Separation of Chromium(III) & Chromium(VI) from Their Binary Mixture by Paper & Thin Layer Chromatographic Techniques

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Optimum conditions for getting quantitative separation of Cr(III) and Cr(VI) from their binary mixture by paper and thin layer (alumina) chromatographic techniques have been worked out. In the case of paper chromatography, both quantitative separation and quantitative recovery are possible with basic eluents, binary and ternary solvent systems. On alumina layers, quantitative separation only is possible with aq. ammonia and aqueous solutions of complexing and polyvalent anions but no quantitative recovery of Cr(III) is possible as the latter has greater affinity towards the adsorbent. Explanations have been offered for the observed migratory behaviour.

THE separation of Cr(III) and Cr(VI) from their binary mixture in solution assumes importance in biological systems[1-3] and in catalytic oxidation-reduction reactions[3]. Not much work has been done[3-7] on chromatographic separation of Cr(III) and Cr(VI) and in many instances, adequate explanations for the differential migratory behaviour of Cr(III) and Cr(VI) have not been presented. To bridge this gap, the title investigation has been undertaken.

Materials and Methods

Approximately decimolar solutions of the ions were prepared afresh by dissolving AR grade chrome alum and potassium chromate in de-ionized and de-oxygenated water, keeping the pH at 3.0 using dil. H_2SO_4. The solutions were standardized using standard Fe(II) and potassium dichromate solutions[8].

Rutter's technique[9] of circular paper chromatography and ascending technique[10] for TLC using alumina G (Merck) layers, were adopted.

Elutions on paper have been conducted using pure solvents, basic solvents, binary blends of water and organic solvents and ternary mixtures consisting of water, a minimum amount of glacial acetic acid or formic acid (85%) and an organic solvent. Aqueous ammonia or aq. solutions of simple, complexing and polyvalent anions were used as eluents in TLC.

Chromium(III) was detected by its yellow colour on spraying with 5% aq. solution of $K_4[Fe(CN)_6]$ and drying the chromatograms at 60-80°C (refs. 11, 12). Chromium(VI) was identified by the blue colour produced by spraying with 1% solution of benzidine in 50% acetic acid[13].

Results and Discussion

Paper chromatography — The following observations are significant :

(i) Chromium(III) shows either diffusive or no

migration in the pure solvents. On the other hand, chromium(VI) shows sharp migration in water and ethylene glycol but diffusive or no migration in other organic solvents (Table 1; item Nos. 1-5).

(ii) The presence of water or ethylene glycol in organic solvents, viz., EtOH, n-PrOH, t-BuOH, diacetone alcohol, acetone and butylcellosolve (BuCel), results in differential migration of Cr(III) and Cr(VI) (Table 2). Chromium (III) shows diffusive migration whereas chromium(VI) shows sharp migration.

(iii) In one-phase ternary systems of which water is a component, Cr(III) and Cr(VI) migrate

TABLE 1 — PAPER CHROMATOGRAPHIC BEHAVIOUR OF Cr(III) AND Cr(VI) IN PURE AND BASIC SOLVENTS

Sl No.	Eluent	Dielectric constant	R_r value*	
			Cr(III)	Cr(VI)
1.	Ethylene glycol	37.7	1.00d	1.00
2.	Water	78.54	1.00d	1.00
3.	MeOH	32.63	0.25d	0.73d
4.	EtOH	24.55	0.15d	0.42d
5.	†Other aliphatic alcohols, esters, ketones, pyridine and dioxane	2.21-20.7	zero	zero
6.	**Aq. ammonia (25% w/v)	—	zero	1.00
7.	**Aq. NaOH (pH 11)	—	zero	1.00
8.	**Methylamine (40% w/v)	—	zero	1.00

*Average value of four runs.

drefers to diffusion.

†Alcohols : n-PrOH, t-BuOH, i-BuOH & i-AmOH; Esters : MeOAc, EtOAc, n-BuOAc, n-AmOAc & Acetoacetic ester (ROAcAc); Ketones : Acetone, methyl ethyl ketone (MeEtCO), methyl isobutyl ketone (MIBK), cyclohexanone (CyCO) & acetophenone.

**Good separation.

TABLE 2 — PAPER CHROMATOGRAPHIC BEHAVIOUR OF Cr(III) AND Cr(VI) IN SELECTED BINARY AND TERNARY SOLVENT SYSTEMS

Eluent ratio	R_r values	
	Cr(III)	Cr(VI)
WATER-ACETONE*		
10:90	zero	0.29^t
20:80	zero	0.44
40.60	0.44^d	0.63
60:40	0.70^d	0.79
80:20	1.00^d	0.94
ETHYLENE GLYCOL-t-BuOH*		
20:80	zero	0.40^t
30:70	0.23^d	0.46
40:60	0.35^d	0.56
60:40	0.74^d	0.75
80:20	1.00^d	1.00
WATER-AcOH-MeEtCO†		
20:10:70	zero	0.44
30:10:60	0 25	0 58
40:10:50	0.41	0.69
50:10:40	0.68	0.77
60:10:30	0.85	0.83
70:10:20	1.00	0.87
80:10:10	1.00	0.88

t—refers to tailing; d—refers to diffusion.

*The migration trend of the two ions is similar in other binary blends where acetone is replaced by EtOH, n-PrOH, t-BuOH, diacetone alcohol and BuCel or where t-BuOH is replaced by MeEtCO, EtOH, t-BuOH, diacetone alcohol and BuCel.

†Mode of migration of the two ions is similar in other ternary mixtures, viz. (1) H_2O-HCOOH-MeEtCO or MeOAc (x:10:y), (2) H_2O-AcOH or HCOOH-ROAcAc (x:15:y), (3) H_2O-AcOH or HCOOH-i-BuOH or CyCO(x:20:y), (4) H_2O-AcOH or HCOOH-i-AmOH or EtOAc (x:30:y), (5) H_2O-AcOH-MIBK (x:35:y), (6) H_2O-AcOH-n-BuOAc (x:40:y) and (7) H_2O-AcOH-n-AmOAc (x:50:y).

TABLE 3 — MIGRATIONAL CHARACTERISTICS OF Cr(III) AND Cr(VI) ON ALUMINA LAYERS

Sl. No.	Eluent	R_f Value*		$\triangle R_f$
		Cr(III)	Cr(VI)	
1.	Water	0.16^d	0.50^d	—
2.	1M KCl	0.25^d	0.60^d	—
3.	1M KClO$_4$	0.21^d	0.65^d	—
4.	1M KNO$_3$	0.10^d	0.51^d	—
5.	Aq. ammonia (25% w/v)†	zero	0.69	0.69
6.	Water-NaF			
	0.10M	0.09^d	0.43	0.34
	0.50M	0.11^d	0.48	0.37
	1.00M	0.12^d	0.50	0.38
	Sat. solution†	0.13^d	0.50-0.75^d	0.37
7.	Water- K$_2$SO$_4$			
	0.10M†	0.06^d	0.39	0.33
	0.50M†	0.10^d	0.56	0.46
	1.00M†	0.12^d	0.59	0.47
	Sat. solution†	0.13^d	0.63	0.50
8.	Water- K$_3$PO$_4$			
	0.10M†	zero	0.57	0.57
	0.50M†	zezo	0.58	0.58
	1.00M†	zero	0.72	0.72
	Sat. solution†	zero	0.73	0.73
9.	Water- Na$_2$CO$_3$			
	0.10M†	zero	0.49	0.49
	0.50M†	zero	0.56	0.56
	1.00M†	zero	0.73	0.73
	Sat. solution†	zero	0.74	0.74

*Average of four runs; d refers to diffusion
†Good separation

dominantly through ion-association at lower percentages of organic solvent.

Chromium(VI) being anionic, is seldom adsorbed on the negatively charged cellulose in water or binary systems containing high percentages of water. The unadsorbed Cr(VI) is thus simply washed away by the eluents; it migrates to the solvent front in water and to somewhat lesser degree in aq. blends of organic solvents. In solvent mixtures containing higher proportions of organic solvents, migration of Cr(VI) is expected to be sluggish due to physical adsorption via hydrogen bonding between oxygen atoms of Cr(VI) species and —OH groups of cellulose. Contrary to this expectation, sharp migration is observed with the eluents containing upto 80% of organic solvents. This indicates that 20% water in the eluents is enough to provide sufficient number of hydrogen bond-active groups to desorb and solubilize the Cr(VI) species. Chromium(III) being cationic, gets attached strongly to negatively charged filter paper in water or binary blends containing higher proportions of water and hence the diffusive migration. In binary solvent mixtures containing lower proportion of water where physical adsorption is predominant, the sluggish migration of Cr(III) is due to its less solubility in the eluent.

The above mechanism holds good also with eluents containing ethylene glycol in place of water as can be seen from the similarity of migration (vide Table 2).

differentially with increasing R_r values as the percentage of organic solvent decreases; variation of R_r values for Cr(VI) is less marked than for the Cr(III) (vide Table 2).

(iv) With aqueous base solutions, Cr(III) remains at the point of application whereas Cr(VI) migrates to solvent front (vide Table 1; item Nos. 6-8).

At pH 3, Cr(III) exists as cationic species, $Cr(OH_2)_6^{3+}$, $[Cr(OH_2)_6SO_4]^+$ and $[Cr(OH_2)_5OH]^{2+}$ (ref. 14), whereas Cr(VI) exists as anionic species, $[HCrO_4]^-$ and $[CrO_3(OSO_3)]^{2-}$ (refs. 15, 16).

When in contact with water, paper is presumed to be charged negatively due to dissociation of —OH groups of cellulose[17]. This dissociation is less with increase in percentage of organic solvent in the binary solvent mixtures containing water as the other component. Hence, the attachment of solute to cellulose in the case of binary solvent systems is predominantly through physical adsorption at higher percentages of organic solvent, whereas it is pre-

TABLE 4 — ESTIMATION OF Cr(III) AND Cr(VI)

[Quantity spotted : 40.00 µg each of Cr(III) and Cr(VI)]

Sl No.	Eluent	Estimation*		% Error		$\frac{Cr(VI) \times 100}{Cr(III) + Cr(VI)}$†
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
	PAPER CHROMATOGRAPHY					
1.	Aq. ammonia (25% w/v)	40.20	40.35	+0.50	+0.87	50.09
2.	Aq. NaOH (pH 11)	40.15	40.25	+0.37	+0.63	50.06
3.	Methylamine (40% w/v)	40.36	40.28	+0.90	+0.70	49.95
4.	H$_2$O-EtOH (20:80)	39.55	40.12	−1.12	+0.30	50.36
5.	H$_2$O-n-PrOH (30:70)	39.71	39.64	−0.72	−0.90	49.96
6.	H$_2$O-t-BuOH (40:60)	39.63	39.74	−0.92	−0.65	50.07
7.	H$_2$O-Me$_2$COHCH$_2$COMe (30:70)	39.52	40.21	−1.20	+0.52	50.43
8.	H$_2$O-Acetone (20:80)	39.79	40.32	−0.52	+0.80	50.33
9.	H$_2$O-BuCel (30:70)	39.84	39.60	−0.40	−1.00	49.85
10.	(CH$_2$OH)$_2$-EtOH (40:60)	40.34	40.15	+0.85	+0.37	49.88
11.	(CH$_2$OH)$_2$-Acetone (40:60)	39.81	40.33	−0.47	+0.82	50.32
12.	(CH$_2$OH)$_2$-i-BuOH (30:70)	40.45	40.47	+1.12	+1.17	50.01
13.	(CH$_2$OH)$_2$-Me$_2$COHCH$_2$COMe (30:70)	40.41	40.37	+1.02	+0.92	49.98
14.	(CH$_2$OH)$_2$-BuCel (30:70)	39.69	39.62	−0.77	+0.95	49.96
15.	(CH$_2$OH)$_2$-MeEtCO (30:70)	39.45	39.65	−1.37	−0.87	50.13
16.	H$_2$O-AcOH-i-BuOH (20:20:60)	39.78	39.57	−0.55	−1.07	49.87
17.	H$_2$O-AcOH-i-AmOH (20:30:50)	40.27	40.50	+0.67	+1.25	50.14
18.	H$_2$O-AcOH-MeEtCO (20:10:70)	40.39	40.26	+0.97	+0.65	49.92
19.	H$_2$O-AcOH-CyCO (30:20:50)	40.47	40.36	+1.17	+0.90	49.93
20.	H$_2$O-AcOH-MIBK (15:35:50)	39.52	39.61	−1.20	−0.97	50.06
21.	H$_2$O-AcOH-EtAc (20:30:50)	39.59	39.74	−1.02	−0.65	50.09
22.	H$_2$O-AcOH-i-BuOAc (20:40:40)	39.81	39.67	−0.47	−0.82	49.91
23.	H$_2$O-AcOH-n-AmOAc (20:50:30)	39.77	39.81	−0.57	−0.47	50.02
24.	H$_2$O-AcOH-ROAcAc (20:15:65)	39.67	39.89	−0.82	−0.27	50.14
25.	H$_2$O-HCOOH-MeEtCO (10:10:80)	40.21	40.34	+0.52	+0.85	50.08
26.	H$_2$O-HCOOH-MeOAc (10:10:80)	40.27	40.37	+0.67	+0.92	50.06
27.	H$_2$O-HCOOH-ROAcAc (20:15:65)	40.11	40.41	+0.27	+1.02	50.19
28.	H$_2$O-HCOOH-i-BuOH (10:20:70)	39.68	40.51	−0.80	+1.27	50.52
29.	H$_2$O-HCOOH-CyCO (10:20:70)	40.40	40.20	+1.00	+0.50	49.88
30.	H$_2$O-HCOOH-EtOAc (10:30:60)	39.95	39.37	−0.12	−1.57	49.63
	THIN LAYER CHROMATOGRAPHY‡					
31.	Aq. ammonia (25% w/v)	—	39.45	—	−1.37	—
32.	1M NaF	—	39.40	—	−1.50	—
33.	1M K$_2$SO$_4$	—	39.30	—	−1.75	—
34.	1M K$_3$PO$_4$	—	39.52	—	−1.20	—
35.	1M Na$_2$CO$_3$	—	39.60	—	−1.00	—

* Average of four estimations;

† ≈50% Redox ratio on paper indicates that the separation and recovery of the ions are quantitative;

‡ Quantitative separation is possible on alumina layers but not quantitative recovery of Cr(III).

In ternary solvent systems containing acetic acid or formic acid, the electrostatic forces are no more active as the lower dielectric constants and lower pHs of the eluents suppress the dissociation of hydroxyl and carboxyl groups of cellulose. In addition, the lower pH prevents the hydrolysis of Cr(III). Hence, migration is attributed mainly to the solubilizing capacities of the eluents. During solubilization only one molecule of acetate enters into the coordination sphere of Cr(III)[18]; formate has less tendency in this respect than acetate[19]. Most of the coordination sites are occupied already by polar water molecules. Hence, Cr(III) having water in its coordination sphere, prefers more structured solvent (hydrogen bond active solvents) than Cr(VI) which is mostly in the form of HCrO$_4^-$ (refs. 15,16). As the water content of ternary system decreases, the R_f of Cr(III) decreases faster than that of Cr(VI) because, of the two, Cr(III) complex is more hydrophilic.

With basic aqueous eluents, Cr(III) does not migrate because of its precipitaion as hydroxide but Cr(VI) migrates as CrO$_4^{2-}$ under the influence of water of the eluent (Table 1, item Nos. 6-8).

Thin layer chromatography — Alumina retards the migration of both cations and anions depending upon pH conditions[20]. The cation to anion exchange transition point for alumina has been found to occur at pH 8 (refs. 21, 22). In the present work the ion-exchange ability of alumina has been used to achieve quantitative separation of Cr(III) and Cr(VI). Chromium(VI) shows faster migration with eluents containing fluoride, sulphate, phosphate, carbonate and aqueous ammonia than those containing chloride, nitrate and perchlorate (vide Table 3). With eluents containing fluoride, the mechanism of desorption of chromate is one of complexation[20]. Fluoride successfully competes with chromate for the cationic sites of alumina. With eluents containing sulphate, the desorption of chromate is due to outer-sphere

complexation[20], while with aqueous solutions of ammonia and Na_2CO_3 it may be due to higher pH values of the eluents which suppress the basic dissociation of $Al(OH)_3$ but enhance the acidic dissociation[21,22]. The desorption mechanism is contributed in phosphate solution by inner and outer sphere complexation; hydrolysis of triphosphate ion also has a definite influence on the mechanism.

Chromium(III) undergoes hydrolysis easily above pH 3. The hydrolysis coupled with the cation-retarding ability of alumina, results in either no migration or diffusive migration of Cr(III) in aqueous salt solutions (vide Table 3).

Estimation — Chromium(III) and chromium(VI) bands on the paper chromatograms were cut out and extracted with $0.05M$ H_2SO_4. Chromium(III) was then estimated photometrically by EDTA method[23] and chromium(VI) by diphenylcarbazide method[24] (Table 4).

As regards the estimation of thin-layer chromatograms, the separated Cr(VI) was extracted repeatedly with 1:1 ammonia. The extracts were combined and concentrated. Chromium(VI) was determined by diphenylcarbazide method.

It can be seen from Tables 3 & 4, that Cr(III) has great affinity towards alumina. It is adsorbed so strongly that quantitative isolation of Cr(III) from the adsorbent is almost impossible. The degree of separation had, therefore, to be inferred from the estimation of Cr(VI) only.

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