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NOTE

Chromatographic Separations of Metal Ions on Zirconium Tungstoarsenate Impregnated Ion-Exchange Papers

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Abstract

A new heteropolyacid salt ion-exchanger, zirconium tungstoarsenate, has been used for preparing impregnated ion-exchange papers. Twenty-nine metal ions have been chromatographed and R_F values determined in seven different mixed solvent systems containing 1-propanol and HNO_3 or HCl. On the basis of the difference in selectivities for different metal ions on impregnated papers, a large number of binary and ternary separations has been obtained. Some of the important separations achieved are Ag^+–Tl^+, Ag^+–Pt(IV), Zn^{2+}–Hg^{2+}, Sb^{3+}–Bi^{3+}, Zn^{2+}–UO_2^{2+}, Fe^{2+}–Fe^{3+}, Sb^{3+}–Bi^{3+}–Hg^{2+}, Ag^+–Ba^{2+}–UO_2^{2+}, and Ag^+–Zn^{2+}–Cu^{2+}–Sn^{2+}. The results are compared with those obtained on plain papers.

INTRODUCTION

Ion-exchange properties of heteropolyacid salts (*1–5*) are quite well known and have been used in wide-scale separations of radionuclides on their columns as well as on papers impregnated with them. Ammonium molybdophosphate (*6*) was the first inorganic ion exchanger to be used in paper chromatographic separations of inorganic ions. Micro amounts of Li^+, Na^+, K^+, Rb^+, and Cs^+ have been separated on papers treated with this exchanger, and this has also been used for the separation of some fission products (*6, 7*).

Recently, authors have synthesized zirconium tungstoarsenate (ZTA) and found it to possess promising exchange properties, enabling its column to be used for obtaining some important separations of ion pairs (*8*). It was thought worthwhile to exploit the exchange properties of this white-colored heteropolyacid salt for achieving separations of metal ions on papers impregnated with it. A large number of difficult separations of analytical and radioanalytical importance have been carried out using different mixed solvent systems. The results have been compared with those obtained on plain papers.

EXPERIMENTAL

Reagents

All metal salts and acids were of analytical grade. The solvent 1-propanol was purified by distillation.

Apparatus

Chromatography was performed on Whatman No. 3 chromatographic paper strips ($15 \times 5.5\ \text{cm}^2$) using $20 \times 10 \times 28\ \text{cm}^3$ glass jars.

Preparation of Ion-Exchange Papers

Ion-exchange papers were prepared by impregnating paper strips with zirconium tungstoarsenate. For this, the paper strips were first dipped in a freshly prepared solution of sodium 12-tungstoarsenate (*9*) for ~10 sec. This solution was prepared by mixing an aqueous solution of 3.5 g of sodium tungstate with 0.15 g of arsenic pentoxide in aqueous sodium hydroxide and adding concentrated hydrochloric acid until the mixture was strongly acidic. Total volume of the solution was kept to 100 mL. The excess solution on paper strips was blotted out, and the strips were dried at room temperature for 15 min. The strips were again dipped in 0.1 *M* zirconyl chloride solution for ~10 sec. The excess solution was drained off and the strips were dried at room temperature. They were then washed with distilled water to remove the excess reagents and dried at room temperature.

Composition of Impregnated Papers

The impregnated paper strips were analyzed in order to determine the composition of the exchange material formed on papers. These strips were dissolved in a mixture of perchloric, nitric, and sulfuric acids (3:1:4), and the solution was evaporated to dryness. The residue was treated with aqueous sodium hydroxide, and zirconium hydroxide was precipitated. The mixture was filtered, and tungsten in the filtrate was estimated by the thiocyanate method at 398 nm. The white precipitate of zirconium hydroxide on the filter paper was dissolved in 0.1 *M* hydrochloric acid, and zirconium was estimated by the alizarin red-S method at 510 nm.

The above analysis of the ion-exchange papers shows that the Zr/W molar ratio is 0.15. This ratio is almost the same as was found for the zirconium tungstoarsenate exchanger (*8*).

Test Solutions and Detectors

Test solutions of chlorides, nitrates, or sulfates of most of the metal cations (0.1 *M*) were prepared in 0.1 *M* corresponding acids. Bismuth chloride and antimony chloride were prepared in 4.0 *M* hydrochloric acid whereas ceric sulfate was dissolved in 3.6 *M* sulfuric acid. Sodium selenite and molybdate solutions were prepared in water. Mercuric nitrate solution was prepared in 0.5 *M* nitric acid and stannous chloride was prepared in 4.0 *M* hydrochloric acid, with a piece of tin included to prevent oxidation. Metal ions were detected by standard methods (*10*).

Procedure

The test solutions were spotted with thin glass capillaries and the papers were developed by the ascending technique in chromatographic chambers conditioned with the developers. It took 1½ to 2 hr for an 11-cm ascent of the solvent. After detecting the spots, the R_F values were measured. In the case of spreading, the front (R_L) and rear (R_T) limits of the spots are mentioned. For comparison, R_F values on plain papers were also determined.

RESULTS

Twenty-nine metal cations were chromatographed on impregnated as well as on plain papers in the following seven solvent systems:

(a) 1.0 *M* HNO_3 in 33% (v/v) 1-propanol
(b) 1.0 *M* HNO_3 in 50% (v/v) 1-propanol
(c) 0.1 *M* HNO_3 in 50% (v/v) 1-propanol
(d) 0.1 *M* HNO_3 in 80% (v/v) 1-propanol
(e) 1.0 *M* HCl in 33% (v/v) 1-propanol
(f) 1.0 *M* HCl in 50% (v/v) 1-propanol
(g) 0.1 *M* HCl in 50% (v/v) 1-propanol

TABLE 1

R_F and R_t Values of Metal Ions in Various Solvent Systems on Papers Impregnated with ZTA[a]

Metal ion	1-Propanol (33%)–1.0 M HNO_3 (a)		1-Propanol (50%)–1.0 M HNO_3 (b)		1-Propanol (50%)–0.1 M HNO_3 (c)		1-Propanol (80%)–0.1 M HNO_3 (d)		1-Propanol (33%)–1.0 M HCl (e)		1-Propanol (50%)–1.0 M HCl (f)		1-Propanol (50%)–0.1 M HCl (g)	
	R_F	R_t	R_F	R_t	R_F	R_t	R_F	R_t	R_F	R_t	R_F	R_t	R_F	R_t
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
Tl^+	0.36	0.22	0.25	0.30	(0.00–0.39)T	—	0.05	—	(0.00–0.53)T	—	0.00	—	(0.00–0.43)T	—
Mg^{2+}	0.83	0.02	0.78	0.02	0.79	0.02	(0.00–0.40)T	—	0.90	−0.04	0.72	0.02	0.78	−0.03
Ba^{2+}	—	—	0.52	0.09	0.56	0.13	0.10	0.06	—	—	0.42	0.11	0.50	0.14
Fe^{2+}	0.83	0.03	0.70	0.10	0.79	0.02	0.08	0.22	0.87	−0.05	0.65	0.10	(0.37–0.91)T	—
Co^{2+}	0.80	−0.01	(0.45–0.82)T	—	0.77	0.04	0.35	0.00	0.85	−0.03	0.58	0.13	(0.55–0.93)T	—
Ni^{2+}	0.79	0.05	0.69	0.02	0.80	0.01	0.34	0.00	0.84	−0.02	0.61	0.09	0.74	0.03
Cu^{2+}	0.78	0.04	0.68	—	0.83	−0.01	0.38	0.02	0.80	0.02	0.83	−0.12	0.78	−0.02
Zn^{2+}	0.86	−0.01	0.93	−0.16	(0.49–0.81)T	—	0.10	0.17	0.84	0.06	0.89	0.06	(0.50–0.95)T	—
Pd^{2+}	0.77	0.09	0.71	0.06	0.75	0.12	(0.14–0.81)T	—	0.85	0.08	0.78	0.14	0.74	0.20
Cd^{2+}	0.75	0.09	0.65	—	(0.50–0.84)T	—	(0.00–0.57)T	—	0.86	0.06	0.86	0.08	0.66	0.10
Sn^{2+}	0.89	−0.02	0.89	0.03	0.04	—	0.84	—	0.85	—	0.90	0.01	0.06	—
Hg^{2+}	0.82	0.11	0.97	−0.10	0.88	−0.02	0.51	0.42	0.93	0.04	0.96	0.02	0.08	0.17

Pb^{2+}	0.54	—	0.43	—	(0.13–0.59)T	—	0.10	—	(0.00–0.70)T	—	0.11	—	(0.00–0.50)T	—
Al^{3+}	—	—	0.80	0.05	0.94	−0.07	0.42	—	—	—	(0.52–0.88)T	—	0.86	−0.06
Fe^{3+}	0.84	0.03	0.79	0.04	0.84	−0.05	0.44	—	0.91	−0.07	0.72	0.01	0.85	−0.07
La^{3+}	0.73	0.07	0.70	0.04	0.75	0.02	0.19	0.04	0.77	0.06	0.62	0.05	0.71	0.02
Sb^{3+}	(0.00–0.87)T	—	0.09	—	(0.00–0.31)T	—	(0.00–0.48)T	—	0.82	−0.07	(0.30–0.86)T	—	(0.00–0.33)T	—
Bi^{3+}	(0.59–0.90)T	—	(0.51–0.86)T	—	0.67	—	0.26	—	0.88	0.04	0.75	0.18	0.66	0.17
Ce^{3+}	0.79	0.04	0.62	—	0.84	−0.08	(0.11–0.51)T	—	0.82	−0.02	0.64	0.00	(0.44–0.81)T	—
Pt(IV)	0.78	0.14	0.78	0.12	0.61	0.29	0.20	—	0.87	0.03	0.89	0.08	0.69	0.20
Sn^{4+}	0.89	0.00	0.88	0.07	0.08	—	0.86	—	0.84	—	0.92	0.01	0.05	—
Ti^{4+}	(0.00–0.87)T	—	(0.00–0.86)T	—	(0.00–0.66)T	—	0.08	—	(0.00–0.99)T	—	(0.52–0.83)T	—	(0.00–0.74)T	—
Th^{4+}	0.77	0.06	0.75	0.05	0.72	0.07	(0.00–0.50)T	—	0.76	0.07	0.69	0.02	(0.47–0.83)T	—
Ce^{4+}	0.78	0.05	(0.46–0.77)T	—	0.85	−0.07	0.25	0.00	0.81	−0.03	0.61	0.00	(0.45–0.80)T	—
VO^{2+}	0.81	0.06	0.81	−0.02	0.87	−0.07	0.40	0.00	0.90	−0.05	0.73	0.03	0.86	−0.09
Se(IV)	0.86	−0.03	0.06	0.75	0.03	0.77	0.02	0.69	0.90	−0.05	0.06	0.76	0.03	0.76
Mo(VI)	(0.00–0.64)T	—	(0.00–0.71)T	—	0.06	—	0.09	—	(0.00–0.71)T	—	(0.00–0.65)T	—	(0.00–0.28)T	—
UO_2^{2+}	0.79	0.07	0.81	0.01	0.85	−0.02	0.54	−0.01	0.81	0.02	0.70	0.02	0.82	−0.07

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[a] Where the difference between R_L and R_T is less than 0.25, the average is reported as R_F. $R_i = R_F$ on plain paper $- R_F$ on impregnated paper. T = tailing.

TABLE 2

Experimentally Achieved Separations on ZTA Papers

Solvent system	List of separations achieved in different solvent systems
a	$\mathrm{Pb^{2+}/Zn^{2+}}$, $\mathrm{Ag^{+}/Tl^{+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Pb^{2+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Tl^{+}/Cu^{2+}}$, $\mathrm{Ag^{+}/Tl^{+}/Zn^{2+}}$, $\mathrm{Ag^{+}/Tl^{+}/Cd^{2+}}$
b	$\mathrm{UO_2{}^{2+}/Zn^{2+}}$, $\mathrm{Mg^{2+}/Zn^{2+}}$, $\mathrm{Cu^{2+}/Zn^{2+}}$, $\mathrm{Ni^{2+}/Zn^{2+}}$, $\mathrm{Cd^{2+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Al^{3+}}$, $\mathrm{Ag^{+}/Pt(IV)}$, $\mathrm{Sb^{3+}/La^{3+}}$, $\mathrm{Sb^{3+}/Al^{3+}}$, $\mathrm{Sb^{3+}/Zn^{2+}}$, $\mathrm{Sb^{3+}/Sn^{4+}}$, $\mathrm{Sb^{3+}/UO_2{}^{2+}}$, $\mathrm{Ba^{2+}/Mg^{2+}}$, $\mathrm{Ag^{+}/Cu^{2+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Tl^{+}/Bi^{3+}}$, $\mathrm{Sb^{3+}/Bi^{3+}/Hg^{2+}}$, $\mathrm{Sb^{3+}/Pb^{2+}/Th^{4+}}$, $\mathrm{Sb^{3+}/Pb^{2+}/Hg^{2+}}$, $\mathrm{Sb^{3+}/Pb^{2+}/Sn^{2+}}$
c	$\mathrm{Mo(VI)/Fe^{3+}}$, $\mathrm{Mo(VI)/VO^{2+}}$, $\mathrm{Mo(VI)/Ce^{4+}}$, $\mathrm{Mo(VI)/Th^{4+}}$, $\mathrm{Sn^{4+}/Bi^{3+}}$, $\mathrm{Sn^{2+}/Cu^{2+}}$
d	$\mathrm{Tl^{+}/Bi^{3+}}$, $\mathrm{Ti^{4+}/Fe^{3+}}$, $\mathrm{Fe^{2+}/Fe^{3+}}$, $\mathrm{Pb^{2+}/Cu^{2+}}$, $\mathrm{Pb^{2+}/UO_2{}^{2+}}$, $\mathrm{Zn^{2+}/Co^{2+}}$, $\mathrm{Zn^{2+}/Al^{3+}}$, $\mathrm{Zn^{2+}/Hg^{2+}}$, $\mathrm{Zn^{2+}/UO_2{}^{2+}}$, $\mathrm{Bi^{3+}/UO_2{}^{2+}}$, $\mathrm{La^{3+}/UO_2{}^{2+}}$, $\mathrm{Mo(VI)/UO_2{}^{2+}}$, $\mathrm{Ag^{+}/Bi^{3+}/UO_2{}^{2+}}$, $\mathrm{Ag^{+}/Cu^{2+}/Sn^{2+}}$, $\mathrm{Se(IV)/Ce^{4+}/UO_2{}^{2+}}$, $\mathrm{Ti^{4+}/Fe^{3+}/Sn^{2+}}$, $\mathrm{Ag^{+}/Zn^{2+}/Cu^{2+}/Sn^{2+}}$
f	$\mathrm{Ba^{2+}/La^{3+}}$, $\mathrm{Ag^{+}/Pd^{2+}}$, $\mathrm{Ag^{+}/VO^{2+}}$, $\mathrm{Pb^{2+}/Ba^{2+}}$, $\mathrm{Pb^{2+}/Bi^{3+}}$, $\mathrm{Pb^{2+}/Fe^{3+}}$, $\mathrm{Pb^{2+}/Sn^{2+}}$, $\mathrm{Pb^{2+}/Cd^{2+}}$, $\mathrm{Pb^{2+}/Sn^{4+}}$, $\mathrm{Se(IV)/Zn^{2+}}$, $\mathrm{Se(IV)/Th^{4+}}$, $\mathrm{Se(IV)/Al^{3+}}$, $\mathrm{Se(IV)/Bi^{3+}}$, $\mathrm{Co^{2+}/Hg^{2+}}$, $\mathrm{Pb^{2+}/Bi^{3+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Co^{2+}/Hg^{2+}}$, $\mathrm{Tl^{+}/Bi^{3+}/Hg^{2+}}$, $\mathrm{Tl^{+}/Ba^{2+}/Hg^{2+}}$, $\mathrm{Tl^{+}/La^{3+}/Hg^{2+}}$, $\mathrm{Tl^{+}/VO^{2+}/Hg^{2+}}$, $\mathrm{Tl^{+}/UO_2{}^{2+}/Hg^{2+}}$
g	$\mathrm{Se(IV)/Cu^{2+}}$, $\mathrm{Se(IV)/UO_2{}^{2+}}$, $\mathrm{Se(IV)/Hg^{2+}}$, $\mathrm{Sn^{2+}/Mg^{2+}}$, $\mathrm{Sn^{2+}/Hg^{2+}}$, $\mathrm{Ag^{+}/Ba^{2+}/UO_2{}^{2+}}$

The R_F on impregnated papers and R_i (R_F on plain papers − R_F on impregnated papers) values for various metal ions on ZTA papers are given in Table 1. Some important and difficult separations which seemed possible on the basis of R_F values were achieved on these papers, and these are listed in Table 2.

DISCUSSION

A perusal of the results (Table 1) reveals that impregnated papers give more compact spots than plain papers in almost all the solvent systems. From the table it is seen that even though the R_F varies from 0.00 to 1.00, no generalization as to the effect of charge, size, and nature of cation on these values emerges. Further, it is observed that for these ion-exchange papers R_F values decrease as the amount of propanol in the solvent mixtures (a and b; c and d; e and f) is increased. This decrease in R_F values may be due to a decrease in number of H^+ competing for exchange sites. For most of the metal ions, R_i values are small in all the solvent systems, indicating that the migration behavior of metal ions on impregnated and plain papers is not significantly different. This is obviously due to weaker ionization of the exchange material in the presence of propanol. Further, hydrogen ions of the acid present in the solvent tend to suppress (by competition) the adsorption of metal ions on exchange sites. Similar effects have also been observed on stannic tungstate (*11*) papers in nitric acid–acetone solvent systems. For some metal ions in some of the solvent systems, R_i is negative, i.e., the R_F on impregnated papers is more than on plain papers.

A significant decrease in R_F values on both plain and impregnated papers in Solvent d seems to be due to the fact that propanol checks the mobility of ions to a great extent. The type of acid in solvents used also affects the R_F values. This difference seems to be due to the formation of metal chloro complexes in hydrochloric acid. In these solvent systems Ag^+, Tl^+, and Pb^{2+} ions do not move and are retained at the point of application due to formation of insoluble chlorides. However, for Tl^+ and Pb^{2+}, slight tailing is observed from the point of application because $TlCl$ and $PbCl_2$ are less insoluble. The fact that silver ion is retained in nitric acid media, as well as on plain papers, indicates some sort of metal ion–matrix interaction in addition to the formation of silver chloride. Pb^{2+} and Tl^+ are not retained in propanol–nitric acid mixtures (Solvent a) and thus can be separated from Ag^+. Mo(VI) shows tailing only on ion-exchange papers and not on plain papers in almost all of the solvent systems. This may be due to Mo being in anionic form (*12*).

It is seen from Table 1 that R_F values for a number of metal ions are significantly different, thereby indicating the possibility of many separations on these ion-exchange papers. The details of a number of binary and ternary separations carried out are given in Table 2. All these separations were found to be reproducible. Of all the separations achieved, the most important ones are Ag^+–Tl^+, Ag^+–Pt(IV), Ag^+–Pd^{2+}, Tl^+–Hg^{2+}, Zn^{2+}–Hg^{2+}, Sb^{3+}–Bi^{3+}, Bi^{3+}–$UO_2{}^{2+}$, Zn^{2+}–$UO_2{}^{2+}$, La^{3+}–$UO_2{}^{2+}$, Sn^{4+}–Bi^{3+}, Tl^+–Bi^{3+}, Fe^{2+}–Fe^{3+}, Ag^+–Tl^+–Hg^{2+}, Ag^+–Pb^{2+}–Hg^{2+}, Sb^{3+}–Bi^{3+}–Hg^{2+}, Sb^{3+}–Pb^{2+}–Th^{4+}, Ag^+–Bi^{3+}–$UO_2{}^{2+}$, Se(IV)–Ce^{4+}–$UO_2{}^{2+}$, Ti^{4+}–Fe^{3+}–Sn^{2+}, Ag^+–Ba^{2+}–$UO_2{}^{2+}$, and Ag^+–Zn^{2+}–Cu^{2+}–Sn^{2+}.

As for most of the metal ions, R_F values both on plain and impregnated papers are almost of the same order; i.e., the same separations can be achieved on impregnated and on plain papers. However, separations on impregnated papers are better in that they are cleaner because less tailing is observed. In addition to this, some important separations not possible on plain papers can be carried out on impregnated papers. These separations are, of course, due to the selectivity of the impregnated papers. Some of these separations are as follows:

Tl^+ from 24 cations in solvent system f. Interferences are Ag^+, Mo(VI), Se(IV), and Pb^{2+}.

Pb^{2+} from 24 cations in solvent system f. Interferences are Ag^+, Mo(VI), Se(IV), and Tl^+.

Sb^{3+} from 23 cations in solvent system b. Interferences are Ag^+, Tl^+, Ti^{4+}, Mo(VI), and Se(IV).

Se(IV) from 24 cations in solvent system f. Interferences are Ag^+, Tl^+, Pb^{2+}, and Mo(VI).

Mo(VI) from 20 cations in solvent system c. Interferences are Ag^+, Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Sn^{4+}, Ti^{4+}, and Se(IV).

Sn^{2+} from 26 cations in solvent system d. Interferences are Pd^{2+} and Sn^{4+}.

Sn^{4+} from 26 cations in solvent system d. Interferences are Pd^{2+} and Sn^{2+}.

Thus it is obvious that papers impregnated with ZTA are better than plain papers for chromatographic separations of metal ions.

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