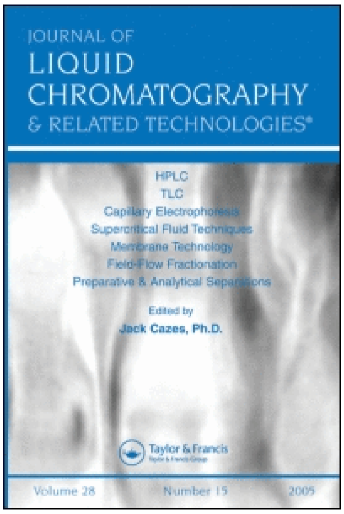

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# TLC Separation of Microgram Quantities of Iron(II) from Milligram Quantities of Iron(III)

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# TLC SEPARATION OF MICROGRAM QUANTITIES OF IRON(II) FROM MILLIGRAM QUANTITIES OF IRON(III)

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## ABSTRACT

A TLC method has been developed for the separation of microgram quantities of Fe(II) from milligram quantities of Fe(III) by using formic acid-butanol-ethyl methyl ketone as mobile phase. The separation is not effected by the presence of chloride, bromide, sulfate, sulfite, acetate and phosphate ions. Good separation was achieved when the pH of the sample solution was kept near to 1.0.

## INTRODUCTION

Separation of the different valence states of iron is important from the theoretical as well as the practical point of view. Several[1-14] methods have been reported for the separation of Fe(II) from Fe(III), most of them dealing with paper chromatography[1-3], electrophoresis[4-7] and ion-exchange chromatography[8-13]. Surprisingly, only one reference[14] is available on the use of TLC for the separation of Fe(II) from Fe(III). In fact, none of these studies refers to the use of formic acid(FA) as an eluent. FA has found some interesting applications[15-18] as an promising medium for chromatographic separations of metal ions in column and paper chromatography in the past, but the emphasis has now shifted to using it in TLC[19-22] for several reasons. It forms complexes with many metals[23,24], does not permit oxidation of cations during analysis, prevents hydrolysis of salts and does not dissolve ion-exchange materials significantly. It has also been reported that the acidic developers containing FA are less affected by silica gel properties and they do not deform the chromatoplates[20].

It was, therefore, considered worthwhile to use mixed organic solvents containing FA to achieve an analytically important separation of Fe(II) from Fe(III) on silica gel thin layers. Butanol was selected because it gives clean separations and ethyl methyl ketone(EMK) was used because of its high resolving potentiality

## EXPERIMENTAL

### Apparatus

A thin layer chromatography apparatus (Toshniwal, India) for the preparation of silica gel layers on 20x3 Cm glass plates was used. The plates were developed in glass jars (20x6 Cm). Beckmann pH meter was used for pH measurements.

### Reagents

FA and Silica gel G of Merck, India, EMK, and n-butanol of BDH were used. All other reagents were of analytical grade.

### Test Solutions and Detectors

0.1M solutions of nitrates, chlorides or sulfates of metal ions were generally used containing a little acid to prevent hydrolysis. 0.1M solutions of the sodium or potassium were taken for the study of anions as impurities. 1% solutions of ferrous ammonium sulfate, ferric chloride and aluminium nitrate were used for studying the effect of loading on the $R_f$ value. 1% potassium ferricyanide and potassium ferrocyanide solutions were used for the detection of Fe(II) and Fe(III) respectively. Other metal ions were detected by using conventional spot test reagents. The ferrous sulfate and ferric chloride solutions were brought to the required pH by the addition of either dilute sodium hydroxide solution or dilute hydrochloric acid.

## Developers

| | |
|---|---|
| $S_1$ | 10M FA in butanol |
| $S_2$ | 20M FA in butanol |
| $S_3$ | butanol saturated with 5M or 10M aqueous FA |
| $S_4$ | 10M FA in butanol saturated with NaCl-EMK(2:1) |
| $S_5$ | 10M FA in butanol-acetic acid(1:1) |
| $S_6$ | 5M FA in butanol-EMK(2:1) and (3:1) |
| $S_7$ | 10M FA in butanol-EMK(1:1),(2:1),(1:2),(3:1) and (1:3) |
| $S_8$ | 10M FA in butanol-acetone(1:1),(2:1) and (3:1) |
| $S_9$ | 10M FA in butanol-acetone-acetic acid(1:1:1) and (2:1:1) |

## Preparation of silica gel plates

The slurry used was prepared by mixing the silica gel in conductivity water in the ratio of 1:3 with constant shaking for 5 min. This 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 first dried at room temperature and then in an electrically controlled oven at 100±5°C for 2 hr. The plates were stored in the oven at room temperature until used.

## Procedure

For qualitative analysis, one or two drops of the cations solutions were spotted on the plates with the help of a micro-pipette. The plates were developed in the chosen solvent system by allowing the solvent to ascend to 10 Cm from the starting line on the plate in all cases. After the development was over, the plates were dried and the cations were detected by using usual reagents. For quantitative separation, various known volumes of standard metal salt solution were spotted on silica gel plate by using a lambda pipette and the development was performed in the chosen solvent. The $R_f$ values were determined after detecting the cations spots with appropriate spraying reagent.

## RESULTS AND DISCUSSION

Results of this study have been summarized in figures 1-2 and tables 1-2. In order to achieve the separation of Fe(II) from Fe(III) several solvent systems were tried. In $S_2$, $S_4$ and $S_5$ solvent systems, Fe(II) and Fe(III) both moved with the solvent front imposing a restriction on their mutual separation. Fe(III) moved faster than Fe(II) in solvents $S_1$, $S_2$ and $S_6$ but they gave a single tailed spot when chromatographed as mixture and thus hampering the separation. However, in $S_7$, $S_8$ and $S_9$ solvent systems Fe(II) was well separated from Fe(III) with reasonable resolution.

Some interesting points emerging out from the study of chromatographic behaviour of Fe(II), Fe(III) and their synthetic mixture in $S_7$-$S_9$ solvent systems are as follows:

(i) In all solvent systems ($S_7$-$S_9$), Fe(II) remained at the point of application and Fe(III) moved with the solvent giving $R_f \approx 0.4$ to 0.5.

(ii) Fe(II) cannot be separated from Fe(III) in the absence of acetone or EMK.

(iii) In solvent systems $S_8$ and $S_9$ good separation of Fe(II) from Fe(III) was obtained only when the proportion of FA was less

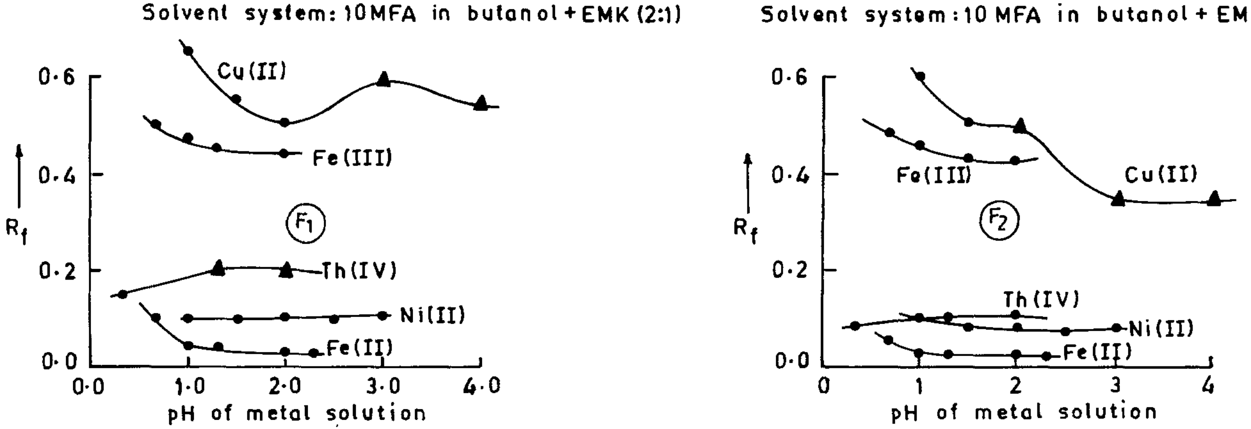

Fig. 1 Plot of $R_f$ values vs. pH of some metal solutions

●—● Compact spots

▲—▲ Tailing spots with $R_L - R_T \geq 0.4$

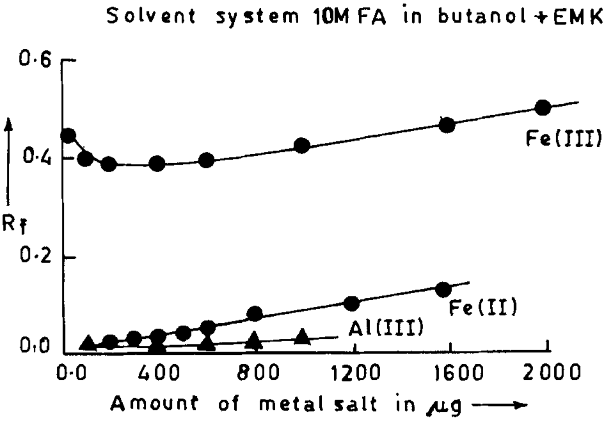

Fig. 2 Plot of $R_f$ values vs. amount of metal salts
—●—● Compact spots
—▲—▲ Tailing spots with $R_L - R_T > 0.3$

than 50%. At higher proportion of FA(>50%), Fe(II) spots started to spread.

(iv) Fe(II) gave more compact spots in solvent $S_7$ than in $S_8$ or $S_9$.

Table 1 indicates the results of separation of Fe(II) from Fe(III) in solvent systems containing various proportions of 10M FA in butanol and EMK. It is evident from the table 1 that the separation of different valence states of iron is possible at all proportions of FA but the solvent systems B and C were found to be better.

Figure 1 summarizes the effect of pH of some metal solutions on their mobility in solvent systems B and C. $R_f$ values of Fe(II), Ni(II) and Fe(III) remain almost constant at all pH values in both the solvent systems. In general, the $R_f$ of Cu(II) decreases as the pH of the sample solution increases. Cu(II) showed considerable tailing at higher pH in both the solvent systems. Thorium solutions of pH 1 showed tailing in solvent B.

## TABLE 1

Separation of Fe(II) from Fe(III) at pH 1.3 in solvent systems containing variable proportions of 10M FA in butanol and EMK

| Solvent System | | $R_f$ Fe(II) | $R_f$ Fe(III) |
|---|---|---|---|
| 10M FA in butanol-EMK | | | |
| A | 1:1 | 0.02 | 0.45 |
| B | 2:1 | 0.03 | 0.47 |
| C | 1:2 | 0.02 | 0.48 |
| D | 1:3 | 0.05 | 0.46 |

## TABLE 2

Separation of Fe(II) from Fe(III) at different pH values of sample solution with solvent system containing 10M FA in butanol-EMK in 2:1 ratio

| pH of the sample solution containing Fe(II) and Fe(III) | $R_f$ Fe(II) | $R_f$ Fe(III) |
|---|---|---|
| 0.7 | 0.08 | 0.48 |
| 1.3 | 0.03 | 0.46 |
| 2.0 | 0.03 | 0.40 |
| 2.3 | 0.02 | 0.35 |

It is clear from figures 1($F_1$,$F_2$) and table 2 that Fe(II) can be successfully separated from Fe(III) in the pH range of 0.7 to 2.3 but the best results were obtained when the pH of the sample solution containing mixture of Fe(II) and Fe(III) was kept near to 1.0.

In order to study the aging effect, the synthetic mixture of Fe(II) and Fe(III) at pH 1.3 was spotted on the chromatoplates and the $R_f$ values for Fe(II) and Fe(III) were determined with time upto 48 h. The $R_f$ values did not show any variation with time.

Figure 2 shows that the $R_f$ value of Fe(II) increases with the increase in its amounts of loading. However, the $R_f$ values of Al(III) and Fe(III) were not effected upto the loading of 1 mg of Al(III) and 600 μg of Fe(III) as their salts. Good compact spots were obtained for Fe(II) and Fe(III) upto the loading of 600 μg of each. At higher loading Fe(II) spot began to spread and Fe(III) showed considerable tailing. It is evident from Fig.2 that large quantities of Al(III) can be separated from considerable amount of Fe(III). Similarly, Fe(II) upto 600 μg can be easily separated from large amount of Fe(III) but the large amount of Fe(II) i.e. >600 μg cannot be separated from Fe(III) because of the spreading of Fe(II) spots at higher loading. As a result, 10 to 500 μg of Fe(II) and 50 μg to 1 mg of Al(III) salts were successfully separated from 5 μg to 3 mg of Fe(III) salt. Thus, the tailing in Fe(III) spots at higher loading did not impair the separation of Al(III) or Fe(II) from Fe(III). Conversely, the tailing in Al(III) or Fe(II) spot did not permit their separation from Fe(III). Fe(III) could not be separated from Cu(II), Zn(II), $UO_2$(II) and Cd(II).

To study the effect of different anions on the separation of Fe(II) from Fe(III), synthetic mixtures containing Fe(II), Fe(III) and the anions concerned in the ratio of 1:1:2 were spotted on the chromatoplates and the $R_f$ of Fe(II) and Fe(III) were determined in solvent C. $Cl^-$, $Br^-$, $SO_4^{2-}$, $CH_3Coo^-$, $IO_4^-$, $PO_4^{3-}$ and $SO_3^{2-}$ did not hurt the separation. However, $I^-$, $NO_3^{2-}$, $MoO_4^{2-}$, $CrO_4^{2-}$, $Cr_2O_7^{2-}$, $BrO_3^-$, $IO_3^-$, $SCN^-$ and $Fe(CN)_6^{3-}$ were found to interfere in the separation of Fe(II) from Fe(III) because of the spreading in Fe(II) spots in the presence of these anions.

The proposed method is fast needing about 30 min. for the separation of micro as well as milligram quantities of Fe(III) from considerable amounts of Al(III) and Fe(II). The lower limits of detection for Fe(II) and Fe(III) were found to be 4 μg and 2 μg respectively.

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