SUMMARY

The work described in this thesis involves the use of thin-layer chromatography (TLC) as the practical analytical technique for the analysis of transition metal and rare earth chlorosulphates. Several thin-layer chromatographic systems were developed for rapid and reproducible qualitative and quantitative analysis of metal chlorosulphates. Some new stationary phases were developed by i) impregnating silica gel, alumina, kieselguhr and cellulose with organic and inorganic impregnants ii) mixing of silica gel, with alumina or cellulose and egg shell powder with cellulose or silica gel and iii) impregnating the mixed adsorbents with 1,4 - dioxane, DMSO, oxalic acid, aniline, ammonium nitrate and aqueous salt solution of alkali metals or aqueous ammonia. These layer materials were used to achieve important separations in combination with proper mobile phases, that include monocomponent solvents (various organic solvents, mineral and carboxylic acids and aqueous salt solutions); multicomponent organic solvents (mixtures of alcohols, alkanes, carboxylic acids, amides or ketones); mixed aqueous organic solvents (carboxylic acids-aqueous salt solutions alcohols-mineral acids of various concentration etc.); aqueous solutions of acids (HCl, formic acid, acetic acid or oxalic acid); bases and salt solutions. The results of the study have been presented under six chapters.

Chapter-I provides general introduction describing the general aspects of science, chemistry, analytical chemistry, thin-layer chromatography (TLC) and metal chlorosulphates. A comparison of TLC and other chromatographic methods has been presented to show the relative advantages of using TLC as highly efficient microanalytical separation method. Being an off-line process, the various steps in TLC are carried out independently with
better control. The principle of TLC is known for more than 100 years now, the reason for performing it is presently shifting from analysing natural mixtures of organic and inorganic substances to the analysis of biological, pharmaceuticals, alloys and environmental samples. In addition to the detailed discussion or principle steps of TLC process a compilation of literature (1973-1996) on TLC of metal complexes is summarized in tabular form in this chapter. The need of developing application oriented TLC method is emphasised.

Chapter-II describes the results of TLC carried out on some transition metal chlorosulphates using mixed (silica gel + cellulose 1:1, 1:2 w/w); impregnated (silica gel, silica gel + cellulose 1:1, 1:2, 1:3 or silica gel + alumina 1:1 w/w) and unmodified (silica gel) layers. The analytical potential of water, a non-toxic and easily available universal solvent as mobile phase was exploited by realizing selective separation of Mn - Ni / Co - Cu / Zn - Fe chlorosulphates on layers prepared from a binary mixture of silica gel and cellulose (2:1). The effect of anions on the separation of Co or Ni chlorosulphates from Fe, Mn and Cu chlorosulphates was examined to widen the applicability of the method in the presence of anionic species. The separation of Ni /Co from Cu is hampered by the presence of SCN⁻ in the sample. The quantitative determination of Ni chlorosulphate was performed by titrimetry and that of Cu chlorosulphate was done by both titrimetry and atomic absorption spectrometry (AAS). The percentage recoveries of Cu (91.6% by titrimetry and 95.5 % by AAS) and of Ni (91.43% by titrimetry) chlorosulphates were obtained using the calibration curves constructed for the standards. The titrimetric method was found suitable for higher concentration of Cu whereas AAS was found useful for
low concentrations. Some validation parameters such as the stability of the
colour intensity of the metal chlorosulphate on the sorbent layers and the
reproducibility of $R_f$ values were assessed. Dependence of $R_f$ values on the
compositional proportion of constituting components in the mixed bed and
the pH of the mobile phase was investigated to select the optimum pH of
mobile phase and the appropriate composition of layer for better separation
of metal chlorosulphates. With a particular chromatographic system, the
mobility of chlorosulphates, acetates and sulphates of the same metals differ
slightly. Number of 3d - electrons of the central metal atoms (transition metals
of Mn, Fe, Co, Ni, Cu & Zn) and magnetic moments of metal chlorosulphates
were correlated with mobility or $hR_f$ values (Figures 1 and 2).

Figure 1 - Variation of mobility with number of 3d electrons
Chapter III summarizes the results of thin-layer chromatographic studies of transition metal chlorosulphates on silica gel, cellulose, kieselguhr, alumina, silica gel + alumina or cellulose layers with mixed acidic solvent systems. Carboxylic acid containing systems were found to provide better separations compared to HCl containing systems. Mixed binary layers of silica gel + cellulose and silica gel + alumina were found suitable for several separations of analytical importance. With most of the stationary phases, propanol and butanol containing solvent systems produced well resolved spots of higher intensity compared to solvents containing lower alcohols (methanol or ethanol). Compared to alumina or kieselguhr, silica gel provided more separation possibilities. Spectrophotometric determination of chlorosulphate of cobalt was worked out and the recovery after elution from silica gel + cellulose (2:1) plates has been estimated at the respective $\lambda_{\text{max}}$ value (620 nm) and it provides a molar absorptivity of 454.5 $\text{mol}^{-1} \text{cm}^{-1}$.
Chapter- IV presents the results of the mobility of single, mixed and impregnated layers with 125 solvent systems. Experimental conditions were optimized and useful chromatographic systems were identified for selective separation of La. For example, 5% aqueous ammonia producing highly compact spot for La on cellulose layer can be utilized for selective separation of La from Ce, Eu, Gd or Yb. Since rare earth chlorosulphates are prepared from rare earth benzoates this particular TLC study is of considerable importance. The information gathered from the behaviour of these rare earth benzoates on new sorbent layers are of immense importance to select proper stationary phase for reliable separations of rare earth chlorosulphates. Out of 125 mobile phase-stationary phase combinations, best separation conditions were achieved with nonimpregnated silica gel + alumina (9:1) as stationary phase and 0.5M aqueous ammonia as mobile phase. All rare earth benzoates have lower mobility (R_f = 0.30) on impregnated alumina layers whereas higher R_f values (except for La) were obtained on silica gel impregnated with aniline. The separation sequence in TLC is influenced by a variety of factors including mode of separation (normal or reversed-phase; cation or anion exchange) and composition of the stationary and mobile phases. A notable variation in the mobility of lanthanide benzoates was observed in silica gel or mixed silica + alumina and cellulose + alumina layers when developed with some organic and nonacidic solvent systems. For rare earth benzoates, both trends of increase and decrease in R_f values with increasing atomic number were observed. The examination of TLC behaviour of rare earth benzoates is also of interest for understanding the ionic bonding properties of the M^{3+} rare-earth (RE) cation (ionic size 8.5-10.6 nm).

Chapter - V summarizes the TLC behaviour of chlorosulphates of rare earth viz. Y^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+} and Yb^{3+} on TLC plates coated with plain, mixed and impregnated adsorbents. Various aque-
ous salt solutions were used as the impregnants. Silica gel H yields more compact spots compared to silica gel G or other conventional coating materials. Aqueous salt solutions were found more suitable eluents compared to organic solvents for selective separations. A general trend of increasing R_f values with increasing salt concentration in the mobile phase was noted with all rare earth chlorosulphates. A linear relationship was obtained when log h_R_f of rare earth chlorosulphates (except Yb), was plotted against the ionic radii of RE cations (Fig. 3)

![Figure 3 - Correlation of the ionic radii of M^{3+} ions with mobility of metal chlorosulphates](image)

Figure 3 - Correlation of the ionic radii of M\(^{3+}\) ions with mobility of metal chlorosulphates

Variation of ionic radii and h_R_f values with magnetic moments of RE cations and chlorosulphates were investigated. A decrease in ionic radii or h_R_f values of some rare earths with increase in their magnetic moments is noticed as shown in Fig 4.
Figure 4 - Variation of magnetic moments of rare earth cations and chlorosulphates with (A) the ionic radii on the $M^{3+}$ ions and (B) the $hR_f$ values of the rare earth chlorosulphates.
The spectrophotometric determination of yttrium chlorosulphate after TLC separation from neodymium and ytterbium using the optimum conditions gives a linear relationship in the concentration range 40.8-285.5 µg of yttrium and resulted in a recovery of 88.5%.

Chapter-VI encapsulates the results of TLC behaviour of metal chlorosulphates on layers prepared from plain chicken egg shell and egg shell mixed with cellulose or silica gel and developed with salt solutions, mineral acids, amine solutions and surfactants. Aqueous salt solutions of alkali metals were found better solvent systems for selective separations of metal chlorosulphates. The effect of acid containing mobile phases towards the stability of TLC plates coated with egg shell was also examined. Layers prepared from egg shell mixed with silica gel H yielded better results, compared to the layers of egg shell mixed with silica gel G or cellulose. A combination of silice gel H + egg shell (2:1 w/w) as stationary phase and 1 M aqueous ammonium sulphate solution as mobile phase was found most suitable for the separation of metal chlorosulphates.

This particular study was intended to develop inexpensive sorbent layer materials for their better utilization in chromatography.