Separation Science and Technology

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

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To cite this Article Qureshi, Mohsin and Husain, Waqif(1969) 'Separation of Metal Ions on Titanium(IV) Tungstate Papers', Separation Science and Technology, 4: 3, 197 — 207
To link to this Article: DOI: 10.1080/01496396908052251
URL: http://dx.doi.org/10.1080/01496396908052251

SEPARATION SCIENCE, 4(3), pp. 197–207, June, 1969

Separation of Metal Ions on Titanium(IV) Tungstate Papers*

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Summary

Papers impregnated with titanic tungstate have been used to chromatograph 52 cations in 45 aqueous and mixed solvents. Experimentally, a large number of complex cation separations have been achieved easily and rapidly—Au^{3+}, Tl^{3+}, Ag^+, Mo^{6+}, K^+, Rb^+, CS^+, Ni^{2+}, Sb^{3+}, Bi^{3+}, Be^{2+}, and Tl^+ can be easily separated from numerous metal ions. Several quaternary, ternary, and binary separations have also been achieved, and some important separations are discussed.

INTRODUCTION

The synthesis of new inorganic ion exchangers and their use for the impregnation of chromatographic papers has been recently reviewed (*1,2*). Since the publication of *Inorganic Ion Exchangers* by Amphlett we have been interested in synthesizing new inorganic ion exchangers and exploring the possibility of using them in inorganic paper chromatography (*3–5*). There are a number of advantages in using these exchangers for paper chromatography: (a) these papers are more selective than untreated papers, since now the R_f values depend on partition as well as on ion exchange (b) they are easy to prepare—their ion exchange material and their ion exchange capacity can be altered at will according to the requirements of a particular separation; (c) the separations on these papers are fast, predictable, and reproducible.

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* Presented in part at the 5th International Symposium on Chromatography and Electrophoresis held in Brussels, Belgium, September, 1968.

These advantages are further enhanced if mixed solvent systems are used for cation separations. Some efforts in this direction have been found fruitful in this laboratory (*4,5*). However, the separation potential of papers impregnated with synthetic inorganic ion exchangers has not been fully explored and it needs further study. As far as we are aware titanic tungstate papers have not been used for cation separations. We have, therefore, studied the chromatographic behavior of 52 cations on titanic tungstate papers using 45 solvent systems. In this communication we have summarized only the important separations achieved.

EXPERIMENTAL

Apparatus

Development 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 (B.D.H.) AnalaR reagents. A 15% titanic chloride solution (B.D.H.) was used.

Preparation of Ion Exchange Papers

A. 0.25 *M* solution of titanic chloride and a 0.25 *M* solution of sodium tungstate were prepared in distilled water. Paper strips were first passed through titanic chloride solution for 3 to 5 sec; the excess titanic chloride was removed by placing the strips on a filter paper sheet. The strips were then dipped in sodium tungstate solution for 5 sec and the excess was drained off. The strips were dried at room temperature overnight, washed 3 times with distilled water in order to remove excess reagent, and were finally allowed to dry at room temperature for 12 hr and used as such.

Cation Solutions

A 0.1 *M* solution of chlorides, nitrates, or sulfates of most of the cations were prepared in 0.1 *M* solution of the corresponding acids. Antimony(III) and Bi(III) chlorides (0.1 *M*) were prepared in 30%

(v/v) HCl solution. One per cent solutions of Au(III) and Ga(III) chlorides were prepared in 4 *M* HCl solution and 1% niobium pentachloride was prepared in 10% tartaric acid. Selenium dioxide was dissolved in water and made alkaline with 1 *N* KOH solution. Ceric sulfate was prepared in 3 *N* H_2SO_4; mercuric nitrate solution was prepared in 0.5 *N* HNO_3; and AS_2O_3 and $Be(NO_3)_2$ were dissolved in 1% HNO_3.

Detectors

Saturated H_2S solution was used to detect Ag^+, Pb^{2+}, Hg_2^{2+}, Hg^{2+}, Bi^{3+}, Tl^+, Cd^{2+}, As^{3+}, Sb^{3+}, Pd^{2+}, and Cu^{2+}; a fresh solution of sodium cobaltinitrite was used to detect K^+, Rb^+, CS^+; a 0.1% alcoholic solution of Alizarine Red S was used to detect La^{3+}, Ce^{3+}, Ce^{4+}, Y^{3+}, Zr^{4+}, Th^{4+}, Hf^{4+}, In^{3+}, Ca^{2+}, Nb^{5+}, Pr^{3+}, Sm^{3+}, and Nd^{3+}; stannous chloride in HCl was used to detect Au^{3+}, Pt^{4+}, Mo^{6+}, Te^{4+}, and Se^{4+}; Al^{3+}, Be^{2+}, and Ga^{3+} were detected by 1% alcoholic solution of aluminon; Diphenyl carbazide was used to detect Mn^{2+}, Cr^{3+}, Ir^{4+}, and Zn^{2+}; Fe^{3+}, V^{4+}, UO_2^{2+} were detected with $K_4Fe(CN)_6$; Mg^{2+} was detected with quinalizarine; a fresh 5% solution of sodium rhodizonate was used to detect Ba^{2+} and Sr^{2+}; Ru^{3+} was detected with 2 *N* HCl solution of thiourea; Sn^{2+} and Sn^{4+} were detected by phosphomolybdic acid solution and dithiozone, respectively; and Ge^{4+} was detected by first dipping the strip into HNO_3 solution of ammonium molybdate and then into acetic acid solution of benzidine and exposing to ammonia vapors.

Procedure

Fine glass capillaries were used to apply the test solutions on papers. The chromatograms were conditioned for 5 to 10 min and then the solvent was allowed to ascend 11 cm from starting line on paper in all cases. Time of development has been specified with each solvent. To obtain a clear picture of the size of the spot, instead of simply giving R_f values of the spot, the R_f of the front limit (R_L) and R_f of the rear limit (R_T) of the spots are given in parentheses. Thus Mn^{2+} (0.00–0.11) means that its R_T is 0.00 and its R_L is 0.11.

RESULTS

In many cases it was found possible to separate one cation from numerous metal ions. These separations are summarized in Table 1.

TABLE 1

Separation of One Cation from Numerous Metal Ions on Titanic Tungstate Papers as Predicted by R_f Values

Metal ion separation (R_T–R_L)	Solvent system	Ions that interfere	Time
Au^{3+} (1.00–0.91) from 47 cations	Acetone + acetic acid + *n*-butanol + 1 *M* NaCl (1:1:1:1)	Sn^{2+}, Sn^{4+}, Hg^{2+}, Nb^{5+}	1.45 hr
Tl^{3+} (1.00–0.93) from 51 cations	Acetone + acetic acid + *n*-butanol + 4 *M* HCl (1:1:1:1)	Au^{3+} only interferes	1.45 hr
Ag^{+} (0.78–0.57) from 47 cations	Piperidine + acetone + methanol + 20% HNO_3 (1:3:1:0.5)	Hg_2^{2+}, Hg^{2+}, Pd^{2+}, Au^{3+}	1.00 hr
Mo^{6+} (0.95–0.70) from 45 cations	2 *M* Ammonium formate + 2 *M* NH_4OH (1:1)	Ag^{+}, Ni^{2+}, K^{+}, Rb^{+}, CS^{+}, Se^{4+}	20 min
K^{+} or Rb^{+} or CS^{+} (0.77–0.56) from 44 cations	2 *M* Ammonium formate + 2 *M* NH_4OH (1:1)	Ag^{+}, Ni^{2+}, Mo^{6+}, Se^{4+}, Nb^{5+}	20 min
Ni^{2+} (0.86–0.36) from 39 cations	2 *M* Ammonium formate + 2 *M* NH_4OH (1:1)	Ag^{+}, Cu^{2+}, Pd^{2+}, Cd^{2+}, Zn^{2+}, Mo^{6+}, Mg^{2+}, K^{+}, Rb^{+}, CS^{+}, Se^{4}, Nb^{5+}	20 min

Sb^{3+} (0.69–0.46) from 38 cations	Acetone + acetic acid + *n*-butanol + 1 *M* NaCl (1:1:1:1)	Hg^{2+}, Bi^{3+}, Pd^{2+}, Al^{3+}, Be^{2+}, Ga^{3+}, Zn^{2+}, Pt^{4+}, Ca^{2+}, Sn^{2+}, Sn^{4+}, Nb^{5+}, UO_2^{2+}	1.45 hr
Bi^{3+} (0.80–0.66) from 38 cations	*n*-Butanol + dioxane + 50% HNO_3 (3:2:3)	Hg^{2+}, Pd^{2+}, UO_2^{2+}, Sb^{3+}, As^{3+}, Be^{2+}, Ga^{3+}, Au^{3+}, Pt^{4+}, Ce^{4+}, Th^{4+}, Sn^{2+}, Sn^{4+}	2 hr
Be^{2+} (0.66–0.48) from 33 cations	*n*-Butanol + dioxane + 50% HNO_3 (3:2:3)	Hg^{2+}, Bi^{3+}, Cu^{2+}, Pd^{2+}, UO_2^{2+}, Sb^{3+}, As^{3+}, Ga^{3+}, Cd^{2+}, Pt^{4+}, Th^{4+}, In^{3+}, Ce^{3+}, Ce^{4+}, Ru^{3+}, Sn^{2+}, V^{4+}, Ge^{4+}	2 hr
Tl^{+} (0.00–0.06) from 22 cations	*n*-Butanol + HCl (7:3)	Al^{3+}, K^{+}, Ca^{2+}, Cr^{3+}, Ni^{2+}, Ge^{4+}, As^{3+}, Se^{4+}, Rb^{+}, Sr^{2+}, Y^{3+}, Zr^{4+}, Nb^{5+}, Ru^{3+}, Ag^{+}, Sn^{2+}, Cs^{+}, Ba^{2+}, La^{3+}, Ce^{3+}, Ce^{4+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Hf^{4+}, Ir^{4+}, Hg_2^{2+}, Pb^{2+}, Th^{4+}	4 hr

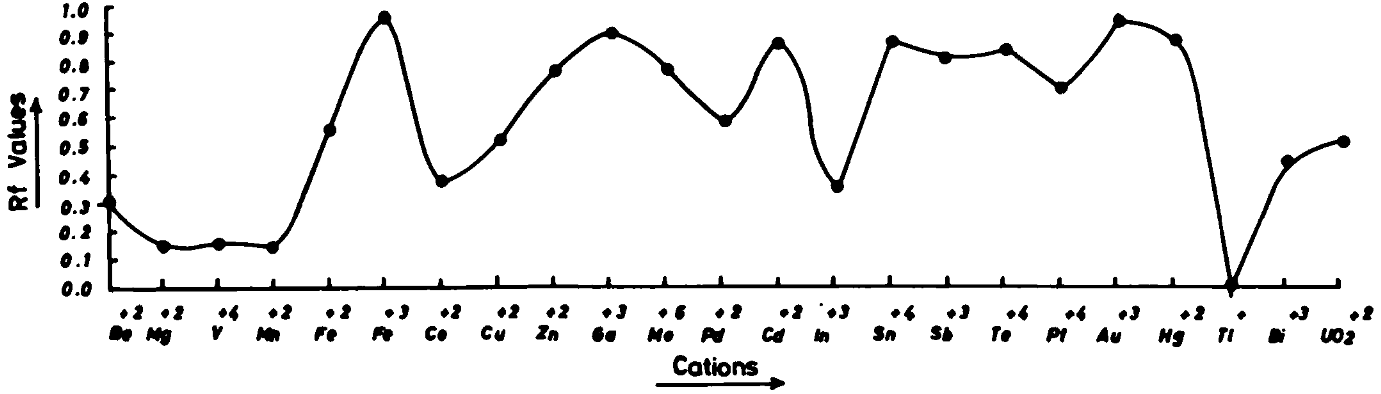

FIG. 1. Separation of thallium(I) from numerous metal ions.

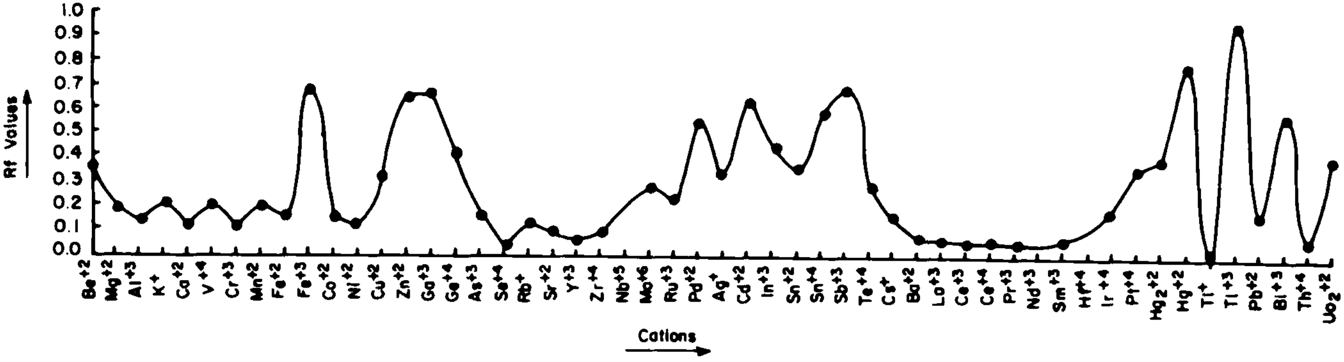

FIG. 2. Separation of thallium(III) from numerous metal ions.

TABLE 2

Separations Achieved Experimentally on Titanic Tungstate Papers

Solvent system	Separations achieved, metal ion (R_T–R_L)	Time
Acetone + acetic acid + *n*-butanol + 4 *M* HCl (1:1:1:1)	Al^{3+} (0.16–0.34)–In^{3+} (0.42–0.59)–Ga^{3+} (0.66–0.70)–Tl^{3+} (0.93–1.00)	2.00 hr
	Al^{3+} (0.15–0.32)–Be^{2+} (0.36–0.58)–Ga^{3+} (0.63–0.69)–Tl^{3+} (0.93–1.00)	2.00 hr
	Ni^{2+} (0.13–0.30)–Pd^{2+} (0.46–0.63)	2.00 hr
	Nd^{3+} (0.00–0.16)–UO_2^{2+} (0.33–0.55)	2.00 hr
	Fe^{2+} (0.18–0.33)–Fe^{3+} (0.64–0.70)	2.00 hr
1 *M* Ammonium formate in 4 *M* NH_4OH	Tl^{+} (0.00–0.06)–Cu^{2+} (0.35–0.58)–Ni^{2+} (0.72–0.94)	25 min
	Fe^{3+} (0.00–0.00)–Cu^{2+} (0.35–0.58)–Ni^{2+} (0.73–0.94)	25 min
	UO_2^{2+} (0.00–0.00)–Mo^{6+} (0.79–1.00)	25 min
	Pt^{4+} (0.00–0.00)–Ni^{2+} (0.73–0.94)	25 min
	Hg^{2+} (0.00–0.23)–Ag^{+} (0.73–0.89)	25 min
0.25 *M* Malonic acid in 3 *M* NH_4OH	Bi^{+3} (0.00–0.00)–Cu^{2+} (0.21–0.45) Ag^{+} (0.72–0.90)	20 min
	Pb^{2+} (0.00–0.00)–Cu^{2+} (0.23–0.48)–Ag^{+} (0.76–0.94)	20 min
	Hg^{2+} (0.00–0.09)–Cd^{2+} (0.27–0.55)–Ag^{+} (0.73–0.90)	20 min
	Mn^{2+} (0.00–0.11)–Ni^{2+} (0.72–0.97)	20 min
	Tl^{+} (0.00–0.08)–Ag^{+} (0.73–0.90)	20 min
n-Butanol + HCl (7:3)	Cr^{3+} (0.00–0.13)–CO^{2+} (0.50–0.72)–Fe^{3+} (0.95–1.00)	4.00 hr
	Ni^{2+} (0.05–0.17)–CO^{2+} (0.52–0.70)–Fe^{3+} (0.95–1.00)	4.00 hr
	Tl^{+} (0.00–0.09)–Bi^{3+} (0.43–0.63)–Hg^{2+} (0.81–0.91)	4.00 hr
Ethyl methyl ketone + acetone + 50% HCl (1:6:1)	Al^{3+} (0.00–0.09)–Be^{2+} (0.16–0.36)–Ga^{3+} (0.81–0.92)	30 min
	Al^{3+} (0.00–0.08)–Be^{2+} (0.14–0.35)–Fe^{3+} (0.70–0.80)	30 min
	Cr^{3+} (0.00–0.09)–UO_2^{2+} (0.71–0.77)	30 min
	Cr^{3+} (0.00–0.09)–Zn^{2+} (0.72–0.83)	30 min
	V^{4+} (0.09–0.21)–UO_2^{2+} (0.68–0.73)	30 min
1 *M* NH_4SCN + 1 *M* HCl (1:1)	Te^{4+} (0.00–0.07)–Pd^{2+} (0.35–0.55)–Ni^{2+} (0.73–0.95)	20 min
	Te^{4+} (0.00–0.07)–Pd^{2+} (0.32–0.55)–Cd^{2+} (0.79–0.93)	20 min
	Te^{4+} (0.00–0.07)–Pd^{2+} (0.35–0.55)–Bi^{3+} (0.79–0.94)	20 min

TABLE 2 (Continued)

Solvent system	Separations achieved, metal ion (R_T–R_L)	Time
	Sb^{3+} (0.00–0.10)–Bi^{3+} (0.75–0.94)	20 min
2 *M* NH_4Br + 2 *M* HBr (1:1)	Te^{4+} (0.00–0.10)–Au^{3+} (0.30–0.50)–Ni^{2+} (0.83–1.00)	25 min
	Se^{4+} (0.00–0.10)–Au^{3+} (0.32–0.52)–Ni^{2+} (0.83–1.00)	25 min
0.1 *M* EDTA + 1 *M* NH_4Cl + 1 *M* NH_4OH (2:1:1)	Cr^{3+} (0.00–0.00)–Mo^{6+} (0.74–1.00)	20 min
	UO_2^{2+} (0.00–0.00)–Pb^{2+} (0.88–1.00)	20 min
	Ge^{4+} (0.00–0.07)–Mo^{6+} (0.71–0.99)	20 min
Acetyl acetone + acetone + 50% HCl (6:3:1)	Mn^{2+} (0.00–0.09)–Zn^{2+} (0.25–0.48)–Ga^{3+} (0.74–1.00)	25 min
	Tl^{+} (0.00–0.00)–Zn^{2+} (0.25–0.47)–Ga^{3+} (0.74–1.00)	25 min
	Y^{3+} (0.00–0.05)–Ga^{3+} (0.75–1.00)	25 min
Ethyl acetoacetate + 20% methylamine hydrochloride + HBr (9:2:4)	Al^{3+} (0.15–0.35)–Zn^{2+} (0.64–0.73)	1.00 hr
	Co^{2+} (0.21–0.41)–Zn^{2+} (0.65–0.73)	1.00 hr
Ethyl methyl ketone + acetone + 50% HCl (6:3:1)	Ni^{2+} (0.00–0.05)–Co^{2+} (0.33–0.42)–Cu^{2+} (0.53–0.74)	25 min
	V^{4+} (0.00–0.10)–Fe^{3+} (0.41–0.54)	25 min
	Cr^{3+} (0.00–0.06)–Fe^{3+} (0.43–0.58)	25 min
n-Butanol + dioxane + 50% HNO_3 (3:1:1)	Ge^{4+} (0.00–0.27)–Sn^{4+} (0.89–1.00)	1.30 hr

In order to emphasize the utility of thallium separations we have also given R_f plots (Figs. 1 and 2).

It was also found possible to achieve experimentally a number of binary, ternary, and quaternary separations. These are summarized in Table 2.

Paper chromatography of those cations that remain at the point of application of titanic tungstate papers was also performed on plain Whatman No. 1 papers to study whether they are precipitated at the point of application, adsorbed after the formation of positively charged species, or retained at the point of application as a result of a low partition coefficient of the solute in the solvent system.

DISCUSSION

Titanium tungstate has been found to exhibit ion exchange (*6*). It is clear from the results recorded in Tables 1 and 2 that titanic tungstate is a useful synthetic ion exchanger. Papers are easily prepared in cold solutions and they are rather opaque so that one can easily see whether impregnation has occurred and also whether the ion exchanger has dissolved in the developing solvent. Some complex separations are achieved easily and rapidly. A few of them are discussed here.

Titanic tungstate papers are so selective that in many cases one metal ion can be easily separated from numerous metal ions (Table 1). In this case, only those separations were verified of which the metal ions had R_f values close to those of the ion separated.

Separation of Tl(I) from Numerous Metal Ions

The Tl^+ can be easily separated from 22 cations including Cu^{2+}, Hg^{2+}, In^{3+}, Bi^{3+}, Mn^{2+}, Au^{3+}, Ga^{3+}, Zn^{2+}, and Fe^{3+}. These are the cations that interfere most in the determination of thallium; n-butanol + HCl in the ratio of 7:3 is used as solvent. Tl^+ is precipitated at the point of application as insoluble TlCl, since it also does not move on plain Whatman No. 1 paper; other cations move forward as their negatively charged chloride complexes. Mn^{2+} forms a weak positively charged complex, $MnCl^{2+}$, and, therefore, moves very little as compared to other cations. V^{4+} and Mg^{2+} behave similarly. In order to have some experimental basis the separation of Tl^+ was tried and achieved practically from binary mixtures of Mn^{2+}, Mg^{2+}, V^{4+} with Tl^+.

Separation of Tl(III) from Numerous Metal Ions

It is evident from Fig. 2 that Tl^{3+} can be easily separated from 51 cations using acetone + acetic acid + n-butanol + 4 M HCl (1:1:1:1) as solvent. It is experimentally verified that Tl^{3+} can be separated from Hg_2^{2+}, Bi^{3+}, UO_2^{2+}, Sb^{3+}, and Fe^{3+}. These are the cations with R_f values very close to Tl^{3+}. This is, therefore, a specific separation.

Many other important separations are performed quickly and with ease on these papers. Thus Al^{3+}–Be^{2+}–Ga^{3+} are separated in 30 mins. This is the fastest separation of these three cations yet reported.

Acknowledgments

The authors are grateful to Dr. S. M. F. Rahman for research facilities and encouragement.

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Received by editor March 11, 1969
Submitted for publication April 8, 1969