.91
Sr ²⁺	0.74	0.67	0.67	0.69	0.72	0.72	0.63	0.54	0.36	0.68	0.41	0.59	0.00	0.21	0.30	0.95	0.97	0.95
K ⁺	0.25	0.42	0.31	0.12	0.12	0.15	0.50	0.65	0.65	0.35	0.57	0.08	ND	0.79	0.25	0.91	0.84	0.92
Rb ⁺	0.20	0.22	0.17	0.24	0.11	0.14	0.47	0.04	0.05	0.17	0.29	ND	ND	ND	ND	0.90	0.91	0.92
Cs ⁺	0.30	0.43	0.27	0.22	0.34	0.09	0.10	0.00	0.41	0.10	0.10	0.10	ND	0.32	0.34	0.95	0.95	0.95
Ni ²⁺	0.16	0.24	0.15	0.56	0.13	0.14	0.43	0.64	0.50	0.28	0.36	0.56	0.22	0.11	0.03	0.97	0.93	0.95
Co ²⁺	0.46	0.20	0.12	0.48	0.20	0.14	0.65	0.68	0.60	0.26	0.36	0.45	0.15	0.08	0.00	0.96	0.94	0.92
Mo ⁶⁺	0.51	0.80	0.71	0.69	0.78	0.75	ND	ND	ND	0.52	ND	0.47	ND	ND	ND	0.93	0.96	0.93
Se ⁴⁺	0.25	0.43	0.38	0.40	T	0.23	0.31	0.06	0.00	0.64	0.12	0.08	ND	ND	ND	0.92	0.94	0.95
W ⁶⁺	0.12	0.76	0.29	0.61	0.81	0.70	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.85	0.90	0.80
Ru ³⁺	0.00	0.71	0.89	0.50	0.04	0.72	0.22	0.20	0.20	0.18	0.84	0.00	ND	ND	ND	0.90	0.85	0.92

* T, tailing.

† ND, not detected.

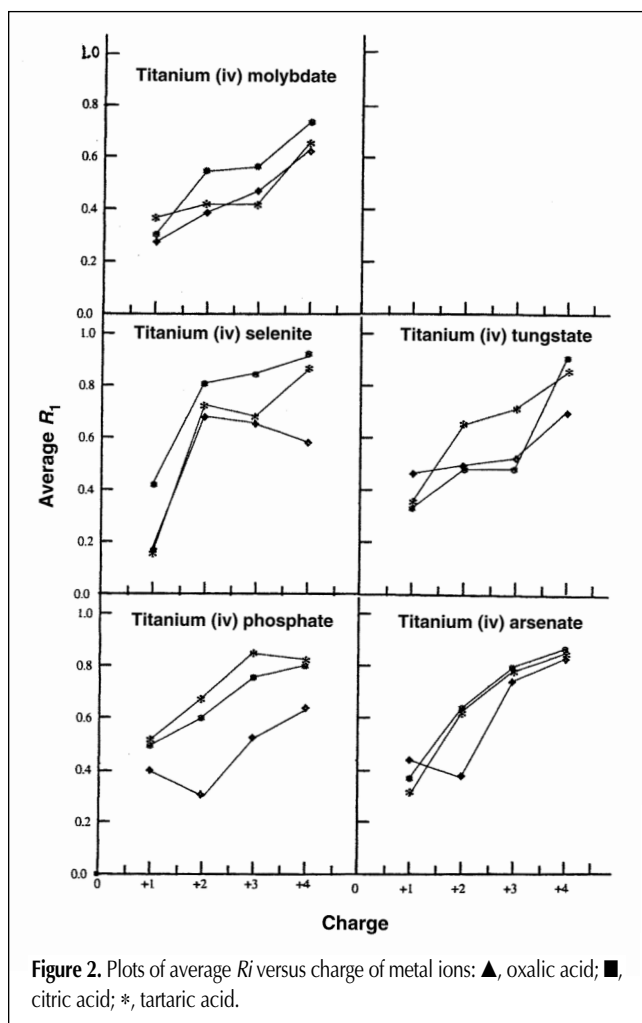


Figure 2. Plots of average R_f versus charge of metal ions: ▲, oxalic acid; ■, citric acid; *, tartaric acid.

ized water. The K_d values for these metal ions are given for comparison in Table IV. In general, the sequence of K_d values is the same as that predicted from R_F values. If it is concluded that the elution sequence can be predicted from K_d values, it follows that the R_F values are not reliable for such a prediction for the following reasons: (a) in paper chromatography, the mobile phase ascent is too fast to achieve equilibrium, (b) some of the ions definitely interact in a different manner with the paper than with the ion-exchanger, and (c) the material obtained by precipitation from solution and the one that deposited on the paper have different composition (i.e., Ti/anion ratio). This view is supported by the earlier studies made by Qureshi et al. (1,13), who determined the composition of various titanium(IV)-based inorganic ion-exchange materials obtained from solution by precipitation and those that were deposited on papers. For instance, the composition of TiAs obtained by the two methods (1,13) were found to be 1:1.8 and 1:0.32, respectively, even when the solutions of Ti(IV) chloride and sodium arsenate (used in the preparation of the ion-exchange material by the two methods) were of the same concentration. Because the K_d values depend on the composition of the material, these are found to be different with respect to the Ti/anion ratio.

Owing to these aforementioned facts, the Alberti and Torraccals (18) view 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 for predicting the elution sequence, especially when the difference in R_F values for the two metal ions is considerable (i.e., $\Delta R_F = 0.3$).

Chromatographic behavior of 3d series metal ions

For 3d series metal ions, the plots of average R_F versus pK_a of complexing acids (Figure 1) are almost similar for all the impreg-

Table III. Precipitation of Metal Ions in Mixtures of Mobile Phases and Impregnating Material

Mobile phase	Metal ion–mobile phase		Metal ion–sodium arsenate–mobile phase		Metal ion–sodium molybdate–mobile phase		Metal ion–sodium phosphate–mobile phase		Metal ion–sodium tungstate–mobile phase		Metal ion–sodium selenite–mobile phase	
	P*	NP†	P	NP	P	NP	P	NP	P	NP	P	NP
	0.1M Citric acid	None	Ag ⁺ , Pb ²⁺	Ag ⁺ , Th ⁴⁺ , Zr ⁴⁺	Ce ⁴⁺ , Hg ₂ ²⁺	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺ , Zr ⁴⁺ , La ³⁺	None	Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Zr ⁴⁺ , Th ⁴⁺ , Ce ⁴⁺	Ag ⁺ , Sb ³⁺ , Pd ²⁺ , Fe ³⁺ , UO ₂ ²⁺	Hg ₂ ²⁺ , Ag ⁺ , Bi ³⁺ , UO ₂ ²⁺ , Zr ⁴⁺ , Th ⁴⁺ , La ³⁺	Al ³⁺	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Sn ²⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Cr ³⁺ , UO ₂ ²⁺
0.1M Oxalic acid	None	Ag ⁺ , Hg ₂ ²⁺ , Pb ²⁺	Ag ⁺ , Hg ₂ ²⁺ , Zr ⁴⁺	Co ⁴⁺	Pb ²⁺ , La ³⁺ , Hg ₂ ²⁺	Ag ⁺	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺ , La ³⁺	Zr ⁴⁺ , Th ⁴⁺	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺	None	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Sn ²⁺ , Zr ⁴⁺ , Th ⁴⁺ , Ce ⁴⁺ , Ba ²⁺	Sr ²⁺
0.1M Tartaric acid	None	Ag ⁺ , Pb ²⁺	Ag ⁺ , Hg ₂ ²⁺ , Fe ³⁺	Ce ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺	Ag ⁺ , Zr ⁴⁺	Bi ³⁺ , Hg ₂ ²⁺ , Fe ³⁺ , UO ₂ ²⁺ , Th ⁴⁺ , Se ⁴⁺	Hg ₂ ²⁺ , Bi ³⁺ , Pb ²⁺ , Ag ⁺ , Zr ⁴⁺	UO ₂ ²⁺ , Fe ³⁺ , Ti ⁺ , Pd ²⁺ , Th ⁴⁺ , Ce ⁴⁺ , Fe ²⁺	None	Ag ⁺ , Hg ₂ ²⁺	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Sn ²⁺ , Fe ³⁺ , Cr ³⁺ , Zr ⁴⁺ , Th ⁴⁺ , Ce ⁴⁺	Ni ²⁺

* P, Metal ions that precipitate

† NP, Metal ions that do not precipitate

nated papers, except for TiW. Thus, from oxalic acid to tartaric acid, the average R_F decreases as the pK_a increases. However, moving from tartaric acid to citric acid, the trend is reversed as the average R_F now increases. The initial decrease in average R_F is more pronounced on TiP papers. This is due to a lower ionization of the acid, thereby causing a lesser degree of complex formation, resulting in lower R_F . However, the increase in average R_F in citric acid media is probably due to the formation of more soluble citrate complexes of these metal ions.

Of all of these impregnated papers, the case of TiW papers is somewhat exceptional, because for them the average R_F increases from oxalic acid to tartaric acid and then decreases from tartaric acid to citric acid.

It is interesting to compare the chromatographic behavior of these metal ions on papers impregnated with inorganic ion-exchangers based on titanium(IV). In an aqueous solution of oxalic acid, the average R_F value of these metal ions on various impregnated papers is in the following order: TiP > TiW > TiAs > TiSe. This may be due to the fact that phosphate papers are less ionized than selenite ones, resulting in low ion-exchange and causing higher R_F . The other papers have their ionization in-between. The pK_1 values (19) of the various anionic acids are in the following order: phosphoric acid (7.21) > tungstic acid (4.2) > arsenic acid (2.22) > selenic acid (1.88). The only exception is TiMO, which gives a maximum average R_F value, though the pK_1 of molybdic acid is 2.54.

Effect of the charge of metal ions on R_F

The plots of average R_i versus charge of metal ions are given in Figure 2. For the majority of cases, the average R_i increases with the increase in charge, which is in agreement with our earlier observation (9).

The increase in average R_i with an increase in charge for such cases is due to the fact that the ions with a higher charge are more strongly adsorbed on impregnated papers and therefore move less; the exceptions being in the case of TiP and TiSe papers in oxalic acid and citric acid media and also in the case of TiAs papers in oxalic acid media. These are due to the fact that in addition to adsorption, various other mechanisms influence the movement of metal ions on impregnated papers.

Metal ion separations

On the basis of significant difference in R_F , a large number of binary and ternary separations are possible. Some of the important ones actually achieved are provided here.

On TiP papers, they are as follows: Fe^{2+} - Fe^{3+} and Ag^+ or Pb^{2+} with Cu^{2+} , Hg^{2+} , or Tl^+ in 0.1M oxalic acid; Se^{4+} - Mo^{6+} and Cr^{3+} or UO_2^{2+} with Mo^{6+} in 0.1M citric acid; and Ag^+ , Hg^{2+} , Pb_2^{2+} , or Pd^{2+} with Hg^{2+} and Ba^{2+} with Sr^{2+} or Ca^{2+} in 0.1M tartaric acid.

On TiMo papers, they are as follows: Cu^{2+} with Ni^{2+} or Cd^{2+} , Hg_2^{2+} with Hg^{2+} or Pd^{2+} , Ag^+ or Cu^{2+} with Tl^+ with Hg^{2+} or Bi^{3+} in 0.1M oxalic acid; Zr^{4+} - Th^{4+} , Ag^+ or Bi^{3+} with Cu^{2+} , Pb^{2+} - UO_2^{2+} with Th^{4+} or Nd^{3+} in 0.1M citric acid; and Rb^+ - Cs^+ in 0.1M tartaric acid.

On TiW papers, they are as follows: Cr^{3+} - Zn^{2+} in 0.1M oxalic acid; UO_2^{2+} - VO^{2+} in 0.1M citric acid; and Th^{4+} with UO_2^{2+} or VO^{2+} , UO_2^{2+} - Pb^{2+} , and Cr^{3+} with Zn^{2+} , Mn^{2+} , Al^{3+} , or Mo^{6+} in 0.1M tartaric acid.

On TiAs(IV) papers, they are as follows: Ni^{2+} - Co^{2+} , Ag^+ with Cd^{2+} or Cu^{2+} - Hg^{2+} on 0.1M oxalic acid and UO_2^{2+} - Mo^{6+} , Ni^{2+} - Pd^{2+} , and Zn^{2+} - Cd^{2+} in 0.1M tartaric acid.

On TiSe papers, they are as follows: Ag^+ with Hg_2^{2+} or Hg^{2+} in 0.1M oxalic acid and Cs^+ - K^+ and Al^{3+} - Cr^{3+} in 0.1M citric acid.

Conclusion

The planar chromatography of metal ions on papers impregnated with titanium(IV)-based inorganic ion exchangers led to many useful separations. The Alberti and Torracalls view for the prediction of elution sequence from R_F values was not found to be applicable. For 3d series metal ions, TiW-impregnated papers exhibit different behavior regarding the effect of pK_a of complexing acids on average R_F values. These values for various impregnated papers in oxalic acid media are in the same order as the respective pK_1 values of the various anionic acids, which corresponds to these papers. An increase in the average R_i is observed with an increase in charge for the majority of metal ions.

Table IV. Comparison of K_d and R_F Values of Some Metal Ions on Titanium Ion-Exchangers

Exchangers	K_d (1,17)	R_F
Titanium(IV) arsenate	$Sm^{3+} > Nd^{3+} > Pr^{3+}$ $Ba^{2+} > Sr^{2+} > Cd^{2+}$ $Al^{3+} > La^{3+}$ $Pb^{2+} > Cd^{2+} > Hg^{2+} > Zn^{2+}$ $Ni^{2+} > Co^{2+} > Cu^{2+}$	$Nd^{3+} \equiv Pr^{3+} > Sm^{3+}$ $Sr^{2+} > Cd^{2+} > Ba^{2+}$ $La^{3+} > Al^{3+}$ $Zn^{2+} \equiv Hg^{2+} > Cd^{2+} > Pb^{2+}$ $Cu^{2+} > Ni^{2+} \equiv Co^{2+}$
Titanium(IV) tungstate	$Sr^{2+} > Ba^{2+} > Ca^{2+}$ $Hg^{2+} > Cd^{2+} > Zn^{2+}$ $Zr^{4+} > Th^{4+}$ $Pb^{2+} > Ni^{2+} > Mn^{2+} > Cu^{2+} > Co^{2+}$ $Sm^{3+} > Nd^{3+} \equiv La^{3+} > Pr^{3+}$	$Sr^{2+} > Ca^{2+} \equiv Ba^{2+}$ $Zn^{2+} > Cd^{2+} > Hg^{2+}$ $Th^{4+} > Zr^{4+}$ $Mn^{2+} > Ni^{2+} > Cu^{2+} > Pb^{2+} \equiv Co^{2+}$ $Nd^{3+} > Pr^{3+} > La^{3+} \equiv Sm^{3+}$
Titanium(IV) selenite	$Cu^{2+} \equiv Pb^{2+} > Hg^{2+}$ $Ba^{2+} > Sr^{2+} > Ca^{2+}$ $Nd^{3+} > Pr^{3+} \equiv Sm^{3+} \equiv La^{3+}$	$Hg^{2+} > Cu^{2+} \equiv Pb^{2+}$ $Ca^{2+} > Ba^{2+} > Sr^{2+}$ $Nd^{3+} \equiv Sm^{3+} \equiv Pr^{3+} \equiv La^{3+}$
Titanium(IV) molybdate	$Pb^{2+} > Ba^{2+} > Sr^{2+} > Al^{3+} > Ca^{2+} > Zn^{2+}$	$Sr^{2+} > Ca^{2+} > Zn^{2+} > Al^{3+} > Ba^{2+} > Pb^{2+}$

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