Thin layer chromatography separation study of certain metal cations with mixture of urea formaldehyde & cellulose as stationary phase system

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ABSTRACT

Various heavy metal ions such as Fe^{3+}, Cu^{2+}, VO^{2+}, UO_2^{2+}, Ni^{2+}, Co^{2+}, Ag^+ & Cr^{6+} have been chromatographed on thin layer of mixture of urea-formaldehyde & cellulose. SDS, urea & thiourea in in different concentration, ratios & at different pH used as mobile phases. Semiquantitative determination of UO_2^{2+} & Fe^{3+} by visual comparison of colour intensities & by spot–area measurement method has been attempted.

Keywords: SDS, Urea formaldehyde, chromatography, separation.

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INTRODUCTION

Because of poor toxicity , low cost , enhanced separation selectivity, non-flammability, capability of simultaneously separating hydrophilic and hydrophobic solutes and non volatility, micellar mobile phases (i.e. solutions containing surfactants) have found interesting applications in liquid chromatography[1-8]. The use micellar mobile (MMP) in thin layer chromatography was first proposed by Armstrong & co-workers [9-10]. MMP have been successfully utilized to separate pesticides and biphenyls[10], polynuclear aromatic hydrocarbons and vitamins[11], phenols[12] amino acids[13-14], alkaloids[15], dyes[16] and drugs[17].

Thin layer chromatography is a very convenient and rapid method for the separation and identification of inorganic ions. Therefore, any attempts to improve TLC for this application seen to be of interest for chromtographers. There are several ways to improve the TLC method. One of them is use of support processing different characteristics than those commonly used in TLC. For that reason number of metal ions were chromatographed on thin layer of synthesized carbamide-formaldehyde polymer,and already used for separation of amino acids[18] and various metal ions were also chromatographed [19] using various organic solvents as mobile phases. Lederer[20],[21] and Xuan et al.[22]-[24] studied the chromatographic behaviour of microcrystalline cellulose thin layer as chiral selector. The microcrystalline cellulose triacetate(MCTA) thin layer plates are commerciable from Antec(Benwil, CH) and Macherey-Nagel. Lepri et al.[25]-[27] proposed the creation of homemade layers using MCTA for coloumn chromatography. The chromatographic behaviour of several racemates and pure optical isomers as N-derivatized amino acids, propionic acid derivatives, alcohols , aromatic amines and lactons were investigated. Aim of our work is to separate and identify the heavy metal ions, binary, tertiary and quarternary mixture of metal ions on thin layer of mixture of synthesized urea formaldehyde polymer and cellulose .

MATERIALS AND METHODS

Apparatus:
Glass plates, Glass jars, glass capillary, electric oven & pH meterwere used.

Chemicals & Reagents:
Sodium Dodecyl Sulphate(SDS), urea, formalin solution, cellulose was obtained from Merck, potassium ferrocynide, dimethyl glyoxime, thiourea, sodium nitrate dithiozone,carbontetrachloride were obtained from SD Fine India. All other chemicals were of analytical reagent grade.

Preparation of stock solutions:
Stock solutions of following salts were used as test solution:
1. Chlorides of Ni^{2+},Co^{2+} & Fe^{2+}
2. Sulfates of Cu^{2+}, VO^{2+} & UO_2^{2+}
3. Nitrate of Ag^+.
4. Potassium salt of Cr^{6+}.

All the solutions were prepared in demineralized water.

Metal Cations studied: Fe^{3+}, Cu^{2+},VO^{2+},UO_2^{2+}, Ni^{2+},Co^{2+},Ag^+ & Cr^{6+}.

Detection Reagents: Various cations were detected by using following reagents.
a. 1% Aqueous potassium ferrocyanide for Fe^{3+},Cu^{2+},VO^{2+} and UO_2^{2+}.
b. 1% Alcoholic solution of dimethyl glyoxime for Ni^{2+} and Co^{2+}.
c. 8×10^{-3} % (w/v) Dithizone in carbon tetrachloride for Ag^+.
d. Saturated alcoholic solution of silver nitrate for Cr^{6+}.

Stationary Phase: Urea-formaldehyde and Cellulose in 1:1(wt/wt) ratio.

Mobile Phase: The following solvent systems were use as mobile phase.

Symbol	Composition
M_1	0.1% SDS
M_2	0.2% SDS
M_3	0.3% SDS
M_4	0.4% SDS
M_5	0.3% SDS pH=1
M_6	0.3% SDS pH=2
M_7	0.3% SDS pH=3
M_8	0.3% SDS pH=4
M_9	0.3% SDS + 1% Urea (9:1,1:1 and 1:9) pH=3
M_{10}	0.3% SDS + 5% Urea (9:1,1:1 and 1:9) pH=3
M_{11}	0.3% SDS + 10% Urea (9:1,1:1 and 1:9) pH=3
M_{12}	0.3% SDS + 15% Urea (9:1,1:1 and 1:9) pH=3
M_{13}	0.3% SDS + 1% Thiourea (9:1,1:1 and 1:9) pH=3
M_{14}	0.3% SDS + 5% Thiourea (9:1,1:1 and 1:9) pH=3
M_{15}	0.3% SDS + 10% Thiourea (9:1,1:1 and 1:9) pH=3
M_{16}	0.3% SDS + 15% Thiourea (9:1,1:1 and 1:9) pH=3
M_{17}	0.3% SDS + 1% $NaNO_3$ (9:1,1:1 and 1:9) pH=3
M_{18}	0.3% SDS + 5% $NaNO_3$ (9:1,1:1 and 1:9) pH=3
M_{19}	0.3% SDS + 10% $NaNO_3$ (9:1,1:1 and 1:9) pH=3
M_{20}	0.3% SDS + 15% $NaNO_3$ (9:1,1:1 and 1:9) pH=3

Chromatography:
Preparation of TLC Plates: TLC plates were prepared by mixing mixture of Cellulose and laboratory prepared Urea-formaldehyde with double distilled water in 1:3 ratio. The resultant slurry was mechanically shaken for 15 min, after which it was applied to well-cleaned glass plates by dipping method. The plated were air dried at room temperature.

Spotting of test solutions: Thin layer chromatography was performed on mixture of cellulose & urea-formaldehyde layer plates. Test solutions were applied on plates with the help of capillary at about 2 cm above the lower edge of the plates. The solvent ascent was fixed to near about 10cm in all cases for the determination of R_f values of all metal cations. Linear ascending development was carried out in TLC chamber.

Limit of Detection: The identification of limits of various cations including Fe^{3+} and UO_2^{2+} were determined by spotting different amounts of cationic solutions on the TLC plates. The plates were developed in M7 and the spots were detected as described The minimum amount of cation that could be detected was taken as the limit of detection.

Semi-quantitative Determination by Spot-Area Measurement: For semiquantitative determination by Spot-Area Measurement method , series of various standard solutions of Cu^{2+}, Fe^{2+} & UO_2^{2+} were spotted on layer of mixture of Cellulose & Urea-formaldehyde. The plates were developed with M_7. After detection the spots were copied onto tracing paper from chromatoplates and then the area of each spot was calculated.

RESULTS AND DISCUSSION

Chromatography of ten metals was performed using various mobile phase systems(M_1-M_{20}) . The mobility pattern of metal cations was found to depend on the composition of mobile phase. Results obtained with different concentrations ,with different pH & ratios of SDS and other organic non-electrolytes compounds solutions reveal the following trends:

Metal ions such as Ag^+ and Cr^{6+} shows mid mobility at all concentration levels as well as entire pH range of SDS solutions. Very high mobility was shown by metal ions such as Fe^{3+}, Cu^{2+},VO^{2+}, Ni^{2+},Co2+ and UO_2^{2+} at all concentration levels as well as entire pH range of SDS solutions.

Table1:- Effect on the mobility of different metal ions at different concentrations of SDS

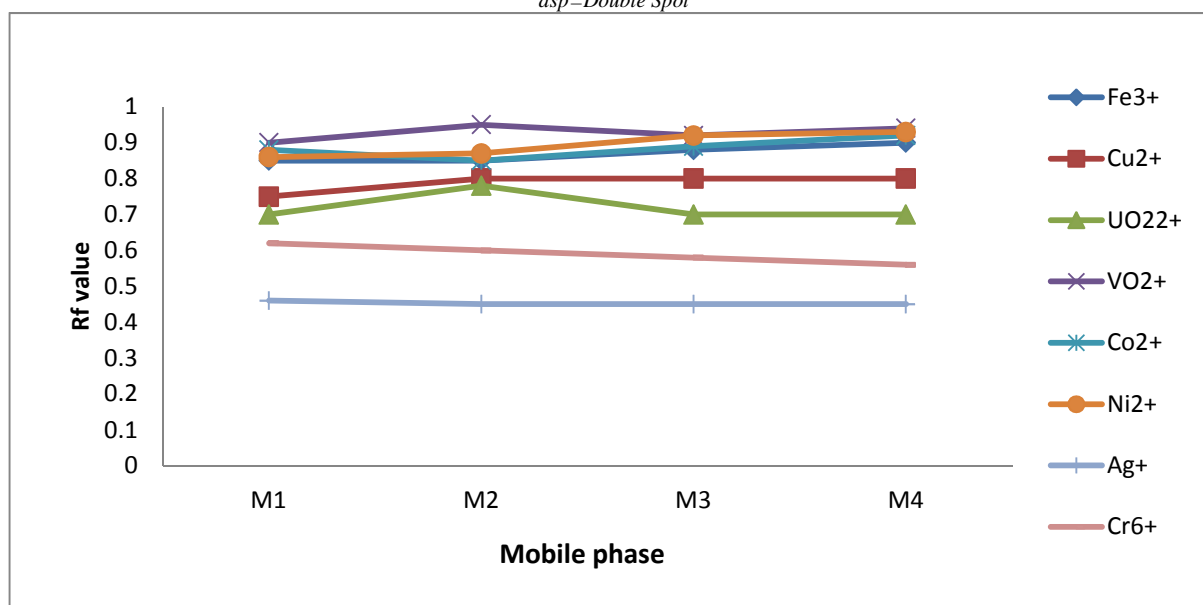| Development time=5 Minutes			
R_f Value			
Metal ions	M1	M2	M3	M4
Fe^{3+}	0.85	0.85T	0.88	0.90T
Cu^{2+}	0.75T	0.80	0.80	0.80T
UO_2^{2+}	0.70T	0.78	0.70	0.70
VO^{2+}	0.90	0.95T	0.92	0.94T
Co^{2+}	0.88	0.85	0.89	0.92
Ni^{2+}	0.86	0.87	0.92	0.93
Ag^+	0.46T	0.45T	0.45	0.45T
Cr^{6+}	0.62 dsp	0.60 dsp	0.58dsp	0.56dsp

T=Tailed Spot
dsp=Double Spot

Figure 1: Separation of metal ions at different concentrations of SDS

Effect of Added Urea:
The effect of addition of organic non-electrolyte e.g. urea at different concentration levels in 0.3% of SDS on the mobility of metal cations was examined as described in table 3.

Mobility of cations were study with increasing concentrations of urea from 1% to 15%. Most of the metal cations show very high mobility at all concentrations of urea. As concentration was increased the mobility of some metal cations such as Fe^{3+},Cu^{2+} was found to be decreased.($Fe^{3+} \approx 0.63$,$Cu^{2+} \approx 0.50$)and also they formed tailed spot in presence of 5% urea.

<div align="center">Table2:- R_f values of different metal ions at 0.3% concentrations of SDS with different pH value</div>

Metal ions	M5	M6	M7	M8
Fe^{3+}	0.79	0.85T	0.88	0.90T
Cu^{2+}	0.80	0.83	0.88	0.90T
UO_2^{2+}	0.78	0.75	0.75	0.72
VO^{2+}	0.90	0.95T	0.95	0.95T
Co^{2+}	0.90	0.92	0.89	0.93
Ni^{2+}	0.90	0.90	0.90	0.90
Ag^{+}	0.47	0.45T	0.43	0.49T
Cr^{6+}	0.63dsp	0.60 dsp	0.58dsp	0.56dsp

(Development time=5 Minutes, R_f Value)

T=Tailed Spot
dsp=Double Spot

Mobility of Ni^{2+},Co^{2+} & VO^{2+} was found to be very high and same at all concentration levels of urea. Mobility of $UO_2^{2+}$was found to be decreased with increase concentration of urea 1% to 15% at all volume ratios with 0.3% of SDS at pH=3. Cr6+ and Ag+ shows mid mobility at all concentrations of SDS+ urea at pH=3. Fe^{3+},Cu^{2+}, Cr^{6+}, Ag^{+} & UO_2^{2+}shows very good spots & separation with increased concentration of urea.

Effect of added Thiourea:
The effect of addition of organic non-electrolyte e.g. thiourea at different concentration levels in 0.3% of SDS at pH=3 on the mobility of metal cations was examined as described in table 4.

Metal cations such as VO^{2+}, Ni^{2+} and Co^{2+} shows high mobility at all concentrations of thiourea. Fe^{3+} and VO^{2+} show tailed spot at M_{14} .The mobility of UO_2^{2+} was found to be decrease with the increase in concentration of thiourea(M_{13} to M_{16}). Conversely the mobility of Fe^{3+} increases with the increase in the concentration of thiourea(M_{13} to M_{16}). However , its mobility decreases with the increase in volume ratio of thiourea in 0.3% SDS.The mobility of Cu^{2+} was found to increase with the increase in concentration of thiourea(M_{13} to M_{16}). Metal ions such as Cr^{6+} & Ag^{+} show mid mobility fromM_{13} to M_{16}.

Effect of added NaNO₃:
The effect of addition of inorganic electrolyte e.g. NaNO₃ at different concentration levels in 0.3% of SDS at pH=3 on the mobility of metal cations was examined as described in table 5 .

<div align="center">Table 3. Mobility trends of metal ions on mixture of Urea formaldehyde and Cellulose developed with 0.3% SDS plus different concentration of Urea at pH=3</div>

Development Time=5 Minutes

Metal ions	0.3% SDS+ 1% Urea			0.3% SDS+ 5% Urea			0.3% SDS+ 10% Urea			0.3% SDS+ 15% Urea		
	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9
Fe^{3+}	0.90	0.90	0.90	0.81	0.70T	0.63	0.71	0.68	0.61	0.70	0.65	0.59
Cu^{2+}	0.90	0.95	0.90	0.50	0.47	0.50	0.82	0.94T	0.88	0.95	0.47	0.94
UO_2^{2+}	0.85	0.80	0.80	0.81	0.78	0.75	0.76	0.75	0.69	0.60	0.50	0.48
VO^{2+}	0.90	0.90	0.90	0.95	0.92	0.95	0.87	0.94	0.94	0.90	0.92	0.94
Ni^{2+}	0.90	0.90	0.90	0.90	0.90	0.85	0.0	0.0	0.0	0.90	0.90	0.0
Co^{2+}	0.90	0.90	0.90	0.96	0.90	0.96	0.92	0.93	0.94	0.90	0.90	0.93
Ag^{+}	0.47	0.45	0.45	0.43	0.48	0.50	0.42	0.45	0.46	0.45	0.45	0.45
Cr^{6+}	0.60	0.58	0.60	0.58	0.56	0.55	0.50	0.58	0.58	0.56	0.55	0.55

T=Tailed Spot

<div align="center">Table 4. Mobility trends of metal ions on mixture of Urea formaldehyde and Cellulose developed with 0.3% SDS plus different concentration of Thiourea at pH=3</div>

Development Time=5 Minutes

Metal ions	0.3% SDS+1% Thiourea			0.3% SDS+5% Thiourea			0.3% SDS+10% Thiourea			0.3% SDS+15% Thiourea		
	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9
Fe^{3+}	0.68	0.59	0.50T	0.78	0.75T	0.72	0.85T	0.83	0.79	0.94	0.89	0.90
Cu^{2+}	0.47	0.52	0.60	0.65	0.69T	0.69	0.82	0.80	0.82	0.85	0.89	0.89
UO_2^{2+}	0.91	0.88	0.85	0.81	0.80	0.78	0.80	0.75	0.70	0.70	0.68	0.65
VO^{2+}	0.94	0.95	0.95	0.95	0.90 T	0.80	0.94	0.92	0.90	0.94	0.88	0.88
Ni^{2+}	0.97	0.93	0.94	0.91	0.90	0.95	0.91	0.77	0.80	0.90	0.86	0.92
Co^{2+}	0.92	0.94	0.93	0.90	0.875	0.90	0.84	0.93	0.82	0.83	0.90	0.87
Ag^{+}	0.44	0.44	0.40	0.45	0.41	0.40	0.44	0.44	0.45	0.42	0.44	0.46
Cr^{6+}	0.63	0.63	0.60	0.56	0.50	0.50	0.65	0.65	0.65	0.63	0.65	0.5

T=Tailed Spot

Table 5. Mobility trends of metal ions on mixture of Urea formaldehyde and Cellulose developed with 0.3% SDS plus different concentration of NaNO$_3$ at pH=3
Development Time=5 Minutes

Metal ions	0.3% SDS+1% NaNO$_3$			0.3% SDS+5% NaNO$_3$			0.3% SDS+10% NaNO$_3$			0.3% SDS+15% NaNO$_3$		
	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9	9:1	1:1	1:9
Fe^{3+}	0.90T	0.89	0.87	0.84	0.84	0.80	0.77	0.72	0.70	0.70	0.63	0.60
Cu^{2+}	0.90	0.90	0.88	0.85	0.82	0.80	0.70	0.66T	0.60T	0.56	0.55	0.50
UO$_2^{2+}$	0.73	0.61	0.60	0.81	0.77	0.71	0.87	0.85	0.85	0.91	0.80	0.80
VO^{2+}	0.87	0.87	0.85	0.88	0.90T	0.86	0.86	0.89	0.87	0.94	0.88	0.88
Ni^{2+}	0.94	0.91	0.89	0.94	0.91	0.89	0.95	0.92	0.91	0.90	0.86	0.92
Co^{2+}	0.71	0.87	0.84	0.81	0.86	0.85	0.92	0.86	0.86	0.83	0.90	0.87
Ag$^+$	0.46	0.44	0.41	0.41	0.41	0.49	0.48	0.45	0.45	0.49	0.45	0.45
Cr^{6+}	0.65	0.63	0.60	0.60	0.60	0.79	0.58	0.55	0.55	0.69	0.65	0.65

T=Tailed Spot

(A) . Volume of added Urea

(B). Volume of added Thiourea
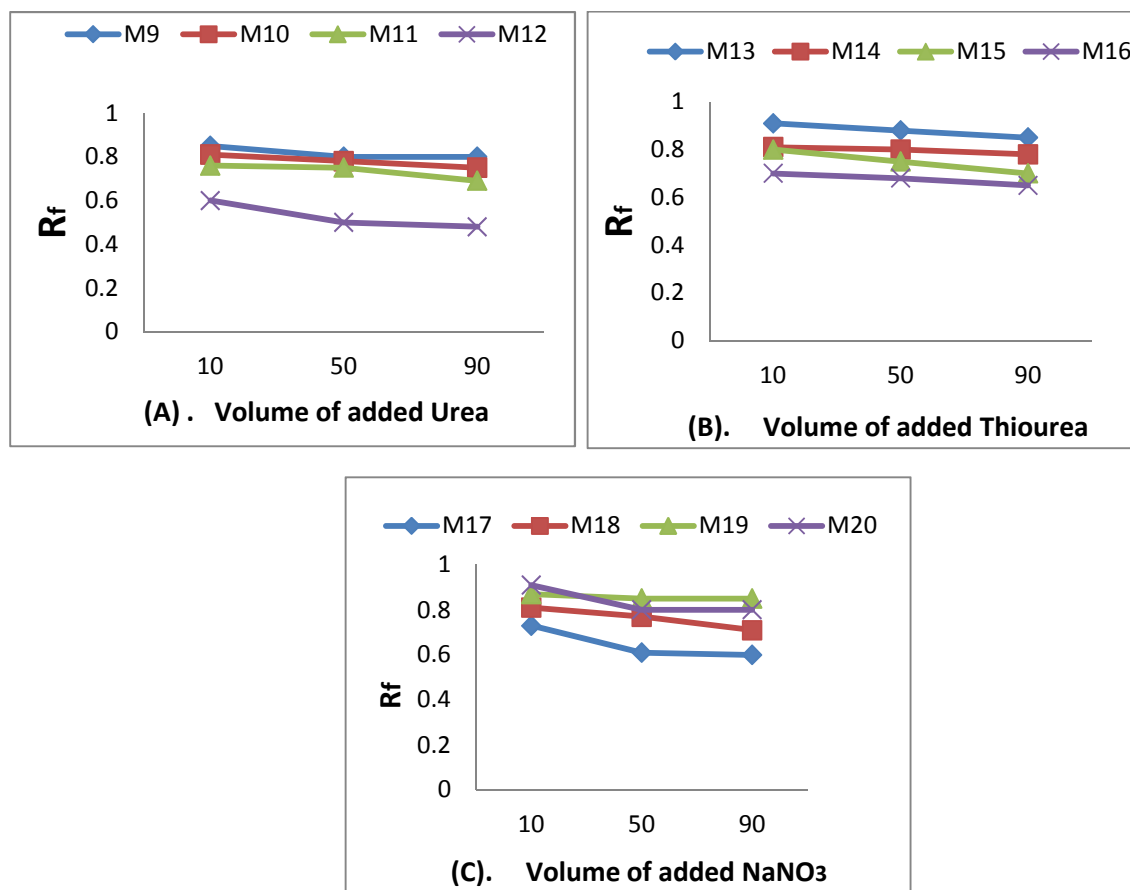
(C). Volume of added NaNO3

Figure 2. Plot of Rf of UO$_2^{2+}$ Vs volume added urea (A), thiourea (B) and NaNO$_3$ (C) in 0.3 % aqueous SDS at pH=3.

Most of the metal cations such as VO^{2+}, Fe^{2+}, Ni^{2+} & Co^{2+}shows very high mobilities in presence of NaNO$_3$ as additives in 0.3% SDS(M$_{17}$ to M$_{20}$). Mobility of Fe^{2+} and Cu^{2+} was found to decrease with the increase of NaNO$_3$ concentration levels. High mobility is associated with tailed spot.The mobility of UO$_2^{2+}$ increases with the increase in concentrationof NaNO$_3$, although its mobility decreases with increase in volume ratio of NaNO$_3$ at their particular concentration in 0.3% SDS(M$_{17}$ to M$_{20}$).Cr^{6+} & Ag$^+$ show mid mobility from M$_{17}$ to M$_{20.}$
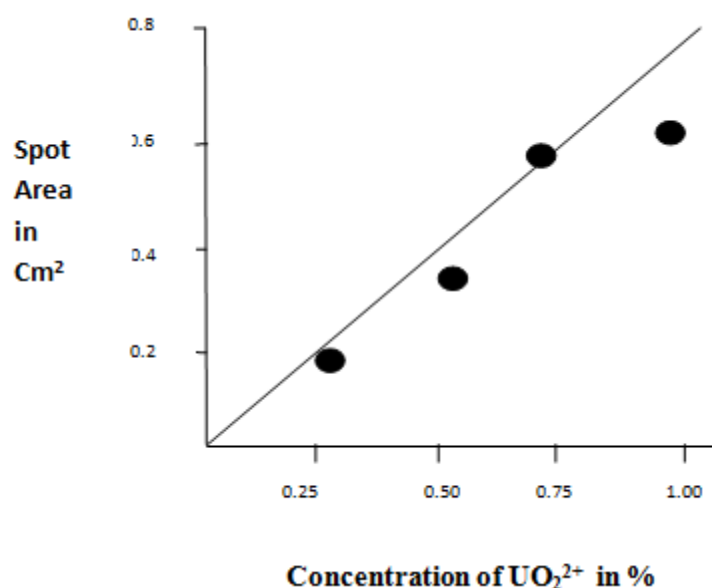
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Figure 3. Calibration curve for semi quantitative determination of UO_2^{2+}

Quantitative analysis by spot area measurement method:
An attempt has been made for semiquantitative determination of metal cations by spot area measurement method. The spots obtained were copied on tracing paper from the chromatoplates and spot area was measured. The relationship between the spot area and microgram quantities of metal cations follows the equation $\tau = km$, where τ is the spot area, m is the spotted amount and k is constant. Representative plots of UO_2^{2+} are shown in Figure 2. A linear relationship was obtained when the area of spot was plotted against the amount of sample spotted.

CONCLUSION

Using above observations we determined the optimum separating condition that is 0.3% SDS+10% thiourea, concentration 1:9 ratio, pH=3 qualitative separation of eight binary mixture & four ternary mixture of metal ions have been carried out. Various binary and ternary separations has been listed in table no. 6 and table no.7 respectively. R_f value of metal cations are given in top to bottom format , as they appear in chromatographic plates. Mixture of urea formaldehyde polymer and cellulose is promising chromatographic adsorbent for the separation of metal cations in inorganic electrolytes and organic non-electrolytes mobile phases.

Experimentally achieved separations on Mixture of urea formaldehyde polymer and cellulose layers developed in 0.3%SDS+10% Thiourea, Concentration 1:9 ratio, pH=3 as mobile phase with optimum separating conditions.

Table 6: Binary Separation
Mobile Phase:- 0.3%SDS+10% Thiourea, Concentration 1:9 ratio, pH=3

Sr. No.	Components	R_f Value of metal ions
1	Cr^{6+};Co^{2+}	Cr^{6+}=0.63 ; Co^{2+}0.84
2	Cr^{6+};Fe^{3+}	Cr^{6+}=0.65 ; Fe^{3+}0.89
3	Cr^{6+};Cu^{2+}	Cr^{6+}=0.65 ; Cu^{2+}0.78
4	Cr^{6+};VO^{2+}	Cr^{6+}=0.60 ; VO^{2+}=0.92
5	Cr^{6+};UO_2^{2+}	Cr^{6+}=0.58 ; UO_2^{2+}=0.85
6	Cr^{6+};Ag^+	Cr^{6+}=0.68 ; Ag^+=0.45
7	Co^{2+};UO_2^{2+}	Co^{2+}=0.89 ; UO_2^{2+}=0.79
8	Co^{2+};Ag^+	Co^{2+}=0.89 ; Ag^+=0.47

Table 7: Tertiary Separation
Mobile Phase:- 0.3%SDS+10% Thiourea in 1:9 ratio at pH=3

Sr. No.	Components	R_f Value of metal ions
1	Cr^{6+};Co^{2+};Fe^{3+}	Cr^{6+}=0.62;Co^{2+}=0.84;Fe^{3+}0.89
2	Cr^{6+};UO_2^{2+};Fe^{3+}	Cr^{6+}=0.65;UO_2^{2+}=0.75;Fe^{3+}=0.92
3	Cr^{6+};Ag^+;UO_2^{2+}	Cr^{6+}=0.58;Ag^+=0.46;UO_2^{2+}=0.78
4	UO_2^{2+};Ag^+;Co^{2+}	UO_2^{2+}=0.79;Ag^+=0.47;Co^{2+}=0.88

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There is a slight difference in the Rf values of metal ions during the separations from their mixtures, due to the mutual interaction of metal ions.

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