Chromatography of Anions on Alumina Thin Layers: Effect of Transition Metals on Cl⁻-Br⁻-I⁻ and NO_2^--NO_3^- Separations

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CHROMATOGRAPHY OF ANIONS ON ALUMINA THIN LAYERS: EFFECT OF TRANSITION METALS ON Cl⁻-Br⁻-I⁻ AND NO₂⁻ -NO₃⁻ SEPARATIONS

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ABSTRACT

Chromatographic behaviour of eighteen anions on thin layers of alumina and alumina mixed with silica gel (1:1, 1:2 and 2:1) has been studied using mixed acidic organic solvent systems containing formic acid. Though the addition of silica gel to alumina enhances the mobility and clarity of detection of anions, but it causes the increased tailing for $Fe(CN)_6^{3-}$, CrO_4^{2-} and $Cr_2O_7^{2-}$. Formic acid is responsible for the differential migration of anions. All the anions remained at the starting line ($R_F = 0$) in pure organic solvents. Formic acid-Ketone systems gave better results compared to formic acid-alcohol systems. Development time increases with the increase of viscosity/mol. wt. of organic solvents. The mutual separation of Cl^-, Br^-, I^- and NO_2^- and NO_3^- were achieved on pure alumina using formic acid-acetone solvent systems. The effect of transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) on $Cl^--Br^--I^-$ and $NO_2^- -NO_3^-$ separations has been studied.

INTRODUCTION

Thin layer chromatography (TLC) is a useful method for the analysis of complex mixture of inorganics as evident by recent literature.[1-3] Compared to cations, TLC of anions has received much less attention probably because of the lack of well defined detection procedures. Our earlier chromatographic

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studies[4-8] showed that silica gel impregnated with inorganic salts opens

numerous possibilities of selective separations at milligram and microgram

levels of some metal ions in formic acid (FA) media. We have also attempted

to use mixed bed obtained by mixing silica gel with alumina in various

ratios to obtain certain separations.   The addition of alumina above 13%

causes tailing of anions.

The purpose of this paper is to study the utility of pure alumina

as well as alumina mixed with silica gel as stationary phases in TLC separa-

tion of anions in mixed organic solvent systems containing FA. Contrary to

the studies on cations[9], clearer detection and increased mobility of anions on

mixed bed were noticed. FA was selected as it does not deform thin layers

and being a good tailing reducer it gives well formed spots.

This report describes the systematic approach on the chromatographic

behaviour of inorganic anions and the mutual separation of Cl^-, Br^-, I^- and of

NO_2^-, NO_3^- in the presence of transition metals. The separation of I^- from Br^-;

Cl^- from IO_3^- and CrO_4^{2-}, and of NO_2^- from NO_3^- are important from practical

point of view. I^-, Cl^- and NO_2^- interfere in most of the detection procedures

of Br^-, IO_3^- and NO_3^- respectively.[10]

EXPERIMENTAL

Apparatus:

A TLC apparatus (Toshniwal, India) was used for the preparation of alu-

mina and alumina mixed with silica gel layers (0.25mm) on glass plates (20x3cm)

which were used for the development of chromatoplates. Glass jars (24x6cm)

were used.

Reagents:

All the reagents were of Analar grade. Alumina (CDH, India); silica gel,

FA, acetone, methanol, ethanol (Qualigens Fine Chemicals, Glaxo, India);

ethylmethyl ketone, Propan-2-ol (Merck, India); n-propanol (Ranbaxy, India);

n-butanol (Sarabhai M. Chemicals, India) and butan-2-ol (BDH, India) were used.

Anions studied:

   Anions as the following inorganic salts were used:

$K_3Fe(CN)_6$, $K_4Fe(CN)_6 \cdot 3H_2O$, Na_2HPO_4, $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, K_2CrO_4,

$K_2Cr_2O_7 \cdot 2H_2O$, $NaVO_3 \cdot H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, K_2SO_4, $NaNO_2$, $NaNO_3$, $NaCl$, KBr, KI,

CH_3COONa, KIO_3, $KBrO_3$, NH_4SCN and $NaIO_4$.

Test solutions:

   All the test solutions were prepared as 1% except Cl^-, NO_2^-, and NO_3^- which were prepared as 5% by dissolving the inorganic salts of anions in double distilled water.

Detectors:

   The following detection reagents were used:

   i)   1% Solution of ferric chloride in 2M HCl for $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$,
        SCN^- and CH_3COO^-.

   ii) Saturated solution of silver nitrate in methanol for CrO_4^{2-}, $Cr_2O_7^{2-}$,
        $S_2O_3^{2-}$, Cl^-, Br^-, I^- and IO_4^-.

   iii) 30 ml of 2% diphenylamine solution in methanol mixed with 20 ml
        of 4M H_2SO_4 for BrO_3^- , VO_3^-, NO_2^-, NO_3^- and IO_3^- .

   iv) 2% alcoholic solution of pyrogallol for MoO_4^{2-} and WO_4^{2-}.

   v)   1% barium carbonate solution in distilled water followed by spraying
        with 2% phenolphthalein solution in methanol for SO_4^{2-}.

Solvent systems:

   The following solvent systems were used as mobile phases:

   1.   Pure ethyl methyl ketone (EMK), FA, acetone and methanol.

   2.   FA + EMK (1:9, 4:6, 1:1, 6:4 and 9:1).

   3.   FA + acetone (1:9, 4:6, 1:1, 6:4 and 9:1).

   4.   FA + methanol (1:9, 4:6, 1:1, 6:4 and 9:1).

5. FA + ethanol (1:9, 4:6, 1:1, 6:4 and 9:1).

6. FA + n-propanol (1:9, 4:6, 1:1, 6:4 and 9:1).

7. FA + iso-propanol (1:9, 4:6, 1:1, 6:4 and 9:1).

8. FA + n-butanol (1:9, 4:6, 1:1, 6:4 and 9:1).

9. FA + butan-2-ol (1:9, 4:6, 1:1, 6:4 and 9:1).

10. FA + 50% picric acid solution in methanol (1:9, 4:6, 1:1, 6:4
    and 9:1).

All the solvent mixtures are by volumes.

Preparation of alumina plates:

To prepare alumina thin layer plates the slurry was first obtained by
homogenizing the alumina in demineralized water in the ratio of 1:3 with
constant shaking for 5 min. The resultant slurry was used immediately to
coat the clean glass plates with the help of an applicator to give a layer
of 0.25 mm thickness. The plates were air dried at room temperature (30°C)
followed by their activation in an electrically controlled oven at 100±5°C
for one hour. The plates were stored in a closed chamber at room tempera-
ture until used.

Preparation of alumina mixed with silica gel plates:

20 gm of synthetic mixture of silica gel and alumina in 1:1, 1:2 and
2:1 ratio were slurried with 60 ml of conductivity water by hand shaking
for 20 minutes. Thin layers (0.25mm thickness) were prepared under the
same experimental conditions as described above for alumina plates.

Procedure:

About 10μl of the anion solution was spotted on the chromatoplates
(plain or mixed adsorbent) with the help of a micropipette. The spots
were completely dried and the plates were developed in desired solvent
system by ascending technique. The solvent ascent was fixed to 10cm in
each case. After the development is over, the plates were withdrawn from
the glass jars, dried and detected using an appropriate detection reagent.

In order to study the effect of transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) on the mobility of I^-, Br^-, Cl^-, NO_2^- and NO_3^-, the synthetic mixtures were prepared by mixing equal volumes of 1% aqueous solution of I^-, Br^- or Cl^-, and 1% solution of transition metal. 10µl of the synthetic mixture thus obtained was spotted on the chromatoplate. The plates were developed in FA + acetone (9:1) solvent system. Similarly the synthetic mixture containing equal volumes of 5% aqueous solutions of NO_2^- or NO_3^- and 1% solution of transition metal ion were prepared and the chromatoplates were developed with FA + acetone (1:1) solvent system. The R_F values of anions were determined in all cases. The effect of the transition metals on I^--Br^--Cl^- and NO_2^--NO_3^- separations was studied by using the synthetic mixture containing Cl^--Br^--I^--M (1:1:1:1 V/V) and NO_2^--NO_3^--M (1:1:1, V/V) where M is transition metal. The mixture was spotted on the chromatoplate and the plates were developed in chosen solvent system. The R_F value for each anion after separation was determined on the plates.

RESULTS AND DISCUSSION

The results of this study have been summarized in figures 1-4 and tables 1-3. The fascinating feature of this study is a considerable difference in the R_F values of chemically similar anions leading to several separations of analytical importance (Table I). Thus, I^- from Br^- and Cl^-; NO_2^- from NO_3^-; IO_3^- from I^- and SCN^- from various other anions have been successfully separated. The development time (10cm run) ranged from 30-60 min with solvent systems containing ethyl methyl ketone, acetone, methanol and ethanol. However, systems containing higher alcohols (butanol or propanol) required longer development time. The development time also increases with increase of FA concentration in the mobile phase.

The main points found from the results shown in figures (1-4) are as follows:

1. $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, IO_3^-, PO_4^{3-}, WO_4^{2-}, MoO_4^{2-}, VO_3^-, $S_2O_3^{2-}$ and BrO_3^- are strongly adsorbed (R_F=0.0-0.1) in all solvent systems.

2. All anions remained at the point of application when chromatographed with pure organic solvent systems. SCN^- and I^- produce tailed spots in methanol.

3. Generally, well formed compact spots for majority of anions were obtained. However, occasional tailed spots for some anions (CrO_4^{2-}, $Cr_2O_7^{2-}$ or I^-) were also noticed.

4. Solvent systems containing 40-50% FA were found more useful for the separation of anions. The best results were obtained in solvent systems containing 50% FA.

5. Ketone – FA systems gave more compact and clearer spots compared to those obtained in FA – methanol or ethanol systems. Though FA – butanol and FA – propanol systems produced highly compact spots similar to FA – acetone system but they need longer development time. Therefore, FA – acetone system has been preferred for detailed study in this paper. FA – acetone system has been utilized for mutual separation of Cl^-, Br^- and I^- on plain alumina and of NO_2^- from NO_3^- on alumina mixed with silica gel layers.

6. In most solvent systems SO_4^{2-}, CH_3COO^-, NO_3^- and IO_4^- failed to produce coloured spots with their respective detection reagents used in this study. However, SO_4^{2-} as blue spot in EMK or methanol eluent and NO_3^- as dark blue spot in FA + EMK (4:6, 6:4 and 9:1) eluents were detected satisfactorily. Similarly, CH_3COO^- produced brown spot in FA + n-propanol (4:6) solvent system whereas IO_4^- gave yellow product when eluted with FA + ethanol (1:9), FA + n-propanol (1:9), FA + iso-propanol (1:1), FA + n-butanol (1:9 and 6:4) and FA + iso-butanol (1:9) eluents.

7. The most useful concentration range in FA – ketone systems is 40-60% for realizing several separations (Fig. 1). The mobility
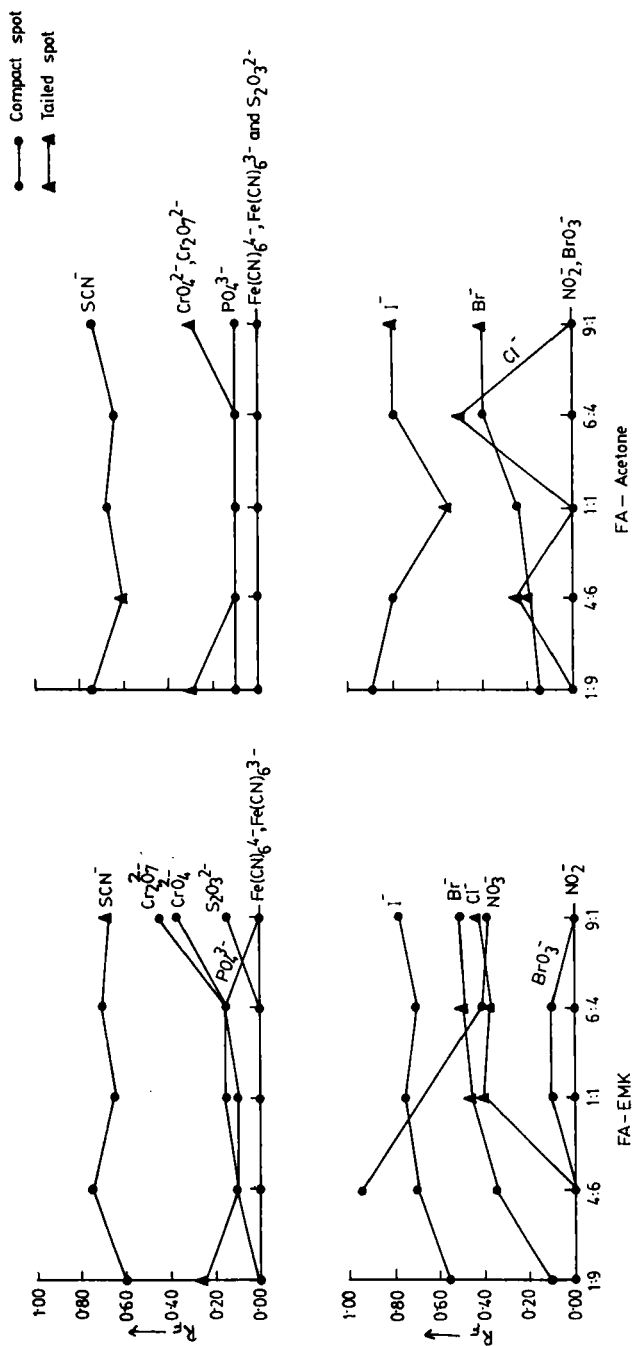
of all anions except NO_3^- is either in the increasing order or remained almost constant with the increase in FA concentration. NO_3^- shows a reversal trend where R_F decreased with increasing FA concentration.

8. FA - ethanol system was found unsuitable while FA - methanol system containing 50-60% FA provides some interesting separations (Fig.2). A double spot (R_F = 0.0 and 0.7) was produced by NO_2^- when chromatographed with FA - methanol (1:9) system. The intermolecular hydrogen bonding or the solvent solvation effect is probably responsible for the formation of double spots.

9. FA - n-propanol system containing 40% FA is useful for some ternary separations (Fig. 3). The mid R_F value (R_F = 0.4) of Br^- can be utilized for its separation from NO_2^-, BrO_3^-, PO_4^{3-}, SCN^- and I^-. However, FA - iso-propanol system gave better results with solvents containing 50% FA concentration. Compared to iso-propanol, n-propanol was found better eluent for anions when used in combination with FA.

10. NO_2^- produced double spots at (R_F = 0.0 and 0.9) in FA-n-butanol (4:6) and FA-butan-2-ol (1:9) solvent systems. However, it could not be detected in other FA-butan-2-ol systems.

11. No significant effect of the alcohol chain length on R_F values of anions was experienced. However, the mobility of SCN^- increases with the decrease in the alcohol chain length causing an increase in its R_F value with the lowering in alcohol chain length. Br^- and I^- showed an increased R_F when chromatographed in FA + methanol or ethanol (1:9) compared to their R_F in FA + propanol or butanol (1:9). A similar trend for Br^- was observed in FA - alcohol (1:1) solvent system. A slight improvement in the compactness of CrO_4^{2-} and $Cr_2O_7^{2-}$ spots results with the increase in alcohol chain length.

TABLE - I

SOME IMPORTANT SEPARATIONS EXPERIMENTALLY ACHIEVED

Stationary phase	Mobile phase	Separation achieved(R_L-R_T)[a]
Plain Alumina	FA+Acetone 9:1	$SCN^-(1.00-0.80)-Br^-(0.50-0.25)-Fe(CN)_6^{4-}, Fe(CN)_6^{3-}, Cl^-$ or $IO_3^-(0.00-0.00)$
		$SCN^-(1.00-0.80)-Br^-(0.60-0.30)-MoO_4^{2-}$ or VO_3^- $(0.00-0.00)$.
		$SCN^-(1.00-0.90)-Br^-(0.70-0.40)-BrO_3^-, WO_4^{2-}, NO_2^-$ or $PO_4^{3-}(0.00-0.00)$.
		$I^-(1.00-0.90)-Br^-(0.50-0.40)-Cl^-(0.00-0.00)$.
		$I^-(1.00-0.85)-Br^-(0.60-0.40)-Fe(CN)_6^{4-}, Fe(CN)_6^{3-}, IO_3^-, NO_2^-, MoO_4^{2-}, VO_3^-$ or $WO_4^{2-}(0.00-0.00)$.
		$I^-(1.00-0.85)-Br^-(0.50-0.40)-PO_4^{3-}$ or $BrO_3^-(0.10-0.00)$.
	FA+acetone 1:1	$SCN^-(0.85-0.60)-Br^-(0.50-0.30)-S_2O_3^{2-}(0.10-0.00)$.
		$I^-(1.00-0.90)-Br^-(0.80-0.30)-Cl^-(0.00-0.00)$.
		$I^-(1.00-0.90)-Br^-(0.80-0.40)-S_2O_3^{2-}(0.10-0.00)$.

Silica gel + Alumina 1:2	FA+acetone 6:4	Cl^-(1.00–0.90)–Br^-(0.60–0.30)–IO_3^-, NO_2^-, $S_2O_3^{2-}$, BrO_3^-, MoO_4^{2-}, VO_3^- or WO_4^{2-} (0.00–0.00).
	FA+isopropanol 6:4	I^-(1.00–0.90)–Br^-(0.70–0.40)–Cl^-, CrO_4^{2-} or $Cr_2O_7^{2-}$ (0.00–0.00).
	FA+acetone 9:1	BrO_3^-(1.00–0.90)–Br^- (0.70–0.60)–$Fe(CN)_6^{4-}$,IO_3^-, MoO_4^{2-}, VO_3^-or WO_4^{2-} (0.00–0.00).
	FA+acetone 1:1	NO_3^- (0.70–0.40)–NO_2^- (0.00–0.00).
Plain Alumina	FA+EMK 1:9	I^-(0.80–0.70)–SCN^- (0.50–0.40)–IO_3^- or NO_2^- (0.00–0.00).
	FA+EMK 1:1	I^-(0.90–0.60)–Cl^- (0.40–0.20)–IO_3^-,MoO_4^{2-} orVO_3^-(0.00–0.00).
	FA+Methanol 1:9	SCN^-or I^-(0.85–0.75)–BrO_3^-(0.30–0.20)–$Fe(CN)_6^{4-}$,$Fe(CN)_6^{3-}$,Cl^-,IO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-} or VO_3^- (0.00–0.00).
	FA+Propan-1-ol 1:9	IO_4^-(0.90–0.60)–I^- (0.40–0.20)–IO_3^-,VO_3^-,Cl^-,Br or CrO_4^{2-} (0.00).
Silica gel+Alumina 1:1	FA+acetone 9:1	Cl^-(0.80–0.70)–BrO_3^-(0.60–0.20)–MoO_4^{2-},VO_3^- or WO_4^{2-} (0.00–0.00).

a. $R_L \rightarrow R_F$ of leading front, $R_T \rightarrow R_F$ of trailing front.

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1. Plot of R_F Vs FA/Ketone mixtures in different ratio

   Compact spot ($R_L - R_T < 0.3$)
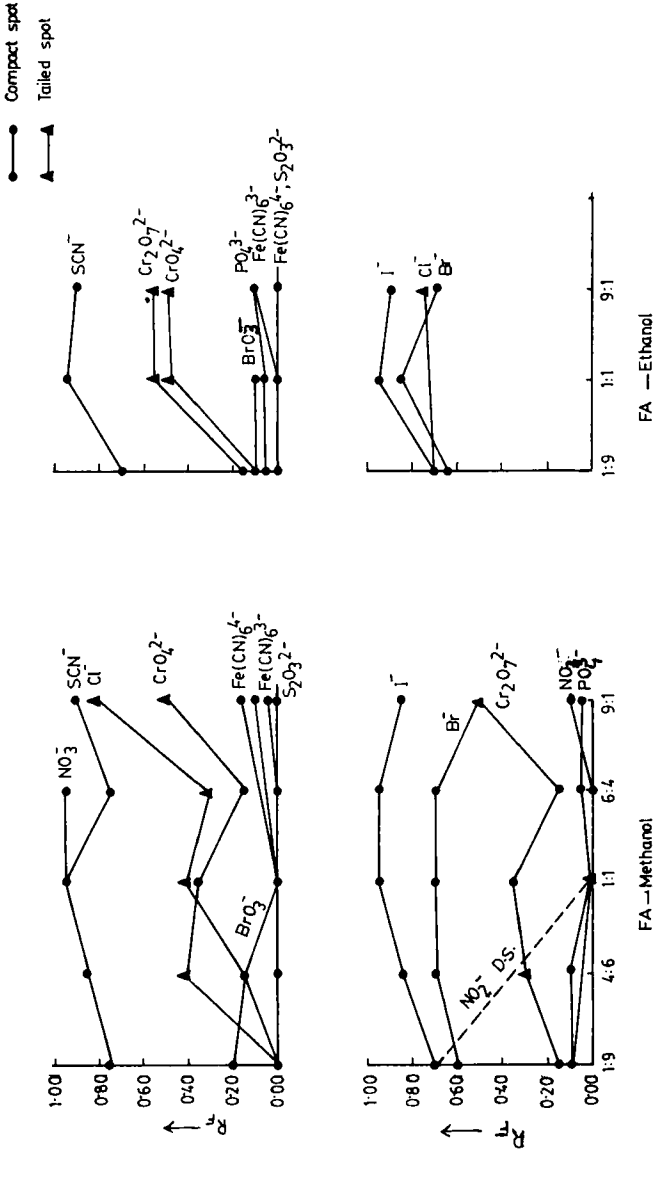
   Tailed spot ($R_L - R_T > 0.3$)

2. Plot of R_F Vs FA/Methanol or ethanol in different ratio.

Compact spot ($R_L - R_T < 0.3$)

Tailed spot ($R_L - R_T > 0.3$)

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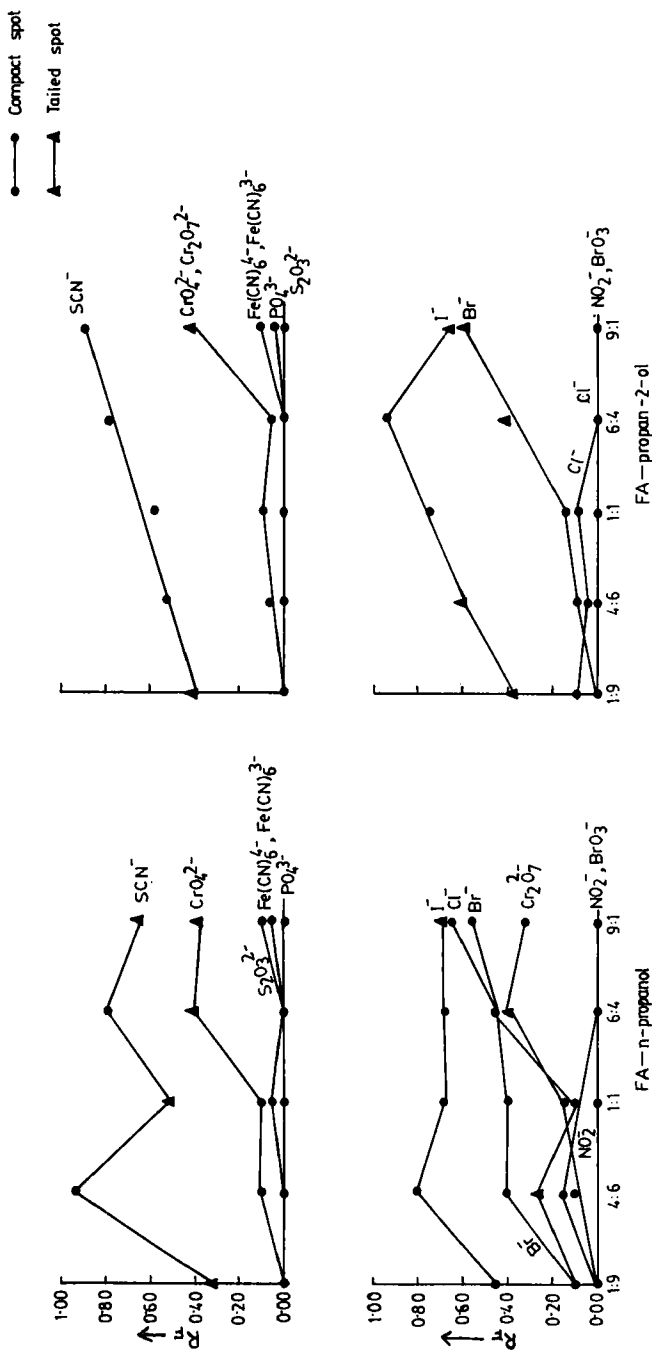
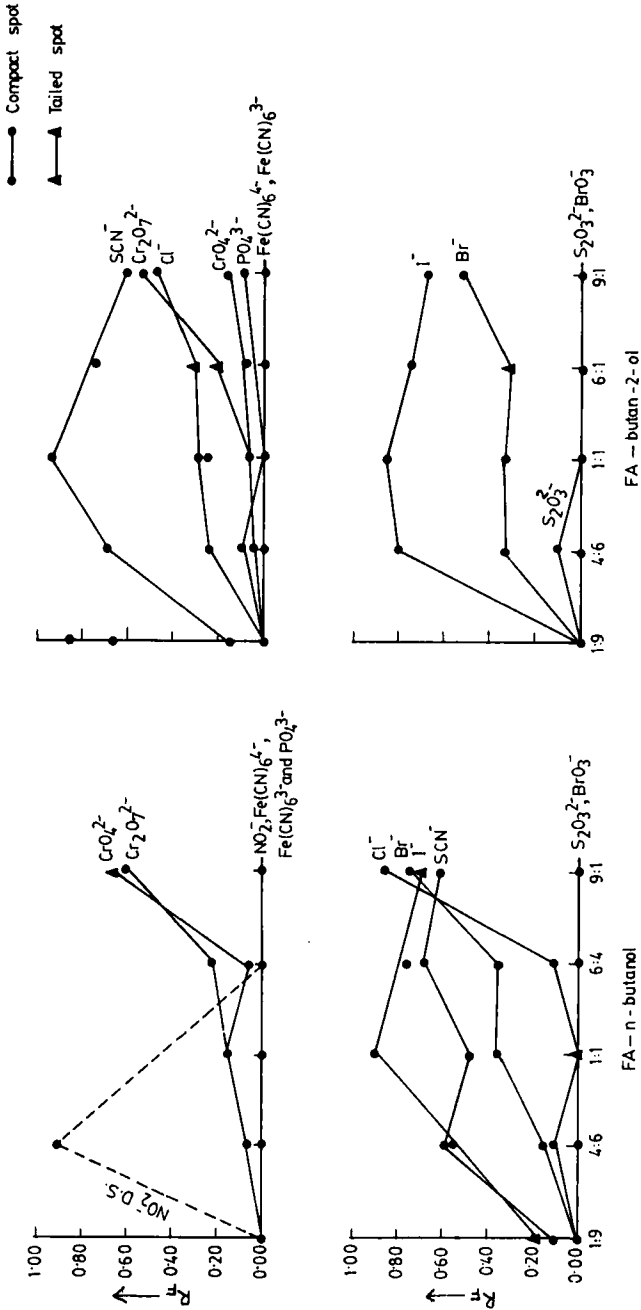3. Plot of R_F Vs FA/n-propanol or isopropanol in different ratio.

Compact spot ($R_L - R_T < 0.3$)

Tailed spot ($R_L - R_T > 0.3$)

4. Plot of R_F Vs FA/n-butanol or Butan-2-ol in different ratio

Compact spot ($R_L - R_T < 0.3$)

Tailed spot ($R_L - R_T > 0.3$)

TABLE - 2

ΔR_F Values(R_F on Plain Alumina - R_F on Alumina mixed with Silica gel)of anions with FA-Acetone solvent systems

Anions	SG+AL (1:1) Stationary phase FA-Acetone					SG+AL (1:2) Stationary phase FA-Acetone					SG+AL (2:1) Stationary phase FA-Acetone				
	1:9	4:6	1:1	6:4	9:1	1:9	4:6	1:1	6:4	9:1	1:9	4:6	1:1	6:4	9:1
$Fe(CN)_6^{4-}$	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
$Fe(CN)_6^{3-}$	0.00	-0.10	-0.10	0.00	-0.10	0.00	-	-	-	-0.10	0.00	-0.15	-0.50	-0.10	-0.10
PO_4^{3-}	-0.10	0.00	0.00	-0.05	-0.10	0.05	-0.20	-	0.00	0.00	0.05	0.00	-0.27	-0.05	-0.30
CrO_4^{2-}	-0.15	-0.10	-0.30	-0.05	-0.20	0.05	-0.65	-0.15	-0.35	-0.25	0.20	0.00	0.00	-0.40	-0.15
$Cr_2O_7^{2-}$	-0.20	-0.20	-0.35	-0.55	-0.50	-0.10	-0.70	-0.35	-0.35	-0.35	0.02	0.00	-0.55	-0.75	-0.60
$S_2O_3^{2-}$	0.00	-0.15	0.00	-0.10	-0.20	0.00	-0.10	-0.05	-0.10	-	0.00	-0.10	-0.10	-	-0.95
Cl^-	-0.15	-0.45	-0.68	-0.20	-0.90	0.00	0.40	-0.85	-0.20	-0.57	-0.10	-0.65	-0.85	-0.35	-0.90
Br^-	-0.15	-0.50	-0.65	-0.30	-0.30	-0.17	-0.50	-0.40	-0.30	-0.17	-0.02	-0.20	-0.52	-0.25	-0.22
I^-	0.10	0.03	-0.45	0.00	-0.10	0.33	-0.15	-0.40	0.05	0.05	0.17	-0.05	-0.35	-0.05	0.08
NO_2^-	0.00	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.90	0.00	0.00
NO_3^-	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-
BrO_3^-	0.00	-0.70	-0.45	-0.90 DS	0.50	0.00	-0.22	-0.30	-	-0.90	-0.08	-0.35	-0.50	-0.95	0.00
SCN^-	-0.05	-0.17	-0.22	-0.25 DS	-0.15	0.05	-0.30	-0.22	-0.25	0.10	0.10	-0.35	-0.27	-0.25	0.10
MoO_4^{2-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SG → Silica gel   AL → Alumina   DS → Double spot

FA - 50% methanolic picric acid (1:9, 4:6, 6:4, 1:1 and 9:1) systems
were found unsuitable for the separation of anions on alumina layers.
PO_4^{3-}, $S_2O_3^{2-}$, Cl^-, Br^-, NO_2^- and NO_3^- could not be detected. SCN^-, I^- moved
with solvent front (R_F=0.9) while $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ remained near the
point of application. R_F value of CrO_4^{2-} or $Cr_2O_7^{2-}$ increase with the in-
crease of FA concentration giving tailed spots in the system containing
90% FA.

The improved chromatographic characteristics of silica gel mixed with
alumina in the separation of cations[9] compelled us to study the chromato-
graphic behaviour of alumina mixed with silica gel (1:1, 1:2 and 2:1)
layers towards anions. The results obtained on the layers of mixed bed
using FA-acetone (1:9, 4:6, 1:1, 6:4 and 9:1) systems as mobile phase are
shown in table 2. It is clear that addition of silica gel, generally
brings about a slight increase in R_F values of anions and also causes
tailing for some anions. The increase in tailing correlates with the in-
crease of silica gel content in the mixed bed. However, some useful res-
ults were obtained on alumina-silica gel (1:2) layers e.g. the detection
of NO_3^- on mixed bed which was practically not detected in most of the
cases on plain alumina and thus leads to its separation from NO_2^- with FA-
acetone (1:1) system. Conversely, the significant increase in the mobi-
lity of Cl^- and Br^- on mixed bed imposes a restriction on the mutual
separation of Cl^-, Br^- and I^- which could be easily achieved on pure alu-
mina.

On alumina - silica gel (1:1 or 1:2) thin layers, MoO_4^{2-} gave double
spots possibly due to the formation of isopolyanionic species e.g. para-
molybdate or octa molybdate.[11] This observation is in consonance to our
earlier studies[12] on plain silica gel where MoO_4^{2-} also produced double
spots in FA - acetone systems.

The results summarized in tables 3A and 3B show that transition me-
tals have a distinct effect on the mobility of anions as well as on their

TABLE - 3A

Effect of transition metals on the R_F values of halogen anions and on their mutual separation

Solvent system : Formic Acid + Acetone (9:1), Stationary phase: Plain Alumina

Transition metals	R_L-R_T values of pure transition metals	R_L-R_T values of anions in the presence of transition metals			R_L-R_T values of halogens in their mixture in the presence of transition metals.
		Cl⁻	Br⁻	I⁻	I⁻-Br⁻-Cl⁻
Ti	0.00 - 0.00	0.40-0.00	0.80-0.40	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.70-0.00)
V	0.00 - 0.00	0.30-0.00	0.80-0.40	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.60-0.00)
Cr	0.40 - 0.00	0.30-0.00	0.80-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.70-0.00)
Mn	0.60 - 0.00	0.30-0.00	0.60-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.70-0.00)
Fe	0.00 - 0.00 & 0.70 - 0.60 DS	0.50-0.00	0.60-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.70-0.00)
Co	0.40 - 0.00	0.60-0.00	0.90-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.60-0.00)
Ni	0.40 - 0.00	0.40-0.00	0.80-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.50-0.00)
Cu	0.80 - 0.10	0.40-0.00	0.70-0.30	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.50-0.00)
Zn	0.50 - 0.30	0.60-0.00	0.70-0.20	1.00-0.90	I⁻(1.00-0.80)-Br⁻ & Cl⁻(0.70-0.00)

R_L - R_T values of Cl⁻, Br⁻ and I⁻ in the absence of transition metals are 0.00, 0.60-0.40 and 1.00-0.30 respectively.

R_L - R_T values of I⁻-Br⁻-Cl⁻ in their mixture in the absence of transition metals I⁻(1.00-0.80)-Br⁻(0.60-0.50)-Cl⁻(0.00-0.00).

TABLE - 3B

Effect of transition metals on the R_F values of NO_2^- and NO_3^- anions and on their mutual separation
Solvent System: FA + Acetone (1:1), Stationary phase: Silica gel + Alumina (1:2)

Transition metals	$R_L - R_T$ values of pure transition metals	$R_L - R_T$ values of anions in the presence of transition metals		$R_L - R_T$ values of anions in their mixture in the presence of metals
		NO_2^-	NO_3^-	$NO_3^- - NO_2^-$
Ti	0.00 - 0.00	0.00 - 0.00	1.00-0.60	NO_3^- (1.00-0.80) - NO_2^-(0.60-0.50)
V	0.00 - 0.00	0.70 - 0.45	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.50-0.40)
Cr	0.30 - 0.00	1.00 - 0.80	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.40-0.30)
Mn	0.00 - 0.00	0.00 - 0.00	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.60-0.50)
Fe	0.40 - 0.00	0.00 - 0.00 0.75 - 0.45DS	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.50-0.40)
Co	0.20 - 0.00	-	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.60-0.50)
Ni	0.20 - 0.00	1.00 - 0.80	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.45-0.40)
Cu	0.10 - 0.00	-	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.55-0.45)
Zn	0.20 - 0.00	-	1.00-0.60	NO_3^- (1.00-0.90) - NO_2^-(0.55-0.50)

R_L-R_T values of NO_2^- & NO_3^- in the absence of transition metals are 0.00-0.00,0.80-0.40 respectively.
R_L-R_T values of NO_2^- - NO_3^- in their mixture in the absence of transition metals NO_3^- (0.70-0.40)-NO_2^-(0.00).

separation. Cl^-, Br^-, NO_2^- and NO_3^- produced badly tailed spots in the presence of transition metals. Conversely, I^- gave an improved compact spot. In spite of the increased tailing in the case of NO_2^-, its separation from NO_3^- is experimentally possible even in the presence of chromium and vanadium (table 3B). However, Cl^- can not be separated from Br^- in the presence of transition metals while the separation of I^- from Cl^- or Br^- is always possible (Table 3A).

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