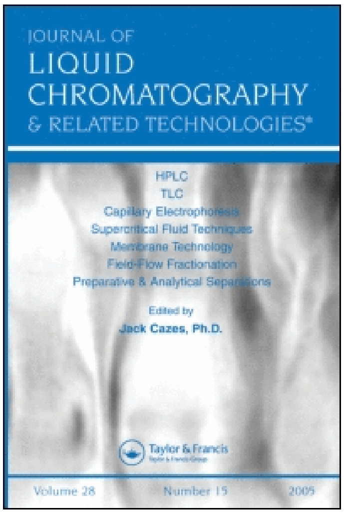

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Paper Chromatographic Separations of Metal Ions on Collidinium Tungstoarsenate Papers

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PAPER CHROMATOGRAPHIC SEPARATIONS OF METAL IONS ON COLLIDINIUM TUNGSTOARSENATE PAPERS.

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ABSTRACT

A systematic study of the chromatography of metal ions on collidinium tungstoarsenate papers has been performed using seven different mixed solvent systems. R_f values of 30 metal ions have been determined by ascending technique and are discussed. The study demonstrates that specific extraction of both Sn(ii) and Sn(iv) is possible in 0.1 mol dm^{-3} HNO_3 in 80 % (v/v) 1-propanol and their mutual separation can be carried out in solvent system 1 mol dm^{-3} HCl in 33 % (v/v) 1-propanol. In addition some binary and ternary separation of metal ions have also been achieved on these papers. For a comparison R_f values on plain papers have also been determined in all the solvent systems.

INTRODUCTION

Ion exchange is the only technique by which separation of very similar ionic species, as different valency states of a particular ion, is possible. In the last two decades inorganic exchangers have been extensively investigated regarding their use as impregnating and column material in the separation of metal ions on papers, thin layers and columns(1-5). Of the various inorganic exchangers, the heteropolyacid salts, being more selective in their exchange properties have been more extensively used for these purposes. Ammonium molybdophosphate (6) was the first exchanger to be used as impregnating material for paper chromatographic separation of alkali metal ions.

Recently(7-11) we have reported on the usefulness of heteropoly tungstoarsenates substituted with different cations for the above purposes. It has been observed that by substituting cations of different valency and ionic size in tungstoarsenate matrix, the structure of resulting compounds and their ion exchange selectivities are changed.

Present studies deal with the chromatographic separation of metal ions on papers impregnated with collidinium tungstoarsenate (CTA) which has been found to possess promising exchange properties (11).

MATERIAL

Reagents

All metal salts and acids were of analytical grade collidinium nitrate was prepared by mixing nitric acid and distilled 2,4,6- collidine in equimolecular quantities. The solvent propanol was purified by distillation.

Metal Ions Studied

The oxidation numbers of the metals used were Ag(i), Tl(i), Mg(ii), Sr(ii), Ba(ii), Fe(ii), Co(ii), Ni(ii), Cu(ii) Zn(ii), Pd(ii), Cd(ii), Sn(ii), Hg(ii), Pb(ii), Al(iii), Fe(iii), La(iii), Sb(iii), Bi(iii), Ce(iii), Pt(iv), Sn(iv), Ti(iv), Th(iv), Ce(iv), VO(iv), Se(iv), Mo(vi), and UO_2(vi).

Apparatus

Chromatography was performed on Whatmann No.3 chromatographic paper strips (15x5.5 cm^2), using 20x10x28 cm^3 glass jars.

Preparation of Ion Exchange Papers

Ion exchange papers were prepared by impregnating paper strips with collidinium tungstoarsenate. The paper strips were first dipped in a freshly prepared solution of sodium 12-tungstoarsenate for ~10 seconds. The solution was prepared by mixing 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 is strongly acidic. Total volume of the solution was kept 100 cm^3. The excess solution on paper strips was blotted out and these were dried at room temperature for 15 minutes. The strips were again dipped in 0.1 mol dm^{-3} collidinium nitrate solution for ~10 seconds. The excess solution was drained off and the strips were dried at room temperature.

Composition of Impregnated Papers

Impregnated paper strips were treated with~0.1 mol dm^{-3} sodium hydroxide solution for some time in order to decompse collidinium tungstoarsenate formed on papers. The strips were then washed with water and the solution was made up to 100 cm^{3} in a measuring flask. Collidine was estimated spectrophotometrically at 263 nm and tungsten was determined by thiocyanate method at 398 nm.

The analysis of the ion exchange papers shows that collidine/tungsten molar ratio is same as was found for collidinium tungstoarsenate exchanger, $(C_8H_{11}NH)_3MO_{12}ASO_{40})$, used for column separation (11).

Test Solutions and Detectors

Test solutions of chlorides, nitrates or sulphates of most of the metal cations (0.1 mol dm^{-3}) were prepared in 0.1 mol dm^{-3}corresponding acids as reported earlier (8,9). Detection of metal ions was carried out by standards methods (12).

Procedure

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 1.5 - 2 hours for 11 cm ascent of the solvent. After detecting the spots, the R_f values were measured. In case of spreading, the front (R_L) and rear (R_T) limits of the spots have been mentioned. For a comparison, R_f values on plain paper strips were also determined.

RESULTS AND DISCUSSION

Thirty metal ions were chromatographed on impregnated as well as on plain papers in seven different solvent systems, i.e.,

(a) 1 mol dm^{-3} nitric acid in 30 percent (v/v)1-propanol,
(b) 1 mol dm^{-3} nitric acid in 50 percent(v/v)1-propanol,
(c) 0.1 mol dm^{-3} nitric acid in 50 percent(v/v)1-propanol,
(d) 0.1 mol dm^{-3} nitric acid in 80 percent(v/v)1-propanol,
(e) 1 mol dm^{-3} hydrochloric acid in 33 percent (v/v)1-propanol,
(f) 1 mol dm^{-3} hydrochloric acid in 50 percent (v/v)1-propanol and
(g) 0.1 mol dm^{-3} hydrochloric acid in 50 percent(v/v)1-propanol.

TABLE 1

Experimentally achieved Separations on CTA Papers

Solvent System	Separations
(a)	Th(iv) (0.40-0.58) - Pd(ii) (0.75-0.91)
	Ce(iv) (0.54-0.68) - Sn(iv) (0.81-0.94)
	Ag(i) (0.00-0.00) - Tl(i) (0.20-0.56)
	- Ni(ii) (0.69-0.91)
(b)	Bi(iii)(0.17-0.56) - Sn(iv) (0.71-0.95)
	Bi(iii)(0.19-0.55) - Hg(ii) (0.90-1.00)
	Ag(i)(0.00-0.00) - Cu(ii) (0.61-0.76)
	- Hg(ii) (0.91-1.00)
	Ag(i)(0.00-0.00) - Ba(ii) (0.33-0.54)
	- Th(iv) (0.65-0.85)
	Ba(ii)(0.35-0.54) - Sr(ii) (0.55-0.65)
	- Mg(ii) (0.69-0.85)
(c)	UO_2(vi)(0.28-0.55) - Zn(ii) (0.85-0.95)
	Fe(iii)(0.25-0.67) - Al(iii)(0.75-0.95)
	Sr(ii)(0.37-0.55) - Mg(ii) (0.65-0.82)
	Cd(ii)(0.50-0.80) - Hg(ii) (0.90-1.00)
	Al(iii)(0.75-0.82) - Zn(ii) (0.88-0.98)
(d)	Pb(ii) (0.00-0.20) - Sn(ii) (0.74-0.85)
	Zn(ii) (0.02-0.18) - Hg(ii) (0.60-0.80)
	Ti(iv) (0.00-0.21) - Se(iv) (0.35-0.63)
	Sn(iv) (0.73-0.87)
(e)	Sn(iv) (0.50-0.75) - Sn(ii) (0.80-0.91)
	Pb(ii) (0.00-0.10) - Sb(iii)(0.40-0.85)
	Th(iv) (0.45-0.58) - VO(iv) (0.76-0.86)
	Th(iv) (0.44-0.60) - UO_2(vi)(0.75-0.95)
	Th(iv) (0.44-0.56) - La(iii)(0.65-0.88)
	Pb(ii) (0.00-0.09) - Th (iv)(0.44-0.60)
	- Bi(iii)(0.77-0.96)
(f)	Ag(i)(0.00-0.00) - Cu(ii) (0.60-0.74)
	Ag(i)(0.00-0.00) - Pd(ii) (0.72-0.94)
	Ba(ii)(0.30-0.47) - La(iii)(0.52-0.70)
	Ba(ii)(0.31-0.47) - Mg(ii) (0.60-0.82)

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 these papers were determined in all the seven solvent systems. Some important and difficult separations, seemed possible on the basis of R_f values, achieved on these papers and are listed in Table 1.

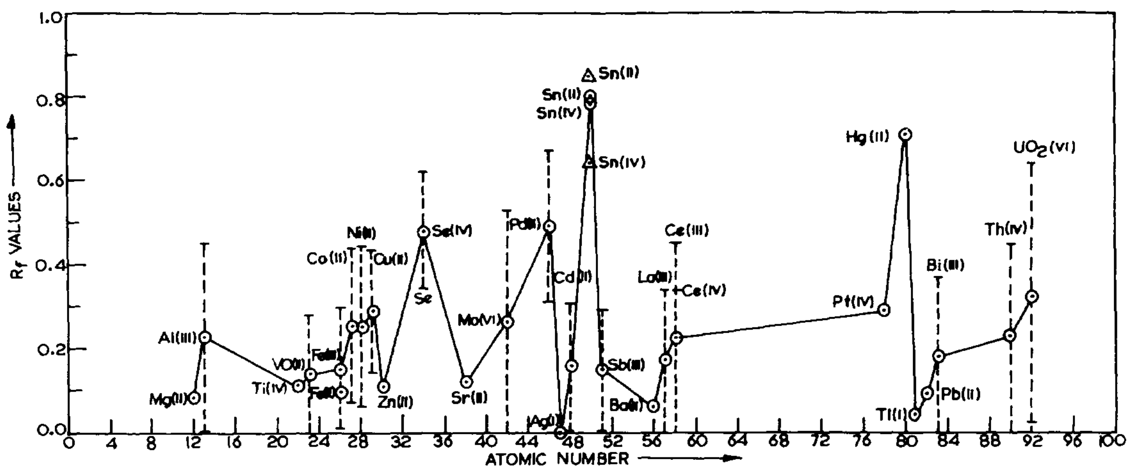

FIGURE 1. Plot of R_f values of metal ions vs. their atomic number in solvent system 0.1 mol dm^{-3} nitric acid in 80 percent v/v 1- propanol, O—O. R_f values of Sn(ii) and Sn(iv) in solvent system 1 mol dm^{-3} hydrochloric acid in 33 percent v/v 1-propanol, Δ—Δ.

The R_f value for Ag(i) is zero in all the solvent systems on impregnated as well as on plain papers. In hydrochloric acid-propanol mixtures, Tl(i) and Pb(ii) show tailing from the point of application (due to their insoluble chlorides) but nitric acid-propanol mixtures move them and can, therefore, be used to separate them from Ag(i). The fact that silver ion is also retained in nitric acid-propanol mixture as well as on plain papers, indicates some sort of metal ion matrix interaction in addition to the formation of AgCl. Sorption studies carried out on this sorbent (static)further confirmed this fact, as Ag(i) is not adsorbed at all from dilute aqueous solutions(11). Apart from Ag(i), Tl(i) and Pb(ii), specific selectivities (low R_f values) in some solvent systems, i.e., Ba(ii) in solvent system(b) and (f); UO_2(vi) and Sr(ii) in solvent system (c); and Th(iv) in solvent system (e) are also observed on these papers. In solvent system (d) R_f values are decreased significantly for almost all the metal ions. In this solvent system Sn(ii), Sn(iv) and Hg(ii) are not retained (showed high R_f) values) and can be separated from other metal ions. The decrease in R_f values in this solvent system on impregnated as well as on plain papers may be due to a check on mobility of ions in higher amount of propanol. This solvant system can, therefore, be used for almost specific extractions of Sn(ii) or Sn(iv) (Fig.1). Separation of Sn(ii) and Sn(iv) can be achieved in solvent system (e).

A comparison of R_f values on impregnated and plain papers showed almost similar pattern for most of the metal ions except that impregnated papers gave more compact spots, i.e., showed less spreading. Therefore, the separations achieved on impregnated papers are cleaner as compared to plain papers. In addition to this, some important separations which are not possible on plain papers can be carried out on impregnated papers. These separations, of course, are due to the selectivity of the impregnating material. Some of these possible separations of one metal ion from numerous others on CTA papers are: Tl(i) from 26 cations in solvent system(e), interferences are Ag(i), Pb(ii), Mo(vi); Pb(ii) from 26 cations in solvent system (e), interferences are Ag(i), Tl(i), Mo(vi); Th(iv) from 20 cations in solvent system (e), interferences are Mo (vi) , Ti(iv), Ce(iv), Ce(iii), Sb(iii), Mg(ii), Ba(ii), Sn(iv), Se(iv); Ba(ii) from 19 cations in solvent system (f), interferences are Tl(i), Sr(ii), Fe(ii), Pb(ii), Fe(iii), Sb(iii), Ce(iii), Ti(iv), Ce(iv), Mo(vi).

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