CHAPTER V

CHROMATOGRAPHIC SEPARATIONS OF METAL IONS AND METAL DITHIZONATES ON PAPERS IMPREGNATED WITH ZIRCONIUM TRIOXALATO ALUMINATE

5.1 INTRODUCTION

Although thousands of research papers on separation of metal ions are appearing every year and that the research activities are confined to about twenty five metal ions, it is surprising that everrising tide of research activities in this field exhibits an exponential growth. A careful thought of this state of affairs explains this situation as not being a contradiction. This partly stems from the fact that every attempt does not give a very positive applied technique. And on the other hand, with the advent of science and technology, new problems are born every now and then and hence the problems in analytical separations are everliving.

Ours is an attempt to systematically investigate the separation of metal ions by chromatographic method. The zirconyl ion with charge density is more and also that of trioxalato aluminate ion, the complex is expected to have good adsorbent character towards metal ions. Hence, we took up the study of separation of metal ions and metal dithizonates by using paper impregnated with zirconium trioxalato aluminate.

5.2 EXPERIMENTAL

The experimental technique, details of preparation of impregnated paper, preparation of reagent solutions and analytical solutions are described in second chapter. No any deviation from the standardized procedure was adopted for any of the following cases.

5.3 RESULTS

5.3.1 Experimental Details

Chromatographic separations of the following metal ions Ni^{+2}, Co^{+2}, Cu^{+2}, Mn^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Bi^{+3} and Fe^{+3} were carried out.

Similarly separations of the following metal dithizonates $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Mn(HDz)_2$, $Zn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$, $Bi(HDz)_3$ and $Fe(HDz)_3$ were also carried out.

The solvent compositions used for the experiment were as follows :

(1) Methanol + 10 M hydrochloric acid + acetone

(2) 10 M Hydrochloric acid + acetone + ethanol

(3) Acetone + 10 M hydrochloric acid + n-butanol

(4) 4 M Nitric acid + acetone + n-propanol

(5) Ethyl methyl ketone + n-butanol + 50 % hydrochloric acid

Zirconium trioxalato aluminate paper was prepared and was used after drying. However, the paper was used within a few days after the preparation. The papers were stored in large flat plastic container. The container was flushed with nitrogen and sealed harmetically by an adhesive tape so as to avoid adsorption of fumes from the laboratory atmosphere.

The experimental results are presented in the following order :

Set I - Methanol + 10 M hydrochloric acid + acetone system for metal ions (Table 5.1) and metal dithizonates (Table 5.2).

Set II - 10 M Hydrochloric acid + acetone + ethanol system for metal ions (Table 5.3) and metal dithizonates (Table 5.4).

Set III - Acetone + 10 M hydrochloric acid + n-butanol system for metal ions (Table 5.5) and metal dithizonates (Table 5.6).

Set IV - 4 M Nitric acid + acetone + n-propanol system for metal ions (Table 5.7) and metal dithizonates (Table 5.8).

Set V - Ethyl methyl ketone + n-butanol + 50 % hydrochloric acid system for metal ions (Table 5.9) and metal dithizonates (Table 5.10).

5.3.2 Observation Tables

(a) For set I, the various compositions of methanol + 10 M hydrochloric acid + acetone (M:H:A) system used are (1:1:1), (1:1:2), (2:1:2), (2:1:1), (1:2:1), (1:2:2) and (2:2:1).

The results of the above compositions are given in Tables 5.1 and 5.2.

(b) For set II, the various compositions of 10 M hydrochloric acid + acetone + ethanol (H:A:E) system used are (1:1:1), (1:2:1), (1:2:2), (1:1:2), (2:1:1), (2:2:1) and (2:1:2).

The results of the above compositions are given in Tables 5.3 and 5.4.

(c) For set III, the various compositions of acetone + 10 M hydrochloric acid + n-butanol (A:H:B) system used are (1:1:1), (2:1:1), (2:1:2), (1:1:2), (1:2:1), (2:2:1) and (1:2:2).

The results of the above compositions are given in Tables 5.5 and 5.6.

(d) For set IV, the various compositions of 4 M nitric acid + acetone + n-propanol (N:A:P) system used are (3:3:3), (2:4:2), (4:2:2), (2:2:4), (4:3:3), (3:4:3) and (3:2:4).

The results of the above compositions are given in Tables 5.7 and 5.8.

(e) For set V, the various compositions of ethyl methyl ketone + n-butanol + 50 % hydrochloric acid (EMK:B:H) system used are (6:3:6), (3:6:1), (6:3:1), (3:6:6), (6:6:3), (3:4:3), and (1:3:6).

The results of the above compositions are given in Tables 5.9 and 5.10.

Table 5.1 Chromatographic separations of metal ions on the paper impregnated with zirconium trioxalato aluminate

Time required - 50 minutes

Compositions of (M:H:A)	R_F values of metal ions								
	Ni^{+2}	Co^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Cd^{+2}	Hg^{+2}	Bi^{+3}	Fe^{+3}
1:1:1	0.93	0.92	0.89	0.71	0.97	0.83	0.93	0.90	0.92
1:1:2	0.82	0.94	0.85	0.55	0.97	0.90	0.89	0.95	0.91
2:1:2	0.89	0.93	0.88	0.77	0.95	0.93	0.95	0.97	0.94
2:1:1	0.91	0.89	0.89	0.60	0.98	0.95	0.92	0.93	0.94
1:2:1	0.90	0.88	0.91	0.67	0.96	0.92	0.67	0.91	0.91
1:2:2	0.88	0.90	0.88	0.60	0.95	0.93	0.91	0.81	0.78
2:2:1	0.93	0.82	0.89	0.76	0.96	0.94	0.90	0.86	0.85

Table 5.2 Chromatographic separations of metal dithizonates on the paper impregnated with zirconium trioxalato aluminate

Time required - 80 minutes

Compositions of (M:H:A)	R_F values of metal dithizonates								
	$Ni(HDz)_2$	$Co(HDz)_2$	$Cu(HDz)_2$	$Mn(HDz)_2$	$Zn(HDz)_2$	$Cd(HDz)_2$	$Hg(HDz)_2$	$Bi(HDz)_3$	$Fe(HDz)_3$
1:1:1	0.33	0.44	0.56	0.62	0.69	0.67	0.72	0.89	0.91
1:1:2	0.26	0.42	0.50	0.54	0.58	0.65	0.70	0.85	0.93
2:1:2	0.50	0.59	0.68	0.73	0.78	0.76	0.82	0.88	0.94
2:1:1	0.58	0.70	0.75	0.79	0.84	0.82	0.88	0.90	0.92
1:2:1	0.55	0.63	0.70	0.73	0.82	0.77	0.83	0.88	0.96
1:2:2	0.45	0.50	0.66	0.73	0.79	0.82	0.85	0.86	0.95
2:2:1	0.43	0.52	0.61	0.64	0.74	0.67	0.75	0.80	0.89

Table 5.3 Chromatographic separations of metal ions on the paper impregnated with zirconium trioxalato aluminate

Time required - 60 minutes

Compositions of (H:A:E)	R_F values of metal ions								
	Ni^{+2}	Co^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Cd^{+2}	Hg^{+2}	Bi^{+3}	Fe^{+3}
1:1:1	0.32	0.70	0.86	0.48	0.93	0.95	0.98	0.94	0.51
1:2:1	0.29	0.79	0.89	0.43	0.92	0.93	0.94	0.95	0.35
1:2:2	0.16	0.60	0.85	0.41	0.98	0.94	0.97	0.94	0.31
1:1:2	0.22	0.50	0.82	0.38	0.97	0.95	0.96	0.94	0.47
2:1:1	0.27	0.66	0.79	0.60	0.83	0.83	0.97	0.94	0.52
2:2:1	0.13	0.17	0.20	0.47	0.80	0.94	0.98	0.96	0.54
2:1:2	0.29	0.49	0.69	0.65	0.98	0.94	0.93	0.93	0.52

Table 5.4 Chromatographic separations of metal dithizonates on the paper impregnated with zirconium trioxalato aluminate

Time required - 65 minutes

Compositions of (H:A:E)	R_F values of metal dithizonates								
	$Ni(HDz)_2$	$Co(HDz)_2$	$Cu(HDz)_2$	$Mn(HDz)_2$	$Zn(HDz)_2$	$Cd(HDz)_2$	$Hg(HDz)_2$	$Bi(HDz)_3$	$Fe(HDz)_3$
1:1:1	0.62	0.69	0.78	0.83	0.92	0.91	0.90	0.95	0.97
1:2:1	0.54	0.62	0.69	0.70	0.93	0.90	0.92	0.94	0.99
1:2:2	0.73	0.78	0.82	0.85	0.90	0.88	0.89	0.96	0.98
1:1:2	0.68	0.72	0.80	0.82	0.94	0.89	0.93	0.95	0.99
2:1:1	0.52	0.61	0.65	0.71	0.90	0.85	0.92	0.98	0.97
2:2:1	0.48	0.51	0.54	0.57	0.83	0.72	0.83	0.90	0.92
2:1:2	0.66	0.76	0.79	0.82	0.93	0.90	0.87	0.90	0.98

Table 5.5 Chromatographic separations of metal ions on the paper impregnated with zirconium trioxalato aluminate

Time required - 90 minutes

Compositions of (A:H:B)	R_F values of metal ions								
	Ni^{+2}	Co^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Cd^{+2}	Hg^{+2}	Bi^{+3}	Fe^{+3}
1:1:1	0.44	0.54	0.71	0.56	0.95	0.94	0.92	0.84	0.84
2:1:1	0.21	0.35	0.73	0.50	0.93	0.95	0.86	0.91	0.96
2:1:2	0.14	0.26	0.63	0.47	0.91	0.95	0.93	0.85	0.85
1:1:2	0.17	0.22	0.55	0.56	0.91	0.90	0.95	0.79	0.79
1:2:1	0.51	0.33	0.77	0.73	0.92	0.94	0.93	0.91	0.91
2:2:1	0.41	0.60	0.76	0.60	0.96	0.94	0.95	0.93	0.92
1:2:2	0.23	0.33	0.53	0.69	0.95	0.94	0.92	0.84	0.94

Table 5.6 Chromatographic separations of metal dithizonates on the paper impregnated with zirconium trioxalato aluminate

Time required - 90 minutes

Compositions of (A:H:B)	RF values of metal dithizonates								
	$Ni(HDz)_2$	$Co(HDz)_2$	$Cu(HDz)_2$	$Mn(HDz)_2$	$Zn(HDz)_2$	$Cd(HDz)_2$	$Hg(HDz)_2$	$Bi(HDz)_3$	$Fe(HDz)_3$
1:1:1	0.41	0.93	0.77	0.54	0.96	0.95	0.94	0.91	0.98
2:1:1	0.30	0.96	0.82	0.27	0.94	0.96	0.96	0.89	0.97
2:1:2	0.15	0.94	0.75	0.60	0.95	0.97	0.95	0.82	0.96
1:1:2	0.18	0.96	0.88	0.55	0.93	0.95	0.95	0.90	0.95
1:2:1	0.24	0.95	0.80	0.47	0.96	0.95	0.97	0.95	0.97
2:2:1	0.36	0.95	0.82	0.45	0.96	0.97	0.94	0.94	0.95
1:2:2	0.17	0.94	0.80	0.33	0.95	0.97	0.92	0.88	0.96

Table 5.7 Chromatographic separations of metal ions on the paper impregnated with zirconium trioxalato aluminate

Time required - 60 minutes

Compositions of (N:A:P)	R_F values of metal ions								
	Ni^{+2}	Co^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Cd^{+2}	Hg^{+2}	Bi^{+3}	Fe^{+3}
3:3:3	0.69	0.71	0.75	0.75	0.71	0.77	0.92	0.96	0.85
2:4:2	0.53	0.78	0.80	0.70	0.65	0.71	0.92	0.94	0.75
4:2:2	0.84	0.79	0.77	0.73	0.68	0.73	0.97	0.79	0.73
2:2:4	0.31	0.78	0.35	0.47	0.85	0.55	0.96	0.86	0.94
4:3:3	0.63	0.64	0.69	0.69	0.68	0.68	0.94	0.81	0.69
3:4:3	0.63	0.65	0.73	0.66	0.60	0.64	0.94	0.88	0.94
3:2:4	0.87	0.40	0.70	0.61	0.73	0.71	0.95	0.80	0.87

Table 5.8 Chromatographic separations of metal dithizonates on the paper impregnated with zirconium trioxalato aluminate

Time required - 75 minutes

Compositions of (N:A:P)	R_F values of metal dithizonates								
	$Ni(HDz)_2$	$Co(HDz)_2$	$Cu(HDz)_2$	$Mn(HDz)_2$	$Zn(HDz)_2$	$Cd(HDz)_2$	$Hg(HDz)_2$	$Bi(HDz)_3$	$Fe(HDz)_3$
3:3:3	0.70	0.73	0.80	0.76	0.79	0.82	0.93	0.97	0.90
2:4:2	0.56	0.80	0.85	0.75	0.73	0.76	0.95	0.97	0.83
4:2:2	0.86	0.88	0.82	0.77	0.71	0.74	0.99	0.82	0.81
2:2:4	0.35	0.80	0.43	0.51	0.88	0.61	0.96	0.88	0.97
4:3:3	0.66	0.69	0.73	0.74	0.70	0.75	0.95	0.86	0.77
3:4:3	0.69	0.70	0.75	0.77	0.66	0.69	0.95	0.90	0.95
3:2:4	0.90	0.49	0.78	0.67	0.78	0.75	0.97	0.88	0.91

Table 5.9 Chromatographic separations of metal ions on the paper impregnated with zirconium trioxalato aluminate

Time required - 65 minutes

Compositions of (EMK:B:H)	R_F values of metal ions								
	Ni^{+2}	Co^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}	Cd^{+2}	Hg^{+2}	Bi^{+3}	Fe^{+3}
6:3:6	0.29	0.38	0.57	0.28	0.92	0.91	0.94	0.90	0.95
3:6:1	0.02	0.06	0.31	0.26	0.87	0.89	0.82	0.79	0.94
6:3:1	0.04	0.12	0.52	0.10	0.96	0.92	0.90	0.72	0.91
3:6:6	0.21	0.31	0.47	0.24	0.93	0.94	0.82	0.79	0.93
6:6:3	0.06	0.11	0.39	0.24	0.92	0.76	0.92	0.79	0.95
3:4:3	0.18	0.27	0.50	0.19	0.88	0.80	0.83	0.91	0.95
1:3:6	0.35	0.44	0.57	0.54	0.80	0.94	0.81	0.72	0.92

Table 5.10 Chromatographic separations of metal dithizonates on the paper impregnated with zirconium trioxalato aluminate

Time required - 70 minutes

Compositions of (EMK:B:H)	R_F values of metal dithizonates								
	$Ni(HDz)_2$	$Co(HDz)_2$	$Cu(HDz)_2$	$Mn(HDz)_2$	$Zn(HDz)_2$	$Cd(HDz)_2$	$Hg(HDz)_2$	$Bi(HDz)_3$	$Fe(HDz)_3$
6:3:6	0.49	0.51	0.63	0.55	0.93	0.95	0.95	0.92	0.96
3:6:1	0.18	0.26	0.49	0.35	0.89	0.91	0.95	0.87	0.96
6:3:1	0.22	0.18	0.55	0.27	0.96	0.93	0.92	0.77	0.95
3:6:6	0.36	0.39	0.52	0.31	0.94	0.95	0.89	0.83	0.93
6:6:3	0.22	0.28	0.47	0.31	0.95	0.81	0.94	0.87	0.98
3:4:3	0.31	0.37	0.56	0.22	0.92	0.84	0.88	0.94	0.97
1:3:6	0.42	0.48	0.62	0.60	0.83	0.94	0.85	0.78	0.94

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5.4 DISCUSSION

Set I -

It is seen that for methanol + 10 M hydrochloric acid + acetone system, there is no significant change in R_F values for the metal ions, Ni^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2} and Bi^{+3} for all the compositions studied. While that for Mn^{+2} there is variation in R_F values for various compositions of this system. Hg^{+2} for composition 1:2:1 and Fe^{+3} for composition 1:2:2 show lowest R_F values. In 1:1:2 solvent composition, the chromatographic separation is quite good for Mn^{+2}, Ni^{+2} and Bi^{+3}. While for 1:2:2 composition, the separation of Mn^{+2}, Fe^{+3} and Zn^{+2} is possible.

When the solvent composition changes, there is significant change in R_F values in cases of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Mn(HDz)_2$ and $Zn(HDz)_2$. Bismuth dithizonate and iron dithiaonate may be unstable in alkaline medium. Therefore, they are dissociated. Hence there is no any change in R_F values. Rest of the metal dithizonates are stable, therefore, they are separated. e.g. 1:1:2 solvent composition shows the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$ and $Bi(HDz)_3$. While 1:1:1 solvent composition shows the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Zn(HDz)_2$ and $Fe(HDz)_3$.

Set II -

For 10 M hydrochloric acid + acetone + ethanol solvent system the R_F values of Co^{+2} and Ni^{+2} differ for each composition. The R_F values are lowest for metal ions Ni^{+2}, Co^{+2}, Cu^{+2} and

Zn^{+2} for the composition 2:2:1 . The variation in R_F values is observed in almost all the compositions for Ni^{+2}, Co^{+2}, Cu^{+2} and Mn^{+2}. While there is no any change in R_F values for Zn^{+2}, Cd^{+2}, Hg^{+2}, Bi^{+3} and Fe^{+3}. The R_F values of Fe^{+3} are lower than any other systems studied. The chromatographic separation can be carried out effectively for Ni^{+2}, Co^{+2}, Cu^{+2} and Mn^{+2} for the compositions 1:1:1, 1:2:1, 1:2:2, 1:1:2 and 2:1:1. Rest of the metal ions are unstable, therefore, separation can not be possible.

The R_F values of metal dithizonates are quite higher than those of metal ions. As there is quite significant change in R_F values of $Ni(HDz)_2$, $Co(HDz)_2$ and $Mn(HDz)_2$, the separation can be carried out successfully. While $Zn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$, $Bi(HDz)_3$ and $Fe(HDz)_3$ are quite unstable, therefore are unable to separate. Still the chromatographic separation is possible for the metal dithizonates namely $Ni(HDz)_2$, $Cu(HDz)_2$ and $Bi(HDz)_3$ for 1:2:1 composition, while it is possible for $Ni(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$ and $Fe(HDz)_3$ for 2:2:1 solvent composition.

Set III -

In acetone + 10 M hydrochloric acid + n-butanol system, the variation in R_F values is obtained in Ni^{+2}, Co^{+2} and Mn^{+2} due to effect of variation in composition of solvents. The R_F values of Ni^{+2} are lowest in 2:1:2 and 1:1:2 compositions. The R_F values are quite higher for Zn^{+2}, Cd^{+2}, Hg^{+2}, Bi^{+3} and Fe^{+3} in almost all compositions of the solvents. Hence separation is difficult. However, separation of Ni^{+2}, Co^{+2},

Cu^{+2}, Mn^{+2}, Bi^{+3} and Zn^{+2} is quite possible for all the compositions of this solvent system.

The R_F values of metal dithizonates are higher than those of metal ions for 2:1:1 solvent composition. $Co(HDz)_2$ shows very high R_F values than Co^{+2} for all the compositions. There is no any change in rest of the metal dithizonates. However, separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Mn(HDz)_2$ and $Bi(HDz)_3$ can be carried out for 2:1:2 composition. Also separation of $Ni(HDz)_2$, $Mn(HDz)_2$, $Cu(HDz)_2$ and $Zn(HDz)_2$ can be carried out for 1:2:2 solvent composition.

Set IV -

For the solvent system, 4 M nitric acid + acetone + n-propanol, the R_F values of metal ions are quite higher than any other systems studied. For 2:2:4 composition, the R_F values of all the metal ions are lowest. Hg^{+2} shows higher R_F value than any other metal ions. The chromatographic separation can be effectively carried out in 2:2:4 solvent composition for the metal ions Cu^{+2}, Mn^{+2}, Cd^{+2}, Co^{+2} and Fe^{+3}. The separation of Ni^{+2}, Fe^{+3} and Bi^{+3} for 3:3:3 composition, the separation of Ni^{+2}, Cu^{+2}, Zn^{+2}, Fe^{+3} and Bi^{+3} for 2:4:2 composition and separation of Co^{+2}, Mn^{+2}, Zn^{+2}, Fe^{+3} and Hg^{+2} for 3:2:4 composition can also be carried out successfully.

Metal dithizonates of this system show quite higher R_F values. The successful chromatographic separations of these metal dithizonates are possible for $Ni(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$, $Co(HDz)_2$ and $Hg(HDz)_2$ for 2:2:4 solvent composition and for $Co(HDz)_2$, $Mn(HDz)_2$, $Cu(HDz)_2$ and $Bi(HDz)_3$ for 3:2:4 solvent composition.

Set V -

For ethyl methyl ketone + n-butanol + 50 % hydrochloric acid solvent system, Ni^{+2} shows lowest R_F values for the compositions 3:6:1, 6:3:1 and 6:6:3. Co^{+2} also shows lowest R_F value for 3:6:1 solvent composition. There is significant change in R_F values for Ni^{+2}, Co^{+2}, Cu^{+2} and Mn^{+2}. While there is no any variation in R_F values for Cd^{+2}, Hg^{+2}, Bi^{+3}, Fe^{+3} and Zn^{+2}. The chromatographic separation of Ni^{+2}, Co^{+2}, Cu^{+2} and Zn^{+2} for 6:3:6 composition, the separation of Ni^{+2}, Co^{+2}, Cu^{+2}, Mn^{+2}, Cd^{+2}, Zn^{+2} and Bi^{+3} for 6:6:3 composition and the separation of Co^{+2}, Ni^{+2}, Mn^{+2}, Hg^{+2}, Bi^{+3} and Cd^{+2} for 1:3:6 composition can be successfully carried out.

The effective and rapid chromatographic separation can be carried out for metal dithizonates than for metal ions in this solvent system. Due to unstability of the complexes, separation can not be carried out in $Fe(HDz)_3$, $Bi(HDz)_3$, $Hg(HDz)_2$, $Cd(HDz)_2$ and $Zn(HDz)_2$. It is observed that for solvent compositions, 6:3:1, 3:4:3 and 1:3:6 the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Mn(HDz)_2$ and $Bi(HDz)_3$ can be carried out.

5.5 CONCLUSION

From all these five solvent systems studied, it is observed that for methanol + 10 M hydrochloric acid + acetone system, Mn^{+2}, Ni^{+2} and Bi^{+3} for 1:1:2 composition and Mn^{+2},

Fe^{+3} and Zn^{+2} for 1:2:2 composition show effective chromatographic separation. Also the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$ and $Bi(HDz)_3$ for 1:1:2 composition and the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Zn(HDz)_2$ and $Fe(HDz)_3$ for 1:1:1 composition can be carried out.

In 10 M hydrochloric acid + acetone + ethanol system, separation can be carried out for Ni^{+2}, Co^{+2}, Cu^{+2} and Mn^{+2} for 1:1:1, 1:2:1, 1:2:2, 1:1:2 and 2:1:1 solvent compositions. Separation is also possible for $Ni(HDz)_2$, $Cu(HDz)_2$ and $Bi(HDz)_3$ for 1:2:1 composition and for $Ni(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$ and $Fe(HDz)_3$ for 2:2:1 composition.

It is observed from acetone + 10 M hydrochloric acid + n-butanol solvent system that, separation of Ni^{+2}, Co^{+2}, Cu^{+2}, Mn^{+2}, Bi^{+3} and Zn^{+2} can be carried out for all the compositions. While $Ni(HDz)_2$, $Mn(HDz)_2$, $Cu(HDz)_2$ and $Zn(HDz)_2$ can be separated for 1:2:2 solvent composition.

From 4 M nitric acid + acetone + n-propanol solvent system, it is seen that separation of Cu^{+2}, Mn^{+2}, Cd^{+2}, Co^{+2} and Fe^{+3} for 2:2:4 composition, separation of Ni^{+2}, Cu^{+2}, Zn^{+2}, Fe^{+3} and Bi^{+3} for 2:4:2 composition and separation of Co^{+2}, Mn^{+2}, Zn^{+2}, Fe^{+3} and Hg^{+2} for 3:2:4 composition can be carried out successfully. The 2:2:4 composition shows the separation of $Ni(HDz)_2$, $Mn(HDz)_2$, $Cd(HDz)_2$, $Co(HDz)_2$ and $Hg(HDz)_2$, while 3:2:4 composition shows the separation of $Co(HDz)_2$, $Mn(HDz)_2$, $Cu(HDz)_2$ and $Bi(HDz)_3$.

It is observed that for ethyl methyl ketone + n-butanol + 50 % hydrochloric acid solvent system, the chromatographic separation of Ni^{+2}, Co^{+2}, Cu^{+2} and Zn^{+2} for 6:3:6 composition, separation of Ni^{+2}, Co^{+2}, Cu^{+2}, Mn^{+2}, Cd^{+2}, Zn^{+2} and Bi^{+3} for 6:6:3 composition and separation of Co^{+2}, Ni^{+2}, Mn^{+2}, Hg^{+2}, Bi^{+3} and Cd^{+2} for 1:3:6 composition can be carried out. It is also observed that for solvent compositions, 6:3:1, 3:4:3 and 1:3:6, the separation of $Ni(HDz)_2$, $Co(HDz)_2$, $Cu(HDz)_2$, $Mn(HDz)_2$ and $Bi(HDz)_3$ can be carried out effectively and rapidly.

Several dithizonates show similar R_F values, because they form unstable complexes. Hence the separation becomes difficult. In all the cases, the time required for the chromatographic separation of metal dithizonates is longer than it is required for metal ions.

The results of the best chromatographic separations of various metal ions and metal dithizonates from other metal ions and metal dithizonates respectively on papers impregnated with zirconium trioxalato aluminate for various solvent systems and various solvent compositions are summarized in table 5.11.

Table 5.11 Chromatographic separations of metal ions/metal dithizonates from other metal ions/metal dithizonates on papers impregnated with zirconium trioxalato aluminate

Metal ions or metal dithizonates	R_F values	Solvent systems	Solvent compositions	Separation from other metal ions or metal dithizonates
Mn^{+2}	0.55	M:H:A	1:1:2	Ni^{+2} and Bi^{+3}
$Co(HDz)_2$	0.44	M:H:A	1:1:1	$Mn(HDz)_2$, $Ni(HDz)_2$, $Hg(HDz)_2$ and $Fe(HDz)_3$
$Cu(HDz)_2$	0.61	M:H:A	2:2:1	$Ni(HDz)_2$, $Hg(HDz)_2$ and $Fe(HDz)_3$
$Mn(HDz)_2$	0.54	M:H:A	1:1:2	$Ni(HDz)_2$, $Hg(HDz)_2$ and $Fe(HDz)_3$
Ni^{+2}	0.16	H:A:E	1:2:2	Mn^{+2}, Co^{+2}, Cu^{+2}, Cd^{+2} and Fe^{+3}
Fe^{+3}	0.35	H:A:E	1:2:1	Co^{+2} and Bi^{+3}
$Cu(HDz)_2$	0.54	H:A:E	2:2:1	$Cd(HDz)_2$ and $Fe(HDz)_3$
Mn^{+2}	0.56	A:H:B	1:1:1	Ni^{+2}, Cu^{+2} and Bi^{+3}

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Metal ions or metal dithizonates	R_F values	Solvent systems	Solvent compositions	Separation from other metal ions or metal dithizonates
Cu^{+2}	0.53	A:H:B	1:2:2	Mn^{+2}, Ni^{+2}, Bi^{+3} and Cd^{+2}
Ni^{+2}	0.14	A:H:B	2:1:2	Co^{+2}, Mn^{+2}, Cu^{+2}, Bi^{+3} and Cd^{+2}
$Ni(HDz)_2$	0.15	A:H:B	2:1:2	$Mn(HDz)_2$, $Co(HDz)_2$ and $Cu(HDz)_2$
$Bi(HDz)_3$	0.88	A:H:B	1:2:2	$Fe(HDz)_3$, $Ni(HDz)_2$, $Cu(HDz)_2$ and $Mn(HDz)_2$
$Mn(HDz)_2$	0.45	A:H:B	2:2:1	$Ni(HDz)_2$, $Cu(HDz)_2$ and $Co(HDz)_2$
Cd^{+2}	0.55	N:A:P	2:2:4	Zn^{+2}, Ni^{+2} and Fe^{+3}
Co^{+2}	0.40	N:A:P	3:2:4	Ni^{+2}, Cu^{+2} and Hg^{+2}
Ni^{+2}	0.31	N:A:P	2:2:4	Mn^{+2}, Cd^{+2}, Co^{+2} and Fe^{+3}
$Mn(HDz)_2$	0.51	N:A:P	2:2:4	$Ni(HDz)_2$, $Zn(HDz)_2$ and $Fe(HDz)_3$

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Metal ions or metal dithizonates	R_F values	Solvent systems	Solvent compositions	Separation from other metal ions or metal dithizonates
Cu^{+2}	0.50	EMK:B:H	3:4:3	Co^{+2}, Ni^{+2}, Cd^{+2} and Fe^{+3}
Co^{+2}	0.12	EMK:B:H	6:3:1	Ni^{+2}, Cu^{+2}, Bi^{+3} and Zn^{+2}
Zn^{+2}	0.80	EMK:B:H	1:3:6	Co^{+2}, Cd^{+2}, Ni^{+2} and Cu^{+2}
Ni^{+2}	0.21	EMK:B:H	3:6:6	Co^{+2}, Cu^{+2}, Bi^{+3} and Cd^{+2}
$Mn(HDz)_2$	0.55	EMK:B:H	6:3:6	$Cu(HDz)_2$, $Ni(HDz)_2$ and $Bi(HDz)_3$
$Co(HDz)_2$	0.37	EMK:B:H	3:4:3	$Mn(HDz)_2$, $Cu(HDz)_2$, $Cd(HDz)_2$ and $Fe(HDz)_3$

From the above studies, it can be concluded that, impregnated paper, especially Whatman No.1 filter paper impregnated with zirconium trioxalato aluminate is more useful for the analytical separations of metal ions and metal dithizonates.