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

Studies on Thorium Phosphate Ion Exchanger. Part III. Paper Chromatographic Behavior and Separations of Metal Ions on Thorium Phosphate Papers

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To cite this Article De, Anil K. and Chowdhury, Kailas(1975) 'Studies on Thorium Phosphate Ion Exchanger. Part III. Paper Chromatographic Behavior and Separations of Metal Ions on Thorium Phosphate Papers', Separation Science and Technology, 10: 5, 639 — 648

To link to this Article: DOI: 10.1080/00372367508058046
URL: http://dx.doi.org/10.1080/00372367508058046

SEPARATION SCIENCE, 10(5), pp. 639–648, 1975

NOTE

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Abstract

Thorium phosphate papers have been prepared by treatment with thorium nitrate and phosphoric acid solutions. Several metal ions have been chromatographed on thorium phosphate paper. The effect of pH on R_F values has been investigated. Some useful analytical separations of metal ions have been achieved by using only dilute mineral acid and a mixed solvent system.

The importance of synthetic inorganic ion exchangers and their use for the impregnation of chromatographic papers has recently been reviewed (*1*, *2*). Papers impregnated with inorganic ion exchangers combine the advantages of ion exchange, adsorption, and partition. Moreover, chromatography of metal ions on inorganic ion exchange papers offers interesting possibilities which are greatly enhanced when these papers are developed with mixed solvent systems. This solvent extraction and ion exchange process is the same as the combined ion exchange–solvent extraction technique introduced by Korkisch (*3*).

In the earlier papers of this series (*4*, *5*) we reported on the synthesis and physicochemical properties of a series of thorium phosphate polymers and also on column chromatographic separations of metal ions on thorium phosphate ion exchangers. Thorium phosphate-impregnated papers are used in our laboratory for the separation of metal ions by the electrophoretic technique (*6*). No previous work has been done on thorium phosphate-impregnated papers for chromatographic studies, and so a comparative study of the chromatographic behavior of metal ions on plain and thorium phosphate-impregnated papers in dilute mineral acids and mixed aqueous–organic systems is reported here. The R_F values of metal ions on thorium phosphate paper are compared with the K_d values of metal ions on a thorium phosphate exchanger (*5*).

EXPERIMENTAL

Apparatus

Development was performed by the ascending chromatographic technique on 25 × 3.5 cm Whatman No. 1 chromatographic paper strips in a 30 × 5.5 cm glass jar.

Reagent

Thorium nitrate tetrahydrate was of Reagent grade (M & B). All other chemicals and solvents were of either E. Merck or B.D.H. AnalaR grade.

Cation Solution

Solutions (4 mg/ml) of chlorides, nitrates, or sulfates of most of the cations were prepared. The pH of the solution was adjusted with the corresponding acid to 2 to 3. Antimony oxide and bismuth nitrate solution were prepared in dilute hydrochloric acid and dilute nitric acid, respectively. Cesium(IV) sulfate solution was prepared in 1.75 *M* sulfuric acid. Palladium chloride and chloroplatinic acid solutions were prepared in dilute hydrochloric acid. All other metal ion solutions were prepared by standard procedures.

Preparation of Ion Exchange Papers

Thorium nitrate (0.1 *M*) in 1 *M* nitric acid solution and 0.25 *M* phosphoric acid solution were prepared. Whatman No. 1 paper strips (25 × 3.5 cm) were first impregnated with thorium nitrate solution for 5 to 6 sec, and then the excess thorium nitrate solution was removed with blotting paper. The strips were then passed through the phosphoric acid solution for 15 to

20 sec, and the excess phosphoric acid was again removed with blotting paper. Then the strips were dried at room temperature, washed with water to pH 3 to 3.5, and finally dried at room temperature.

Procedure

Fine glass capillaries were used to apply the test solution. The paper was conditioned for 15 to 20 min. The front limit R_L and rear limit R_T values were measured.

Detection of the Zones

Yellow ammonium sulfide solution was used for the detection of Ag^+, Tl^+, Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}, and Pd^{2+} zones. Fe^{3+}, UO_2^{2+}, VO^{2+}, and Cu^{2+} were detected with potassium ferrocyanide solution. Fe^{2+} was detected with potassium ferricyanide solution. Cd^{2+} and As^{3+} were detected with dithizone in carbon tetrachloride. Mn^{2+} and Zn^{2+} were detected with a mixture of trisodium pentacyanoamino ferrate and rubeanic acid. Ni^{2+} and Co^{2+} were detected with dimethylglyoxime solution. Sb^{3+} and Sn^{2+} were detected with phosphomolybdic acid solution. Freshly prepared sodium cobaltinitrite solution was used to detect K^+, Rb^+, and Cs^+. Al^{3+} and Be^{2+} were detected with aluminon reagent. $SnCl_2$ (0.1 M) in 4 M HCl and potassium iodide solution mixture were used to detect Pt^{4+}. Alcoholic Alizarin Red S (1%) was used for ZrO^{2+}, Ce^{3+}, Ce^{4+}, and La^{3+} spots. Ba^{2+} and Sr^{2+} were detected with aqueous neutral sodium rhodizonate solution.

RESULTS AND DISCUSSION

Twenty-nine metal ions have been chromatographed by using the following solvents:

(1) 0.1 M Nitric acid
(2) 0.1 M Hydrochloric acid
(3) n-Butanol + 6 M nitric acid
(4) n-Butanol + 6 M nitric acid + acetone

The R_T and R_L values of metal ions on thorium phosphate-impregnated paper and Whatman No. 1 paper are given in Table 1. Distribution

TABLE 1

R_T and R_L Values of Metal Ions on Thorium Phosphate Paper and Whatman No. 1 Paper at 22 ± 2 °C (time, 1 hr)

Metal ion	K_d values at pH 2 to 3 (ml/g)	(R_T–R_L) value on thorium phosphate paper	(R_T–R_L) value on Whatman No. 1 paper	Solvent (0.1 M)
K^+	—	(0.81–0.88)	(0.92–0.96)	HCl
Rb^+	—	(0.80–0.88)	(0.90–0.95)	HCl
Cs^+	—	(0.78–0.90)	(0.90–0.98)	HCl
Ag^+	—	(0.00–0.00)	(0.71–0.77)	HNO_3
Tl^+	—	(0.50–0.65)	(0.78–0.83)	HNO_3
$Hg_2{}^{2+}$	—	(0.00–0.00)	(0.00–0.00)	HNO_3
Pb^{2+}	5225	(0.01–0.02)	(0.85–0.93)	HNO_3
Cu^{2+}	85	(0.90–0.97)	(0.94–1.00)	HCl
Cd^{2+}	140	(0.91–0.98)	(0.89–0.97)	HCl
Hg^{2+}	0	(0.75–0.83)	(0.75–0.85)	HCl
Bi^{3+}	T.A.[a]	(0.00–0.25)	(0.82–0.91)	HCl
Pd^{2+}	—	(0.85–0.93)	(0.83–0.93)	HCl
Pt^{4+}	—	(0.88–0.99)	(0.88–1.00)	HCl
Fe^{3+}	2550	(0.04–0.10)	(0.93–0.99)	HCl
Fe^{2+}	—	(0.80–1.00)	(0.95–1.00)	HCl
Mn^{2+}	12	(0.90–0.97)	(0.92–0.95)	HCl
$UO_2{}^{2+}$	557	(0.30–0.45)	(0.88–0.92)	HCl
VO^{2+}	1588	(0.71–0.88)	(0.94–0.99)	HCl
ZrO^{2+}	—	(0.00–0.03)	(0.95–0.99)	HCl
Cr^{3+}	—	(0.80–0.85)	(0.83–1.00)	HCl
Sb^{3+}	—	(0.00–0.19)	—	HCl
Al^{3+}	170	(0.72–0.80)	(0.95–0.98)	HCl
As^{3+}	—	(0.91–1.00)	(0.90–0.96)	HCl
Ni^{2+}	0	(0.87–1.00)	(0.98–1.00)	HCl
Co^{2+}	0	(0.80–0.93)	(0.93–1.00)	HCl
Zn^{2+}	27	(0.93–1.00)	(0.97–1.00)	HCl
Be^{2+}	—	(0.85–0.95)	(0.95–1.00)	HCl
Ba^{2+}	—	(0.92–0.97)	(0.91–0.97)	HCl
Sr^{2+}	4	(0.85–0.92)	(0.94–1.00)	HCl

[a] T.A.—total adsorption.

coefficient (K_d) values of metal ions on fibrous thorium phosphate (batch No. 2) (*5*) at pH 2 to 3 are also given.

From Table 1 it follows that thorium phosphate paper yields different R_F values than Whatman No. 1 paper because thorium phosphate paper behaves as an ion exchange paper which strongly adsorbs some metal ions. These results may be compared with other inorganic ion exchange papers, e.g., zirconium phosphate and cerium phosphate papers (*7–12*). In our earlier paper (*5*) it was reported that distribution coefficient values are higher in the case of lead, bismuth, and iron (ic) on a thorium phosphate ion exchanger. This is in agreement with the lower R_F values for these metal ions on thorium phosphate paper. Only in the case of VO^{2+} do the R_F values show a different trend, presumably because there is a sharp variation of R_F with pH in this case, strong adsorption occurring at pH 2 to 5 (the K_d value is high at pH 2), but at 0.1 M HCl (pH 1) the R_F value is higher because the adsorption is less. On the basis of the R_F values in Table 1, some important separations have been achieved by using only simple dilute mineral acids as the developing solution as shown in Table 2.

An important ternary separation has been achieved on thorium phos-

TABLE 2

Separations Achieved on Thorium Phosphate Papers at 22 ± 2°C (time, 1 hr)

	Separations achieved by metal ions				
No.	of	(R_T–R_L)	from	(R_T–R_L)	Solvent (0.1 M)
1.	Fe^{3+}	(0.00–0.06)	Fe^{2+}	(0.94–1.00)	HCl
2.	Fe^{3+}	(0.00–0.07)	Mn^{2+}	(0.90–0.97)	HCl
3.	Fe^{3+}	(0.00–0.07)	Cr^{3+}	(0.85–0.90)	HCl
4.	Fe^{3+}	(0.00–0.08)	Cu^{2+}	(0.89–0.91)	HCl
5.	Fe^{3+}	(0.00–0.06)	Co^{2+}	(0.90–0.96)	HCl
6.	Fe^{3+}	(0.00–0.08)	Zn^{2+}	(0.90–0.99)	HCl
7.	Fe^{3+}	(0.00–0.06)	Hg^{2+}	(0.89–0.91)	HCl
8.	Fe^{3+}	(0.00–0.07)	$UO_2{}^{2+}$	(0.40–0.46)	HCl
9.	Pb^{2+}	(0.00–0.12)	Tl^{+}	(0.50–0.54)	HNO_3
10.	Pb^{2+}	(0.00–0.12)	Cd^{2+}	(0.85–0.91)	HNO_3
11.	Sb^{3+}	(0.00–0.06)	Cu^{2+}	(0.89–0.96)	HCl
12.	Sb^{3+}	(0.00–0.07)	Cd^{2+}	(0.88–0.93)	HCl
13.	Sb^{3+}	(0.00–0.06)	Cr^{3+}	(0.90–0.92)	HCl
14.	Sb^{3+}	(0.00–0.07)	Hg^{2+}	(0.79–0.89)	HCl
15.	Sb^{3+}	(0.00–0.08)	Ni^{2+}	(0.86–0.92)	HCl
16.	Sb^{3+}	(0.00–0.08)	Co^{2+}	(0.89–0.93)	HCl
17.	Sb^{3+}	(0.00–0.06)	Zn^{2+}	(0.91–1.00)	HCl

phate paper by using only 0.1 *M* hydrochloric acid, the development period being 1 hr: Fe^{3+}(0.00–0.08)– UO_2^{2+}(0.30–0.40)– Mn^{2+}(0.90 1.00).

R_F values of metal ions are plotted against the pH of the solution in Fig. 1. The pH of the solution was adjusted with dilute nitric acid solution. Figure 1 shows that there is no change in R_F values for ZrO^{2+} and Ag^+, but Sb^{3+}, Pb^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Be^{2+}, Pt^{4+}, Cr^{3+}, Co^{2+}, Mn^{2+}, Cd^{2+}, and Fe^{3+} show slight changes in their R_F values with pH. Abrupt changes occur for UO_2^{2+}, VO^{2+}, Tl^+, and Pb^{2+}, where the R_F values become lower as the pH of the solution increases. In the case of Fe^{3+}, a trail is obtained at pH 0. For Bi^{3+} in all cases (pH 0 to 6), an elongated spot was found on thorium phosphate paper. Silver shows trailing at all pH values when the metal ion concentration is 4 mg/ml, but when the metal ion concentration is 1mg/ml the R_F values are zero in most cases. Figure 1 also shows that there are slight change in R_F values up to pH 2 for UO_2^{2+}, VO^{2+}, Tl^+, and Pb^{2+}, but a sudden increase of R_F values is observed where the pH changes from 2 to 1.

In the case of lead, only the cation diffuses at pH 1. When the pH is changed from 1 to 0, there is a negligible increase in R_F value. This can be explained in the following way. There is an increase in the concentration of hydrogen ions and a decrease in exchange sites when the pH is changed from 2 to 1, but the exchanger is slightly ionized when the pH is changed from 1 to 0 (*13*).

A new quantity R_i is defined according to Qureshi et al. (*13*) as $R_i = R_{FU} - R_{FT}$, where R_{FU} denotes the R_F value on untreated paper and R_{FT} on thorium phosphate-impregnated paper. Thus the R_i value is a measure of the ion exchange effect. R_i values were taken from Fig. 1 and are tabulated in Table 3. From Table 3 it is seen that there are large R_i values for Ag^+, Fe^{3+}, Pb^{2+}, UO_2^{2+}, VO^{2+}, and ZrO^{2+} because these are adsorbed strongly by thorium phosphate paper.

Papers impregnated with inorganic ion exchangers are useful in the rapid evaluation of the analytical potential of an ion exchange material. A mixed solvent system increases the selectivity of the materials because both solvent extraction and the ion exchange mechanism play an important role (*14*). We have therefore studied the chromatography of some metal ions in butanol–nitric acid systems. No significant differences are observed between thorium phosphate-impregnated paper and untreated paper when butanol–nitric acid is used as developing solvents. However, some separations have been achieved on thorium phosphate paper by using the butanol–nitric acid system as shown in Table 4. These separations are not possible on ordinary Whatman No. 1 paper.

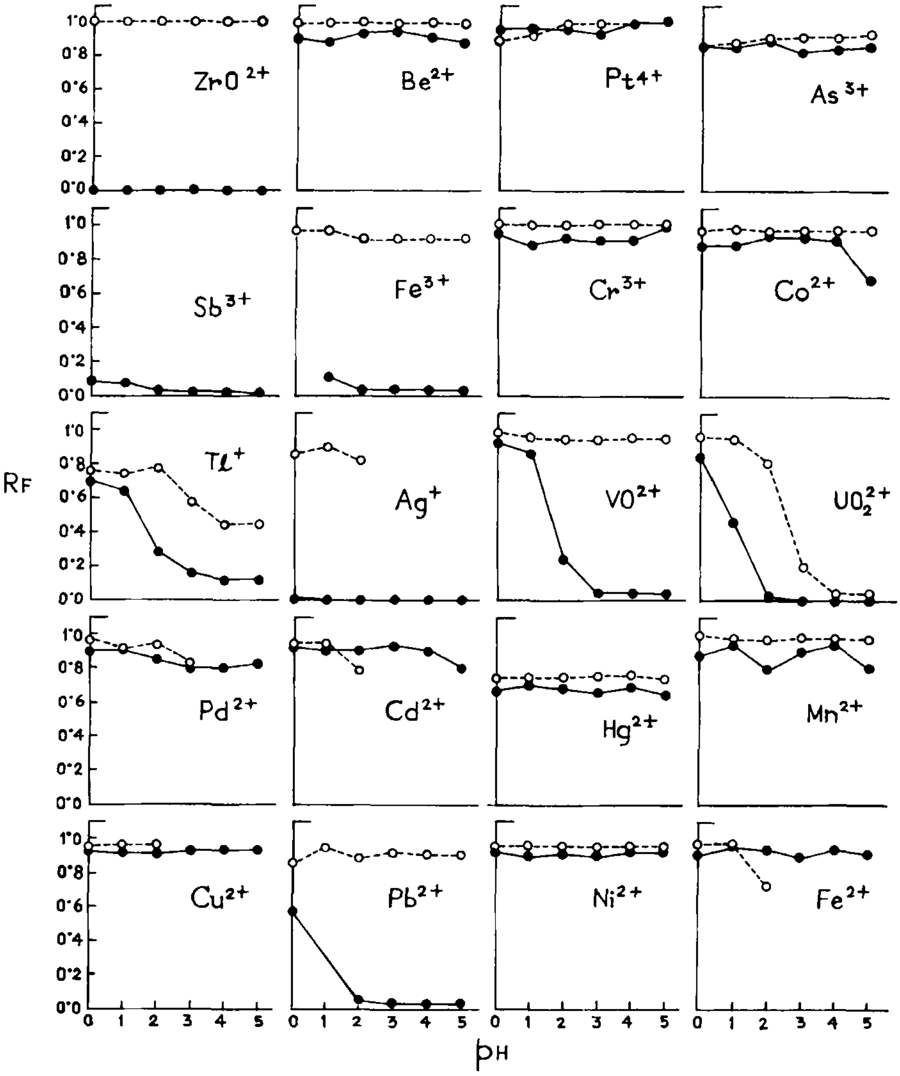

Fig. 1. Plot of R_F vs pH on thorium phosphate paper: (○) Whatman No. 1 paper, and (●) thorium phosphate paper.

TABLE 3

R_f Values of Metal Ions

Metal ion	pH = 0	pH = 1	pH = 2	pH = 3	pH = 4	pH = 5
Ag^+	+0.85	+0.89	+0.81	—	—	—
Tl^+	+0.06	+0.09	+0.49	+0.41	+0.32	+0.31
Hg^{2+}	+0.08	+0.04	+0.07	+0.09	+0.07	+0.07
Pb^{2+}	−0.28	—	+0.82	+0.87	+0.89	+0.85
Be^{2+}	+0.10	+0.11	+0.06	+0.04	+0.08	+0.11
Cu^{2+}	−0.03	+0.04		—	—	—
Cd^{2+}	+0.03	+0.04	−0.02	—	—	—
Ni^{2+}	+0.05	+0.08	+0.05	+0.07	+0.04	+0.05
Co^{2+}	+0.09	+0.10	+0.03	+0.03	+0.07	+0.30
Fe^{2+}	+0.06	0.00	−0.20	—	—	—
Pd^{2+}	+0.08	−0.03	+0.08	+0.03	—	—
$UO_2{}^{2+}$	+0.12	+0.40	+0.77	+0.20	+0.08	+0.08
VO^{2+}	+0.07	+0.08	+0.69	+0.90	+0.90	+0.91
Mn^{2+}	+0.14	+0.03	+0.17	+0.08	+0.01	+0.18
As^{3+}	+0.01	+0.02	+0.03	+0.08	+0.06	+0.06
Fe^{3+}	—	—	+0.87	+0.90	+0.89	+0.90
Cr^{3+}	+0.05	+0.12	+0.09	+0.10	+0.10	+0.02
ZrO^{2+}	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00
Pt^{4+}	−0.06	−0.03	+0.04	+0.07	−0.06	−0.01

The combined effect of the alcohol and ketone system shows that it is somewhat different from that of a single solvent (Table 5).

From earlier results it has been shown that thorium phosphate-impregnated paper is useful for some difficult analytical separations. Also, reproducible results are obtained on thorium phosphate-impregnated paper, and compact spots were obtained in most cases, which is not possible on ordinary Whatman No. 1 paper.

Acknowledgment

The authors are thankful to the Council of Scientific and Industrial Research (India) for financial assistance to one of them (K.C.).

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TABLE 4

Separations Achieved on Thorium Phosphate Papers at 22 ± 2°C (time, 2 hrs)

	Separations achieved by metal ions				Solvent system, butanol: 6 *M* HNO_3
No.	of	$(R_T–R_L)$	from	$(R_T–R_L)$	
1.	Ni^{2+}	(0.00–0.08)	Pd^{2+}	(0.50–0.60)	8 : 2
2.	VO^{2+}	(0.00–0.12)	Pd^{2+}	(0.48–0.58)	8 : 2
3.	Cr^{3+}	(0.00–0.11)	Pd^{2+}	(0.51–0.62)	8 : 2
4.	Fe^{2+}	(0.00–0.13)	Pd^{2+}	(0.50–0.57)	8 : 2
5.	Fe^{3+}	(0.00–0.07)	Pd^{2+}	(0.48–0.54)	8 : 2
6.	Cu^{2+}	(0.00–0.14)	Bi^{3+}	(0.46–0.54)	7 : 3
7.	Ni^{2+}	(0.00–0.11)	Bi^{3+}	(0.47–0.55)	7 : 3
8.	Fe^{3+}	(0.00–0.07)	Bi^{3+}	(0.48–0.56)	7 : 3

TABLE 5

R_F values of Metal Ion on Thorium Phosphate Paper at 22 ± 2°C [time, 2 hr; developing solvent, butanol: 6 *M* HNO_3: acetone (1 : 1 : 1)]

Metal ion		$(R_T–R_L)$	Metal ion		$(R_T–R_L)$
1.	K^+	(0.14–0.30)	17.	Cr^{3+}	(0.02–0.20)
2.	Rb^+	(0.25–0.32)	18.	Hg^{2+}	(0.80–0.93)
3.	Cr^+	(0.16–0.31)	19.	ZrO^{2+}	(0.00–0.04)
4.	Ag^+	(0.00–0.00)	20.	Ni^{2+}	(0.11–0.25)
5.	Tl^+	(0.19–0.29)	21.	VO^{2+}	(0.28–0.40)
6.	$Hg_2{}^{2+}$	(0.60–0.70)	22.	Co^{2+}	(0.16–0.30)
7.	Pb^{2+}	(0.10–0.28)	23.	Zn^{2+}	(0.14–0.28)
8.	Cu^{2+}	(0.34–0.45)	24.	Ba^{2+}	(0.00–0.05)
9.	Cd^{2+}	(0.22–0.31)	25.	Sr^{2+}	(0.13–0.27)
10.	Bi^{3+}	(0.56–0.78)	26.	Sb^{3+}	(0.57–0.68)
11.	Pd^{2+}	(0.67–0.80)	27.	Al^{3+}	(0.15–0.30)
12.	Pt^{4+}	(0.54–0.73)	28.	Be^{2+}	(0.50–0.68)
13.	Fe^{3+}	(0.15–0.31)	29.	Ce^{3+}	(0.00–0.17)
14.	Fe^{2+}	(0.16–0.37)	30.	Ce^{4+}	(0.00–0.10)
15.	Mn^{2+}	(0.14–0.25)	31.	La^{3+}	(0.09–0.30)
16.	$UO_2{}^{2+}$	(0.55–0.82)	32.	As^{3+}	(0.42–0.54)

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Received by editor November 14, 1974