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Chromatographic Separation of Metal Ions on Stannous Ferrocyanide Papers

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NOTE

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Abstract

Ascending paper chromatography of the inorganic metal ions has been performed on papers impregnated with the ion exchanger, stannous ferrocyanide, using 19 solvent systems. On the basis of the difference in the migration of the spots on the paper, twenty-three difficult separations have been achieved. Arsenic has also been separated from numerous metal ions on these papers.

INTRODUCTION

Synthetic inorganic ion exchangers are of great interest today because of their use for the separation of metal ions. A large number of separations have actually been achieved on the columns of these ion exchangers. Chromatography on papers impregnated with inorganic ion exchangers has been reviewed by Alberti (*1*). Studies in this direction have also been made in these laboratories (*2–7*), and many important and useful separations have been achieved. However, all these studies have been made on papers impregnated with inorganic ion exchangers of the zirconium phosphate type. The use of metal ferrocyanides as ion exchange materials in paper chromatography has been lacking, although they have been widely used as scavangers for fission products and alkali metals. Our earlier researches on ferrocyanides of tin(IV) (*8*) and tin(II) (*9*) revealed their potentialities for the separation of metal ions because of their high ion exchange capacity and high selectivity for the metals. This report

summarizes our efforts to use stannous ferrocyanide for the impregnation of papers in order to achieve some difficult separations.

EXPERIMENTAL

Apparatus

Ordinary glass jars, 20 × 5 cm, were used to develop the paper strips, 14 × 3 cm, for chromatography.

Reagents and Chemicals

All the reagents and chemicals were of Analar grade and were obtained from B.D.H. (England) or E. Merck (Darmstadt).

Preparation of Ion Exchange Papers

Stannous ferrocyanide papers were prepared by dipping them in a 0.25 *M* solution of tin(II) chloride, drying, and then dipping in a 0.25 *M* solution of potassium ferrocyanide. After drying, the strips were washed thoroughly in distilled water to remove any excess tin(II) chloride or potassium ferrocyanide. They were finally dried and used as such.

Preparation of Cation Solutions and Detectors

They were prepared as described in an earlier paper (*3*).

Procedure

The ascending technique was applied in these studies. The papers were spotted for the cations, hung in the glass jars, developed in the solvent, and the spots were detected as usual (*3*).

RESULTS

The chromatographic behavior of the following 36 metal ions has been studied: Ag(I), Pb(II), Hg(II), Hg(I), Cd(II), Cu(II), Bi(III), As(III), Sb(III), Al(III), Cr(III), Ni(II), Co(II), Mn(II), Zn(II), Ca(II), Ba(II), Sr(II), Mg(II), Pd(II), Pt(IV), Ir(IV), Ru(III), Mo(VI), Au(III), Rb(I), La(III), Ce(IV), Zr(IV), Th(IV), Ga(III), In(III), Tl(I), UO_2(II), and Nb(V).

The solvent systems used were

1. Distilled water
2. 0.1 *M* HNO_3
3. 1 *M* NH_4NO_3

4. 1 *M* NH_4Cl
5. 1 *M* NaCl
6. 1 *M* $NaNO_3$
7. Dioxane + 0.1 *M* HNO_3 (1:1)
8. Dioxane + 0.2 *M* HNO_3 (1:1)
9. Acetone + 0.2 *M* HNO_3 (1:1)
10. *n*-Butanol + Conc HNO_3 (8:2)
11. 0.2 *M* NH_4NO_3 + 0.1 *M* HNO_3 (1:1)
12. 0.2 *M* NH_4NO_3 + 0.1 *M* HNO_3 (1:2)
13. 2 *M* NH_4NO_3 + 0.5 *M* HNO_3 (1:1)
14. 2 *M* NH_4NO_3 + 1 *M* HNO_3 (1:1)
15. 2 *M* NH_4NO_3 + 2 *M* HNO_3 (1:1)
16. 1.0 *M* $NaNO_3$ + 0.1 *M* HNO_3 (1:1)
17. 0.8 *M* $NaNO_3$ + 4 *M* HNO_3 (1:1)
18. 0.5 *M* NH_4Cl + 1 *M* HCl (1:1)
19. H_3PO_4 + H_2O (1:10)

TABLE 1

Binary Separations Achieved

Solvent system	Separations		
0.2 *M* NH_4NO_3 + 0.1 *M* HNO_3 (1:2)	Ca^{+2}	(0.82–0.66)–Ba^{+2}	(0.58–0.32)
	Mg^{+2}	(0.98–0.84)–Sr^{+2}	(0.40–0.18)
	Mg^{+2}	(0.92–0.80)–Ba^{+2}	(0.70–0.34)
	Ca^{+2}	(0.00) –Sr^{+2}	(0.93–0.81)
2 *M* NH_4NO_3 + 0.5 *M* HNO_3 (1:1)	Cr^{+3}	(0.00) –Al^{+3}	(0.96–0.87)
	Ga^{+3}	(0.87–0.00)–Al^{+3}	(1.0 –0.93)
	In^{+3}	(0.21–0.00)–Al^{+3}	(1.0 –0.87)
	Zr^{+4}	(0.21–0.00)–Th^{+4}	(0.93–0.68)
	Ca^{+2}	(0.00) –Ba^{+2}	(1.0 –0.93)
	Sb^{+3}	(0.15–0.00)–Pb^{+2}	(1.0 –0.75)
	Pt^{+4}	(0.00) –Pb^{+2}	(0.75–0.31)
2 *M* NH_4NO_3 + 2 *M* HNO_3 (1:1)	Au^{+3}	(0.34–0.00)–Pb^{+2}	(0.93–0.46)
	Cu^{+2}	(0.25–0.00)–Pb^{+2}	(0.93–0.75)
	Cd^{+2}	(0.50–0.03)–Pb^{+2}	(0.93–0.75)
	Ag^{+}	(0.12–0.00)–Pb^{+2}	(1.0 –0.84)
	Ru^{+3}	(0.00) –Pb^{+2}	(0.97–0.75)
	Ir^{+4}	(0.12–0.00)–Pb^{+2}	(0.87–0.59)
	Pb^{+2}	(0.31–0.00)–Pb^{+2}	(0.89–0.56)
	Hg^{+2}	(0.25–0.00)–Pb^{+2}	(0.86–0.62)
	As^{+3}	(0.12–0.00)–Pb^{+2}	(1.0–0.86)
	Ga^{+3}	(0.40–0.00)–Al^{+3}	(0.97–0.68)
0.8 *M* $NaNO_3$ + 4 *M* HNO_3 (1:1)	Ag^{+}	(0.13–0.00)–Tl^{+}	(0.92–0.34)
	Zr^{+4}	(0.50–0.00)–La^{+3}	(1.0 –0.75)

The ascent of the solvents was fixed as 11 cm in all cases.

On the basis of the differential migration of the metal ions on paper, 23 binary separations have been achieved using different solvent systems (Table 1). R_L and R_T of the spots are given in parentheses.

DISCUSSION

It is clear from this study that stannous ferrocyanide has a high potentiality in the separation of inorganic metal ions by paper chromatography. Twenty-three binary separations have actually been achieved on these papers (Table 1). It is quite interesting to note that arsenic(III) can be separated from numerous metal ions by simply using water as the developer (Fig. 1). Thus As^{+3} has been separated from a synthetic mixture containing Ag^{+}, Pb^{+2}, Hg_2^{+2}, Al^{+3}, Ni^{+2}, Co^{+2}, Mn^{+2}, Ru^{+3}, Mo^{+6}, La^{+3}, Ce^{+4}, Ga^{+3}, In^{+3}, Tl^{+}, UO_2^{+2}, and Nb^{+5} by developing the strips with water. A greater movement of As^{+3} on stannous ferrocyanide papers is confirmed by the fact that this ion is not adsorbed on the beads of stannic (*8*) or stannous (*9*) ferrocyanide. This may be explained by saying that in solution As^{+3} is present as AsO_3^{-3} because its solution was prepared by dissolving As_2O_3 in dilute HNO_3. Since stannous ferrocyanide is a cation exchanger, AsO_3^{-3} anion is not exchanged, and hence a zero k_d value on

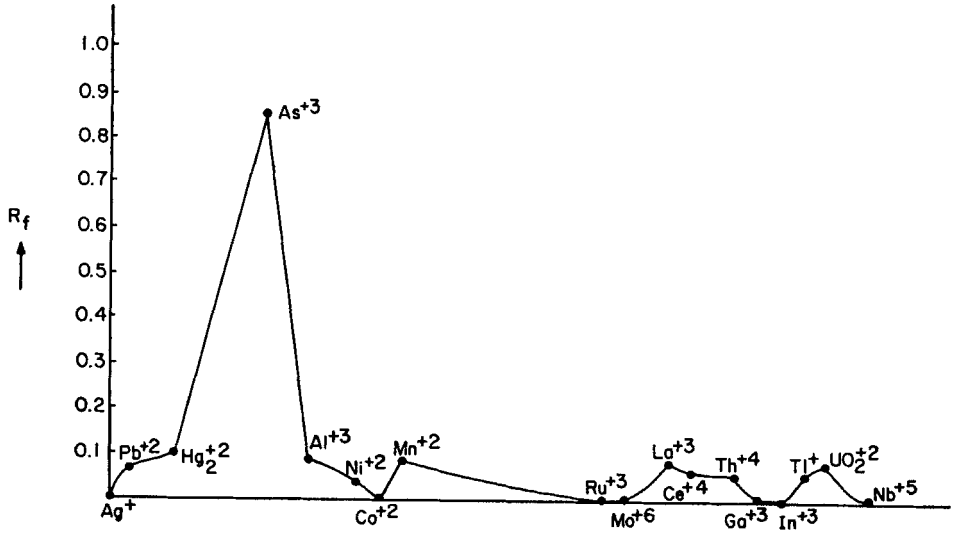

FIG. 1. Movement of cations in distilled water.

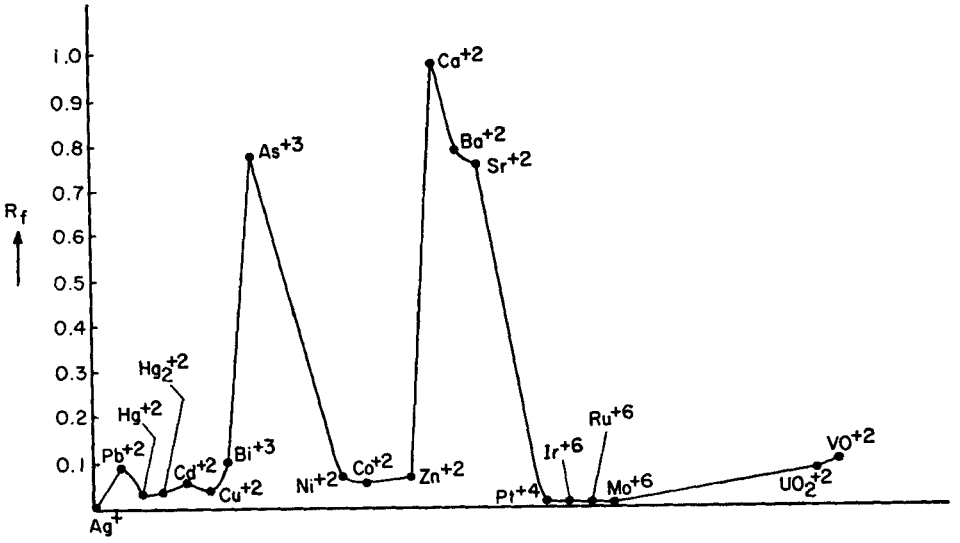

FIG. 2. Movement of cations in 0.1 *M* HNO_3.

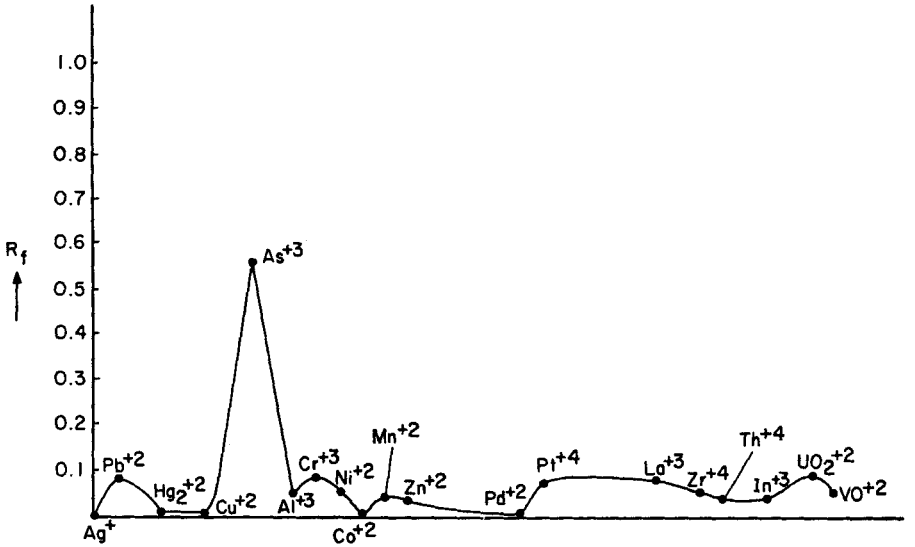

FIG. 3. Movement of cations in dioxane +0.1 *M* HNO_3 (1:1).

its beads and a large R_f value (0.9) on its papers are observed. On increasing the $[H^+]$ of the solvent, the selectivity of the metal ions for the ion exchanger decreases and hence they start moving (Fig. 2). However, the addition of dioxane with HNO_3 suppresses the movement of almost all the cations, and arsenic(III) can again be separated from 18 other metal ions (Fig. 3).

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