CHAPTER I
GENERAL INTRODUCTION
1. INTRODUCTION

Science is a study of systematically arranging and classifying man's knowledge of the world. The first step in the generation of science is the collection of indisputed facts relating to its subject and has been divided into several compartments for the purpose of in-depth study. Chemistry is a branch of physical sciences, closely related to physics and deals essentially with the composition and behaviour of the natural world. It is the study of substances, their structure, properties and reactions. During 19th century, the knowledge of chemistry has grown so vast and the field has become so wide and complex that it is necessary to divide it into different branches for proper understanding of the subject. The major branches of chemistry are organic chemistry, inorganic chemistry, physical chemistry and analytical chemistry. Organic chemistry is confined to the chemistry of carbon compounds. Inorganic chemistry relates to the study of metallic and non-metallic elements and their compounds. Physical chemistry concerns with the study of physical properties and constitution of matter, the laws of chemical reactions and the theories governing these reactions. Analytical chemistry deals with the determination of the chemical composition of matter. The other branches of chemistry are nuclear chemistry, biochemistry, soil chemistry, industrial chemistry, high polymer chemistry, pharmaceutical chemistry, etc., are at present fast developing. Perhaps no other science today is so broad in it's scope as chemistry.

1.1. ANALYTICAL CHEMISTRY

Analytical chemistry is one of the most important branches of chemistry. It is being used for detection, determination and separation of traces of organic and inorganic substances in air, water and soil environments. Owing
to the greater importance of pollution in modern life, the environmental chemistry is becoming more and more relevant to us. The increasing environmental pollution and explosive technological development have created analytical problems needing introduction of increasing instrumentation for their solution. Consequently, the need for analytical chemistry is increasing as the newer problems are arising owing to different demands of the modern world.

By analytical chemistry we understand the development of new methods suited for the requirements of mankind. The classical methods have to be modified according to need of the situation and new methods have to be developed for solving the problems such as the purification of the environment, recovery of precious metals from the spent fuel or sea water, analysis of ores, determination of pesticides and toxic metals in food products and identification of traces of impurities in ultra pure semi-conductors. Thus analytical chemistry plays significant role in chemical technology which is growing rapidly at present. The use of a particular substance in various fields of science (chemical, biochemical, physiological and engineering etc.) depends solely on its chemical analysis which may be qualitative or quantitative.

A qualitative analysis deals with the methods used for the determination of the nature of the constituents of a substrate whereas the quantitative analysis is concerned with the methods dealing with the determination of actual amount of a given species present in a sample. Both instrumental and non-instrumental (classical) methods are used in analytical chemistry. Instrumental methods are usually faster and more sensitive, whereas non-instrumental methods which form the basis of standardization of the
instruments are considered more accurate. However, it is difficult to draw a clear border line between instrumental and non-instrumental analytical methods. For example, a simple volumetric analysis involves the use of a balance and all instrumental methods are based on the principles of physical chemistry and physics. Thus, the difference between two types of analytical methods is only in the complexity of the instrumentation and not a fundamental one. Despite distinct advantages of instrumental methods in many directions, their wide spread adoption has not rendered the classical methods obsolete. The non-instrumental methods should be strengthened because they are simple, inexpensive and versatile. In fact, a close critical comparison of all available analytical methods demonstrate the truth of that well known rule of life and work: nobody (here: nothing) is perfect. The team is always stronger than the individual. Nothing can be replaced completely without loss. Co-operation is best.

There are several methods for the analysis of elements but the simplest of them, characterized by high selectively, rapidity and reliability and requiring no expensive reagent and instrumentation is usually preferred. To an analytical chemist, developing methods for a particular study is the challenging part of the research and usually chooses the most selective method suitable for the case, i.e. the one involving the least number of stages so that the risk of contamination introduced with the reagent is minimized. This is especially important in the determination of very small quantities of elements. Many reagents are not sufficiently selective and separation methods based on properties of compounds become important. One has to look into the possibilities of using various separation techniques such as precipitation, distillation, dialysis, ring-oven technique, ion-exchange,
electrophoresis, solvent extraction and chromatography while handling a new system.

The most general separation techniques include ion-exchange, electrophoresis and chromatography. Ion-exchange can be preferred to separate ionic and non-ionic impurities or similar pairs of cationic and anionic species. The selectivity of exchanger depends upon the nature of exchanger and composition of the eluent. Ion-exchangers are regarded as insoluble solid or liquid materials which carry exchangeable cations or anions. Accordingly, they are called cation or anion exchangers. The materials capable of exchanging both cations and anions are called amphoteric ion-exchangers. Ion-exchange is a process which involves reversible and stoichiometric interchange of ions of the same sign between an electrolyte solution (or molten salt) and a solid phase. The mechanism of the separation is based on the ion-exchange equilibria. The use of electrophoresis was first reported in 1937 by Konig (1). It's use has been limited to ionic species and the separation largely depends on the particle size.

The work embodied in this thesis involves the use of thin-layer chromatography (TLC), a simple, reliable and sensitive chromatographic method as the prime analytical technique for the analysis of “metal chlorosulphates”. It is appropriate to encapsulate necessary information available till date, about metal chlorosulphates (MCSs) and chromatography in general and planar chromatography in particular.

1.2 METAL CHLOROSULPHATES

The diversity of compounds, particularly transition metal compounds has increased rapidly in recent years. One of the reasons for this growing interest has been a recognition of the value of these compounds as inorganic
synthons. The synthesis of various coordination (2-5) and organometallic (6-10) compounds incorporating covalently bound $\text{RSO}_3^-$ ($R = \text{F, CF}_3$) became important in view of the above reason, i.e. precursors to a wide range of derivatives formed by substitution of relatively labile ligand by ligands of greater nucleophilicity. It has been reported (11-15) that $\text{RSO}_3^-$ acts as a better leaving group due to the electron withdrawing properties of the $\text{F}^-$, $\text{CF}_3^-$ and $-\text{SO}_2^-$ groups. It has also appeared in the literature that the variety of compounds with metals in their low oxidation state having covalently bound $\text{RSO}_3^-$ ($R = \text{CF}_3$) have received particular attention due to their use as efficient catalysts in various organic reactions (16-20). These synthetic applications of bound $\text{RSO}_3^-$ ($R = \text{F, CF}_3$) anions makes it imperative to begin with the synthetic utility of chlorosulphuric acid (HSO$_3$Cl) for the synthesis of novel compounds of transition metals, rare earth metals and organometallic compounds. Coordinated SO$_3$Cl anion is also used as a catalyst for number of organic and biochemical reactions and potential precursors for the synthesis of compounds including organometallic compounds.

**i) Role of Chlorosulphuric Acid in the Synthesis of Metal Chlorosulphates and Nature of Bonding**

Survey of literature reveals that alkyl and aryl chlorosulphates have been known for over a century (21). These organo-chlorosulphates were generally prepared (22-26) by the reaction of various types of alcohols with sulphuryl chloride being used as chlorosulphonating agent. It was later realized that chlorosulphate derivatives (27-33) may readily be obtained using chlorosulphuric acid as a reagent for chlorosulphonation.

Chlorosulphuric acid, the starting reagent for the present work is a strong ionizing solvent which is of intermediate strength compared to sulphuric or
fluorosulphuric acid. It has been well established (34-49) that HSO₂Cl could be used as an ionizing solvent for the formation and stabilization of variety of cationic species. There have been a large number of reports on chlorosulphonating behaviour of HSO₃Cl and a variety of metal chlorosulphates. M(SO₃Cl)₂ [M=Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg] (43, 45, 46) and M (SO₃Cl)₃ [M=Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb,Dy] (48) have been prepared by carrying out solvolytic reactions on corresponding metal acetates and benzoates respectively, where HSO₃Cl acts both as medium of reaction as well as chlorosulphonating agent. A number of oxymetal chlorosulphates (41, 42, 50) mixed metal chlorosulphates (34, 35, 37), organometallic chlorosulphates (51, 52) and complexes of the type ML₂(SO₃Cl)₂, ML₄(SO₃Cl)₂ (41, 42, 50), and ML₂(SO₃Cl) (51, 52), [M=Transition metals or rare earth metals L=Pyridine, pyridine N-oxide, triphenyl phosphine methyl cyanide, 2, 2'-bipyridine, acridine and triphenyl phosphine oxide] have also been prepared and characterized in order to examine their stereochemistry and extent of coordination of SO₃Cl anion to the complex cations. The mode of bonding of SO₃Cl⁻ in the metal chlorosulphates as well as their complexes have been confirmed by comparing the IR spectra of these compounds with that of the free SO₃Cl⁻ group. The observed low conductivity values of these compounds further confirm that SO₃Cl⁻ group is covalently bonded to the metal ions and/or complex cations in metal chlorosulphates and/or metal chlorosulphate complexes.

ii) Need of Analytical Studies on Metal Chlorosulphates

Though it is an explicit fact that metal chlorosulphates are an important class of compounds, no work has been reported on their analytical study that can be used for their separation. Details about the physical properties like
magnetic moment, specific conductance, colour etc., and IR data are available. The stereo-chemistry of these compounds has also been fully examined to understand the mode of vibration and cation-anion interactions. The use of chlorosulphates, however, have been limited only to the field of synthetic chemistry as a potential base for various reactions. The chromatography of metal chlorosulphates appeared in the literature very recently (53) and a selective separation of nickel from cobalt as their chlorosulphates has been achieved on thin-layers of silica. It was therefore thought worthwhile to begin with one of the simple and reliable separation techniques, i.e. thin-layer chromatography to achieve selective separation of chlorosulphate complexes of transition and rare earth metals. Table 1.1 gives information about the physical properties of some transition metal and rare earth chlorosulphates.

Table 1.1

Physical Properties of Metal Chlorosulphates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Magnetic moment $\mu_{\text{eff}}$</th>
<th>Molar conductance ohm$^{-1}$cm$^2$ mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (SO$_3$Cl)$_2$</td>
<td>White</td>
<td>5.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (SO$_3$Cl)$_2$</td>
<td>Red</td>
<td>5.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co (SO$_3$Cl)$_2$</td>
<td>Blue</td>
<td>5.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (SO$_3$Cl)$_2$</td>
<td>Light green</td>
<td>3.60</td>
<td></td>
<td>(54)</td>
</tr>
<tr>
<td>Cu (SO$_3$Cl)$_2$</td>
<td>Green</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (SO$_3$Cl)$_2$</td>
<td>White</td>
<td>Diamagnetic</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pb (SO₃Cl)₂  Dirty white
Sn (SO₃Cl)₂  White
Fe (SO₃Cl)₃  Reddish brown  5.58
La (SO₃Cl)₃  White  Diamagnetic  39
Ce (SO₃Cl)₃  White  2.85  45
Pr (SO₃Cl)₃  Green  3.90  60
Nd (SO₃Cl)₃  Reddish violet  3.75  35
Sm (SO₃Cl)₃  White  35
Gd (SO₃Cl)₃  White  8.30  59  (48)
Tb (SO₃Cl)₃  White  42
Dy (SO₃Cl)₃  Grey  10.41  65
Ho (SO₃Cl)₃  White  10.20  40
Er (SO₃Cl)₃  White  36

1.3. CHROMATOGRAPHY

Chromatography is a physical method for separating a mixture in which the separating components are distributed between two phases, one of which constituting a stationary bed of large surface area and the other being a fluid that percolates through the stationary phase. The paper presented by Michael Tswett in 1903 at the meeting of Biological Section of the Warsa Society of Natural Science is generally accepted as the beginning of chromatography. He published his work (55) on the separation of plant pigments in the form of two papers. The pioneering work of Martin and Synge
(56) set a precedent for the development of other forms of chromatography.

**i) Chromatographic Systems and their Classification**

A combination of stationary and mobile phases is termed as chromatographic system. Depending on the geometry of the stationary support employed, a chromatographic system may be columnar or planar. The planar system can further be classified according to the mode of development as ascendent, descendent, horizontal, centrifugal and circular. The classification of chromatography is more easy when the stationary phase is a solid or liquid and mobile phase is a liquid or gas. Thus liquid-liquid, liquid-solid, gas-solid or gas-liquid combination arised. Of these, liquid-liquid and liquid-solid systems constitute liquid chromatography. This includes column chromatography, paper chromatography and thin-layer chromatography (TLC). Out of these TLC is more efficient and rapid. It can be used to simply check the purity of a substance, to separate and identify the components in a mixture or to obtain a quantitative analysis of one or more of the components present in a mixture.

As the development of chromatogram proceeds, the components of the sample interact with the stationary phase. There are different types of interactions which may occur during the separation and these are often referred to as modes of separation; e.g. adsorption, partition, ion-exchange etc. Since these terms refer to the basic mechanism of physico-chemical process which occur, it is convenient to describe a separation as being due to adsorption, partition, ion-exchange etc., even though these may not be the only mechanisms operative. The various methods of classifying chromatographic separations are brought together in Figure 1.1.
Figure 1.1 Classification of chromatographic systems
1.4 PLANAR CHROMATOGRAPHY

Planar chromatography is a collective term applied to all analytical, preparative and micropreparative separation processes where the mobile phase migrates through the stationary phase (paper or porous sorbent) in planar or flat-bed arrangement. The movement of the compounds to be separated is governed by two opposing forces, the driving force of the solvent system and the retarding action of the stationary phase. Depending on the nature of stationary phase, planar chromatography may be classified as paper chromatography (mobile phase migrates through a strip of paper) and thin-layer chromatography (mobile phase moves through a layer of porous sorbent coated on an inert support).

Amongst planar chromatographic methods, TLC has been regarded as a simple, inexpensive and rapid separation technique. TLC is an open and fully off-line system, where the principle steps (sample application, development, drying of plates and densitometric evaluation) can be performed as separate operation steps.

1.5 HISTORY OF TLC

The history of TLC has been reviewed by Stahl (1969), Heftmann (1975), Kirchnar (1975, 1978, 1980), Pelick et al. (1966), Jork and Wimmer (1986), and Wintermeyer (1989). TLC is about 108 years old technique, as Beyerinck (57) first referred it’s use in 1889, when he studied the diffusion of a mixture of HCl and H₂SO₄ through a thin - layer of gelatin. In 1898, Wijsman (58) showed the presence of two enzymes in a malt diastase by using a gelatin layer containing starch and a fluorescent bacteria obtained from seawater, he was the first to introduce the fluorescence phenomenon for detecting the zone on thin layers. In 1938, Izmailov and Schraiber (59), two Soviet
Scientists, developed a method called drop chromatography for the analysis of pharmaceutical preparations on aluminium oxide thin layers. Meinhard and Hall (60) in 1949 separated Fe$^{2+}$ from Zn$^{2+}$ on microscope slides. TLC as presently known began to attract attention through the work of Kirchner and his associates (61-63). Stahl, in the 1950's introduced the term "thin-layer chromatography" for the first time. His major contribution (64,65) was the standardization of materials, procedures and nomenclature. He described an ingenious and practical device for preparing layers. This method is now one of the most frequently described separation techniques in quantitative and qualitative analysis.

Dallas et al. (66) first reported the use of densitometry in TLC in the mid 1960's. A symposium on quantitative TLC held in 1968 in Great Britain led to the publication of the first book on this topic (67). High Performance TLC plates (68) came into use in the mid 1970's. The improvements in practice and instrumentation in the late 1970's led to the development of high performance TLC (HPTLC) (69); instrumental HPTLC (70); centrifugally accelerated preparative layer chromatography (71) and over pressured layer chromatography (OPLC) (72). These and other high performance and quantitative methods have caused a break through in the field of TLC.

1.6 COMPARISON OF TLC WITH OTHER CHROMATOGRAPHIC METHODS

Comparison of TLC and HPTLC have been described by Fenimore and Devis (1981), Bormann (1982), Goddens et al. (1983), Costanzo (1984), Jork and Wimmer (1986), Geiss (1987) and Sherma (1991). Although the mechanisms governing separations in HPLC and TLC/HPTLC are identical, differences in practical aspects lead to the following comparisons of the performance of TLC/HPTLC and HPLC.
i) HPLC is more efficient than HPTLC.

ii) Capacity factors (K') are more reproducible in HPLC than R_p values in TLC.

iii) HPLC is more readily automated than TLC.

iv) Mobile phase velocity in TLC is determined by capillary forces and hence cannot be controlled whereas it is easily adjusted and controlled in HPLC.

v) The number of samples processed in a given time (sample throughput) is higher in TLC than HPLC.

vi) The development and detection steps are much more flexible and versatile in TLC than HPLC.

vii) The choice of sample solvent is less important in TLC than HPLC.

viii) In TLC there is wider choice for commercially available stationary phases and detection reagents.

ix) Solvent use is much lower in TLC than HPLC.

x) Detection limits are approximately the same for TLC and HPLC.

xi) TLC is inexpensive than HPLC and GC.

xii) TLC offers superior resolution, speed and sensitivity compared to paper chromatography.

xiii) Compared to GC, TLC can be used for the analysis of thermally labile compounds.
1.7 TLC PROCEDURE

Basic TLC is carried out as follows: The stationary phase in TLC involves coating a thin layer of some appropriate adsorbent on a plate in the form of a slurry. This is dried at room temperature and activated for a specified time and temperature, then kept in a glass chamber until use. An initial volume of mixture (0.50-10μL) containing 0.50-50μg of the solute is applied on TLC plate at about 3 cm from the lower edge of the TLC plate. The sample is dried at room temperature and the end of the plate is placed in a suitable mobile phase inside a closed chamber. The components of the mixture migrate at different rates as a result of varying degree of affinity for the stationary and mobile phases during movement of the mobile phase through the stationary phase, which is termed development of chromatogram. When the mobile phase has moved to desired distance, the chromatoplate is removed, from the closed chamber and the plate is dried at room temperature and the separated zones of the components of mixture are detected using suitable visualization reagents.

In a TLC system the $R_f$ coefficient is a basic quantity used to express the exact position of the solute on the developed chromatogram. It is calculated as the ratio

$$R_f (Retardation factor) = \frac{\text{Distance travelled by the solute from the starting line}}{\text{Distance travelled by the solvent from the starting line}}$$

$R_f$ varies from 0 (solute remains at the point of application) to 0.999 (solute migrates up to the solvent front). The entire scheme for a typical thin-layer chromatographic process can be summarized as in Figure 1.2.
Figure 1.2  Scheme of a typical thin-layer chromatographic process
1.8 BASIC PRINCIPLE, TECHNIQUE AND THEORY

In classical TLC, the capillary action of the sorbent in the layer controls the rate of migration of the mobile phase. Thus, spot broadening is controlled by molecular diffusion in different sizes according to the interactions between the solvent and sorbent.

Efficiency in TLC is calculated with a compound with median $R_p$, and measured by determination of the theoretical plate number as in the equation

$$N = 16 \left(\frac{x}{w}\right)^2$$

where 'x' is the distance from the origin to the separated zone centre and 'w' is the width of this zone. By convention, the efficiency of a thin-layer plate measured or calculated for a substance having $R_p$ values 0.5, 1.0 or some average value (73). C.F. Poole and S.K. Poole (74) have admirably summarized theories of separation in TLC.

Another important factor which determines the separation efficiency of ions is resolution. It is defined as the ratio of the centre-to-centre distance ($X$) between the two components (A and B) and the average diameter of the two spots (Figure 1.3). Thus it can be expressed mathematically as

$$R_s = \frac{X}{0.5 (d_1 + d_2)}$$

The values of $R_s$ serves to define the separation of components from mixture. For $R_s = 1$, the two components are reasonably well separated; for $R_s > 1$ better separation and for $R_s < 1$ poor or no separation.

In TLC, separation of components in a mixture is achieved by homogenizing the experimental conditions involving stationary and mobile phases. The desired separation can be achieved by proper selection of stationary (sorbent) and mobile (solvent) phases.
Figure 1.3 - Schematic diagram showing resolution of two-component mixture on chromatogram
1.8.1 Nature of Phase Interactions

Some of the important physical and chemical characteristics that determine the degree of interactions of mobile phase-solute, solute - sorbent and mobile phase-sorbent are given in the following paragraphs.

i) **Intramolecular Forces**: which hold neutral molecules together in the liquid or solid state. These forces are physical, characterized by low equilibrium and result in good chromatographic separation.

ii) **Inductive Forces**: exist when a chemical bond has a permanent electrical field associated with it (e.g. C-Cl, C-NO₂ groups). Under influence of this field, the electrons of an adjacent atom, group or molecule are polarized so as to give an induced dipole moment. This is a major contributing factor in the total adsorptive energy on alumina.

iii) **Hydrogen Bonding**: makes a strong contribution in adsorption energies between solute or solvents having a proton donor group and a nucleophilic polar surface such as that of alumina or silica gel.

iv) **Charge Transfers**: between components of the mobile phase and the sorbent can also take place to form a complex of the type S⁻A⁺ (Where S= solvent or solute, and A= surface site of sorbent). This is prominent in ion-exchange chromatography.

v) **Covalent Bonds**: can be formed between solute and/or the mobile phase and the sorbent. These are strong forces and result in poor chromatographic separation.

1.8.2 The Solvent Strength Parameter

The solvent strength parameter (ε⁰) was defined by Snyder (75) as the adsorption energy per unit of standard sorbent. The physical and chemical forces, described just above, are involved in determining the level of interaction of the sorbent and mobile phases. The higher the mobile phase
strength (greater interaction with the sorbent) the greater will be the $R_f$ of the solute in simple liquid-adsorption TLC. Usually one tries to select a mobile phase so as to obtain $R_f$ values of the order 0.30-0.70, to achieve well separated zones. Stronger mobile phase offers greater interaction with the solute and will decrease adsorption, thus causing faster migration. Decreasing the solvent strength can increase resolution. Thus, the difficult separations can be achieved by varying the selectivity (changing interactions) of the mobile phase. Solvent strength is dependent on its reactivity with the sorbent. With a large number of sorbents available, one has to resort to some trial and error operations to find the best mobile phase for separating the components of interest. Trappe (76) described a series of solvents in the order of eluting power. In the expression of mobile phase strength the "eluotropic series" has been widely used.

For the separation of complex mixtures, systematic computer-assisted mobile phase optimization methods are preferable to trial and error methods. The systematic schemes that have been used in TLC are mostly adapted from HPLC. Different approaches for systematic optimization of the solvent system include window diagrams, overlapping resolution maps, simplex methods, pattern recognition procedures and the PRISMA system. These optimization methods have not been widely used for routine practical TLC till date.

1.8.3 Adsorbents

There are many experimentally proven sorbent materials suitable for separating organic and inorganic substances, when used as thin-layers on an inert support. The factors to be considered when coating a sorbent for TLC are type of compounds to be separated; visualization technique to be employed, thickness and stability of the layer described and mobile phase characteristics. The commonly used sorbents are silica gel, alumina, cellulose and kieselguhr (diatomaceous earth) etc.

Silica gel or silicic acid has become the most widely used sorbent for TLC since being described by Kirchner et al. (61). It is slightly acidic in
nature and the free valencies of the oxygen at it's surface are connected either with hydrogen (Si - OH, silanol group) or with another silicon atom (Si - O-Si, siloxane group). The hydroxyl groups on silica surface are considered to be adsorption active centres which are capable to interact with solute molecules. The ability of the silanol groups to react chemically with appropriate reagent is used for controlled surface modifications. Hence silica gel is considered as the most favourable layer material in chromatography.

Aluminium oxide, commonly called alumina, is the second largely used TLC sorbent. Chemically, it is basic and more reactive than silica gel but for a given layer thickness it is not capable to separate quantities of analyte as large as can be separated by silica layer. Adsorption is the separation mechanism in both silica gel and alumina.

Kieselguhr (diatomaceous earth) is a chemically neutral sorbent, that does not separate or resolve as well as alumina or silica gel. The most frequently used kieselguhr (kieselguhr G) contains approximately 15% gypsum binder and is used as an aqueous slurry.

Cellulose is used as a layer material in TLC when it is convenient to perform a given paper chromatographic (PC) separation by TLC in order to decrease the amount of time necessary for the separation and increase the sensitivity of detection. The developing solvents and visualization reagents employed in PC can most readily be used in cellulose TLC. Because of its tenacious nature, cellulose is usually coated on TLC plates without binder unlike the above three sorbents.

Other substances used as sorbents include a variety of ion exchange cellulose powders, polyamide powders and fluorocil. In addition, mixed, impregnated and chemically modified layer materials have been used by researchers to increase the resolution. Thin-layer plates with concentration zones have been proved more efficient than traditional TLC plates (laboratory made or precoated). The concentration zone converts the original sample
spot into a streak or band by sorbing the sample solution.

The various types of sorbent layers used are depicted in Fig. 1.4.

Figure 1.4 - Classification of sorbent phases.
1.8.4 Coating Procedure

The easiest way to coat a plate with a thin-layer of sorbent is to simply pour the slurry on the plate and spread it evenly across the plate with a glass rod. However, this will not produce a layer of uniform thickness. Other methods that may be used are spreading, immersing and spraying. Spreading methods are preferred for a number of reasons, including good reproducibility, ease of adjustment of layer thickness and simple operation.

Glass or plastic sheets and aluminium foils are the most commonly used support for holding sorbent materials in the form of thin-layers. Both laboratory made and commercially precoated layers have been used. Procedures and devices for preparing laboratory made plates are well described by Fried and Sherma (77).

1.8.5 Selection of Sample Solvent

The first consideration before any chromatography to be performed is to decide which solvent should be used to dissolve the sample. Samples and standards are best prepared in a solvent that dissolves the analyte completely, is volatile, has low viscosity, wets the sorbent layer and is a weak chromatographic solvent for the analyte.

1.8.6 Sample Preparation

Often it is necessary to use a number of sample preparation methods together as dissolving of samples, extraction, column chromatography, centrifugation and evaporation to make a sample ready for chromatographic analysis, especially biological samples in order to sufficiently purify a sample so that it is suitable for chromatography. Cations are generally dissolved in distilled water maintaining a concentration such as 1% or 0.1M. Solutions of rare earths are prepared by dissolving in 0.1M HNO₃ or by fusion followed by dissolution in dil. HCl or HNO₃. Anions are taken as their water soluble salts of alkali metals. Methanol or ethanol is generally used as solvent for preparing the sample solutions of organometallics.
1.8.7 Sample Application

It was Kaiser (78) who first realized that the resolution power of the layer depends on the quality of sample application. Improperly applied samples result in poor chromatograms. Sample solution (0.01-1.00%) is prepared in least polar solvent in which sample is soluble. Normally, 1-5 μL of sample solutions is applied as spot or streak on the sorbent layer, about 2-3 cm from the lower edge of the TLC plate in order to avoid the direct contact (or dissolution) of sample with the mobile phase. The sample is completely dried before placing the plate in the developing chamber. Dilute solutions can be applied to the layer either with sorbent drying between successive applications, or after bringing the sample solution to proper concentration.

Micropipette, melting point capillaries, microsyringe etc. are used to apply the sample on the plate. A number of automatic spotters of varying design are also available in the market.

1.8.8 Development

Development is the process in which the mobile phase moves across the sorbent layer to effect separation of the sample substances. Ascending development or linear development is the commonly used mode of development in TLC in which the mobile phase moves upwards through the stationary phase. Any closed container that will hold the plate upright is suitable for development of TLC plate. While performing the development one should take care of the angle of development and saturation of chamber apart from other factors. It has been observed that the angle of development (the angle at which the plate is supported) effects the rate of development as well as the shape of the spots (79). An angle of 75° has been found optimum for development.

If a desired separation is not achieved by simple development, one can follow the options available in the technique. These are summarized in Table 1.2.
## Table 1.2
### Methods for Development of Chromatogram

<table>
<thead>
<tr>
<th>Mode of development</th>
<th>Method of operation</th>
<th>Significance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple development</td>
<td>Development is repeated after drying the plate between each development to achieve satisfactory separation</td>
<td>The process in effect increases the effective length of the layer so as to enhance the possibility of separation. The technique was first applied to TLC in 1955</td>
<td>(80)</td>
</tr>
<tr>
<td>Stepwise development</td>
<td>Plate is developed successively with different mobile phases having different selectivities</td>
<td>Useful for the separation of components with large polarity difference. The procedure was first used by Stahl</td>
<td>(81,82)</td>
</tr>
<tr>
<td>Continuous development</td>
<td>A continuous flow of mobile phase along the length of the plate with the mobile phase being allowed to evaporate off at the end of the plate</td>
<td>The technique was introduced by Mottier and Potterat</td>
<td>(80)</td>
</tr>
<tr>
<td>Two-dimensional development</td>
<td>The plate was developed in a different mobile phase at angle $90^\circ$ to the first development after usual TLC procedure</td>
<td>Applicable for normal, multiple or stepwise mode of developments. The technique is applied for the separation of clinically important substances. First applied in TLC by Kirchner</td>
<td>(83-87)</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
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<td></td>
</tr>
<tr>
<td>Circular development</td>
<td>Mobile phase is carried to the centre of the layer by means of a wick and its flow is towards the centre of the plate. Useful in TLC for the separation of compounds whose $R_f = 1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugal chromatography</td>
<td>Plates are made from circular glass or aluminium with a hole in the centre and is bolted on to the centrifuge. Mobile phase is delivered from a reservoir to the plate at a specified rate while the plate spins. First applied to paper chromatography and has also been used in TLC</td>
<td>(88,89)</td>
<td></td>
</tr>
<tr>
<td>Gradient elution development</td>
<td>Solvent composition of the mobile phase is changed either in steps or continuously. Commonly used in column chromatography, occasionally used in TLC for the separation of lipid mixtures having wide range of polarity</td>
<td>(90,91)</td>
<td></td>
</tr>
<tr>
<td>Reversed-phase partition development</td>
<td>Development employs a relatively nonpolar stationary phase. Mobile phase is relatively polar. Used for the separation of long-chain molecules such as triglycerides, esters, fatty acids, and carotinoids</td>
<td>(92)</td>
<td></td>
</tr>
</tbody>
</table>
1.8.9 Detection or Visualization

After development, TLC plates are dried at or above room temperature to completely remove the mobile phase. The method of visualization is then carried out by physical, chemical or biological means.

An ideal visualization procedure should be able to i) visualize nanogram quantities of separated substances ii) to give a visualized area that is firm on its appearance iii) to give satisfactory contrast between the visualized area and back ground and iv) to give a visualized area that is stable enough and suitable enough for quantitative measurement, if desired.

Physical methods of detection involve spectroscopy, radiography, X-ray fluorescence micro analysis with a scanning collimated primary X-ray beam, UV radiation etc. Among these UV radiation is commonly used due to its high sensitivity.

Chemical methods of detection involve the spraying of TLC plate with a suitable reagent which forms coloured compounds with separated species.

Nanda and Devi have reported an enzymatic method (93) for the detection of heavy metals in fresh water. Nicolaus and Coronelli (94) have reported a microbiological method (i.e. bioautography) for the detection of antibiotics on TLC plates using triphenyl tetrazolium chloride (TTC).

A comprehensive list of detection reagents is available in Volume II of the Handbook of Chromatography, edited by Zweig and Sherma (95). Reagents for specific compounds are found in the data tables of Volume I and in later volumes of this series. In TLC, the qualitative identification of species in a sample is based on the characteristic colour formed with specific spraying reagent in combination with \( R_f \) values (96). The reproduc-
ibility of $R_f$ values of the separated zone is very important for the exact identification of compounds. A high degree of reproducibility of $R_f$ values can be achieved by keeping close control over the following parameters: Sample preparation, volatility and purity of mobile phase, direction and flow rate of mobile phase, chamber saturation, laboratory temperature, sample size, relative humidity, $pH$ of the medium, layer activation temperature, layer thickness and solvent demixing.

### 1.8.10 Documentation

The process of documenting a developed chromatogram consists of evaluation and recording of chromatogram. After noting spot location and colours, $R_f$ values may be measured. Details about development chambers, mode of development, type of thin-layer and mobile phase, sample application, location reagents and methods should be reported while recording a chromatogram. The important ways for documenting a chromatogram are i) documenting by photography, ii) densitometry and, iii) printout from video monitor.

Methods for documentation and storage of chromatograms are best described by Fried and Sherma in one of the chapters of his book, *Thin-Layer Chromatography Techniques and Applications* (77).

### 1.8.11 Quantitation

The three main approaches related to quantitative TLC include i) visual estimation, ii) zone-elution and, iii) *in-situ* densitometry.

**i) Visual Estimation and Spot-size Measurements,**

This is the simplest form of semiquantitative analysis. The accuracy and reproducibility of which fall in the range 10-30%. A definite volume of sample
is chromatographed alongside standards containing known amounts of analyte. After detection, the weight of analyte in the sample is estimated by visual comparison of the size and intensity of the sample zone in the standards. The visual comparison works well if the applied amounts of sample are kept close to the detection limit and the sample is accurately bracketed with standards.

In an attempt to standardize the quantification methods in TLC, Mohammad and Tiwari (97); Shadrin et al. (98); Nanda and Devi (99) and Mlodzikowski (100) have established a linear relationship between the size of the spot and the amount of the analyte.

ii) Zone-Elution and Spectrophotometry

It involves drying the layer, locating the resolved analyte zones, scraping of the separated zones of sample and standards and elution of the analyte from the layer material with a suitable volatile solvent. The eluates are concentrated and analyzed by any independent microanalytical method. Scanning and elution processes are usually performed manually. Spectrophotometry has been the most widely used technique for quantification of eluted species.

iii) In-Situ Densitometry

It is the most preferable technique for quantitation. Substances separated by TLC or HPTLC are quantified by in-situ measurement of absorbed visible or UV-light, or emitted fluorescence upon excitation with UV-light. Absorption of UV-light is measured either on regular layers or on layers incorporated with phosphor. Video densitometers are now available for quantitative densitometric analysis because of their high sensitivity, linear range of calibration curve and better selectivity.
1.9 DEVELOPMENT AND APPLICATION OF INORGANIC TLC

In its early stage TLC was used mainly for the separation of organic compounds. Though the application of inorganic TLC was reported in 1949 by Meinhard and Hall (60), the developments in TLC of inorganic ions appeared in the literature after the work of Seiler (101-103). The work on inorganic TLC up to the end of 1972 has been admirably documented by Brinkman et al. (104) and the work carried out during 1972-1980 has been presented by Kuroda and Volynets (105). The work on TLC of inorganics and organometallics covering the period 1978-1994 has been described by Mohammad and Varshney in chapters of the Handbook of Thin-Layer Chromatography edited by J. Sherma and B. Fried (106-107). A series of review articles (108-112) dealing with different aspects of inorganic TLC have also appeared.

Some of the most interesting recent applications of inorganic and organometallic TLC include, the separation of anions as counter ions of metal diantipyrilmethane cationic complexes and diantipyrilmethane cations (98); identification and separation of metal ions in human placenta (113) and in wool materials (114); preconcentration of geological samples for subsequent ICP-AAS determination (115); separation of heavy metals followed by their determination at ppm levels using square wave anodic stripping voltammetry (116); *in-situ* fluorescence spectra and detection of fluorescent cations on porous glass sheet (117); separation of Zn from Hf (118); effect of heavy metals on separation of periodate from other oxoanions (119); analysis of RE ores (120); complete separation of all noble metals (121); analysis of toxic metals in sea water and industrial wastewater (122); solid state dissociation of metal chelates and reagent in silica gel stationary phase (123); identification of Zn complex formation in a particular silica layer containing
fluorescent indicator during the chromatography of porphyrins (124). Use of N,N-dialkyl-N-benzoyl-thiourea as new selective chelating agents for complexation and enrichment of Pt metals from strongly interfering matrices (125-127); separation of anions in the form of diantipyrilmethane (DAPM) complexes and salts of protonated DAPM; use of reversed - phase salting out TLC to transition metal coordination chemistry (128) and use of polyacrylonitrile as sorbent phase for the separation of mixed amino carboxylato cobalt (III) complexes (129).

Literature published in the period 1973-1996 on the TLC analysis of metal complexes is presented in Table 1.3. The relative proportions of publication on the analysis of metals and metal cations (curve I), anions (curve III) and of metal complexes (curve II) are compared in Figure 1.5. The growth in TLC of metal ions reflected by the shape of the curves (curves I and II) slowed down during 1981-1982 when metal complexes became the choice of investigators. A decline in the number of publication on metal complexes and a subsequent increase in the number of publications on metal ions up to 1987, is, however, noticeable. After 1987, the number of publications on metal ions decreased and the number of publications on metal complexes has increased with the exception of 1994. The number of publications in the field of anion TLC has been lower than that for metals and metal ions and for metal complexes.

The number of publications appearing during 1973-1996 in important chromatographic and analytical journals is shown in Figure 1.6. Investigators have preferred to publish their findings in journals dealing exclusively with chromatography rather than more general analytically oriented journals.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Stationary phase</th>
<th>Mobile phase</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl thiocarbamates of Bi, Cu, Co, Ni</td>
<td>Silica gel G</td>
<td>Dichloromethane-petroleum ether (5+3)</td>
<td>Run 20-30 min. plate activation at 110-120°C for 30 minute</td>
<td>130</td>
</tr>
<tr>
<td>Monothio - β - diketonates Rh (STTA)₃, Co (STTA)₃, Cu (STTA)₂, Pd (STTA)₂, Ni (STTA)₂</td>
<td>Silica gel D</td>
<td>Chloroform - n - hexane (3+7)</td>
<td>Ascending technique; run 10 cm; good separation of metal chelates by elution with CHCl₃; limit of determination is 10 ng for Co and 50 µg for Cu, Ni, Rh and Pd</td>
<td>131</td>
</tr>
<tr>
<td>D and L isomers of tris-ethylenediamine Co (III) complexes</td>
<td>Cellulose, water, d-quartz and Na, K d-tartrate blended in the ratio 40g : 218ml : 10g : 5g</td>
<td>Aqueous mixture of sodium or potassium D -tartrate and / or AlCl₃</td>
<td>TLC of optically active complexes</td>
<td>132</td>
</tr>
<tr>
<td>STTA and its metal chelates</td>
<td>Silica gel (Wakogel B-5)</td>
<td>Monocomponent and bicomponent solvent systems containing alcohols, ketones and esters</td>
<td>Ascending technique; run 10 cm. Separation of Co, Ni, Cu, Zn, Hg, Pb and Cd as their 1,1,1-Trifluoro-4-(2-thienyl) - 4 - mercapto - 3 - buten -2 - one (STTA) chelates.</td>
<td>133</td>
</tr>
<tr>
<td>Sulphate complexes of Pt, Pd, Ir, and Rh</td>
<td>Commercial silufol plates, silica gel Woelm, silica gel KSK</td>
<td>0.1, 1.0 and 6.0N H₂SO₄, 0.2 or 0.5M tetraacetylamine in benzene</td>
<td>Ascending technique, run 7 cm, TLC of the noble elements and their sulphate complexes</td>
<td></td>
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<td>----------------------------------------</td>
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<td>----------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Co(\text{NH}_3)_3^3, Co(\text{en})_3^3, Co(\text{en}_2\text{dip})_3^3, Co(\text{en}_2\text{ophen})_3^3, Co(\text{dip}_2\text{ophen}_2)_3^3, Co(\text{dip}_2\text{ophen}_3)_3^3\</td>
<td>Silica gel G (MN Polygram), silica gel Woelm, aluminium Oxide</td>
<td>Aqueous solutions of various inorganic salts and acids</td>
<td>TLC of cobalt (III) complexes on alumina and silica gel</td>
<td></td>
</tr>
<tr>
<td>β - Diketonates of Fe, Cr and Co</td>
<td>Silica gel</td>
<td>CCl₄, toluene, benzene, dichloro methane, diethyl ether</td>
<td>Ascending technique, run 12 cm; separation of β-diketonates and their metal chelates</td>
<td></td>
</tr>
<tr>
<td>2,2 - Dihydroxy - 5,5 - dimethyl azobenzene complexes of V, Co, Cr, Cu, Ni and Mn</td>
<td>Silica gel G</td>
<td>Benzene - ethanol - 25% aqueous ammonia</td>
<td>Plate development in saturated chamber</td>
<td></td>
</tr>
<tr>
<td>Tetra phenyl porphyrin (TPP) complexes of Cd, Hg, Pb, Rh, Mn, Fe, Co, Ni, Cu and Zn</td>
<td>Silica SHR MN Polygram silica gel, alumina</td>
<td>Benzene - ethanol - 25% aqueous ammonia</td>
<td>TLC development at room temperature; run 15 cm: separation of trace metals</td>
<td></td>
</tr>
<tr>
<td>Complexes of Y, La, Pr, Sm, Dy, Nd, Gd, with the p-</td>
<td>Silica gel - starch (19:1)</td>
<td>Various organic solvents</td>
<td>Development time 0.5 to 4.5 h</td>
<td></td>
</tr>
</tbody>
</table>
dimethylaminoanil of 4-hydroxy-1 naphthyl glyoxal and the p-dimethylaminoanil of 4-acetyl-1-naphthol

<table>
<thead>
<tr>
<th>Substance</th>
<th>Adsorbent</th>
<th>Solvent</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthates of Cu, Ni, Co, Mo, Bi, Pb and Zn</td>
<td>Silica gel</td>
<td>Various organic solvents</td>
<td>Ascending technique; run 10 140 cm</td>
</tr>
<tr>
<td>Diphenylthiovioluric (DPHTV) acid chelates of Ni, Co, Cu, Fe, Pd, Pt and Ru</td>
<td>Silica gel</td>
<td>Carbon tetrachloride-chloroform (10+1), toluene-benzene (10+1)</td>
<td>Ascending technique; run 15 141 cm</td>
</tr>
<tr>
<td>Mixture of Hg Cl₂ and ethyl mercury chloride</td>
<td>Silica gel G and KSK</td>
<td>Hexane - diethylether or acetone (9+1), hexane-acetone (4+1)</td>
<td>Run 10 cm. 142</td>
</tr>
<tr>
<td>Dithizonates of Hg, Ag, and traces of Cu, Bi, Zn, Co, Ni, Pb</td>
<td>Silica gel</td>
<td>Dichloromethane - methanol (9+1), benzene</td>
<td>Ascending technique; run 6 143 cm, application to hydrology and biological samples.</td>
</tr>
<tr>
<td>Cd, Hg, Rh, Pd, Co, Ni, and Zn complexed with acetylthio acetanilide, acetylthio acetate - p - chloroanilide and thiodibenzoyl methane</td>
<td>Alumina</td>
<td>Various organic solvents</td>
<td>Ascending technique; run 10 144 cm</td>
</tr>
<tr>
<td>Anil complexes of Mn, Fe, Cu and Zn</td>
<td>Silica gel - starch (19+1)</td>
<td>Various organic solvents</td>
<td>Ascending technique; layer thickness 0.10 cm. 145</td>
</tr>
<tr>
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<td>Silica gel</td>
<td>Various organic solvents</td>
<td>Ascending technique; layer thickness 0.10 cm.</td>
</tr>
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</tr>
<tr>
<td>Tris (acetylacetonato) Co (II)</td>
<td>Styrargel 60A (polystyrene-divinyl benzene copolymers)</td>
<td>Dioxane</td>
<td>Descending technique; use of polystyrene as an internal standard</td>
</tr>
<tr>
<td>Tc (V) cysteine, Tc (IV) cysteine, Tc (IV) Sn - DTPA</td>
<td>Silica gel H, cellulose (MN-300)</td>
<td>Ethyl methyl ketone, methanol-water (17+3), 0.3N HCl</td>
<td>Qualitative analysis of $^{99m}$Tc species on silica gel and cellulose layers</td>
</tr>
<tr>
<td>Cu, Cd, Hg, Pb, Pd, Fe, Co, Ni and Zn complexes with 3-mercapto 1,3-diphenyl 1,2-propenone (SDBM)</td>
<td>Silica gel</td>
<td>Mono-and two-component organic solvents</td>
<td>Ascending technique: run 10 cm, qualitative separations</td>
</tr>
<tr>
<td>Hg dithizonate</td>
<td>Aluminium foil - backed plates</td>
<td>Carbon tetrachloride - benzene-ethylene dichloride (1+2+2)</td>
<td>Quantitative determination of Hg (I) and Hg (II) by AAS</td>
</tr>
<tr>
<td>Cu, Cd, Pb, Pd, Co, Ni and Zn glyoxal dithiosemicarbazone chelates</td>
<td>Silica gel G</td>
<td>Ethanol-benzene or toluene (1+1 to 1+4)</td>
<td>Ascending technique; glyoxal dithiosemicarbazone as a complexing and chromogenic spray reagent for inorganic TLC</td>
</tr>
<tr>
<td>Metal oxinates (OX),</td>
<td>Chloroform, p-dioxane, benzene, 10⁻³ M H_2O in chlo-</td>
<td>Ascending technique; run 8⁻⁴ C,</td>
<td>152</td>
</tr>
<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>HOX, Cu(OX)₂, Zn(OX)₂, Al(OX)₃, In(OX)₃</td>
<td>roform, 10⁻² M H_2O in CHCl₃</td>
<td>temperature 35 ± 1 °C; TLC of</td>
<td>153</td>
</tr>
<tr>
<td>Silica gel - starch (19:1)</td>
<td>Several organic, mixed organic and mixed aqueous-organic solvent systems.</td>
<td>-</td>
<td>154</td>
</tr>
<tr>
<td>L₁ Cd₁, L₁ AsCl₁, L₁ SbCl₅, L₁ AlCl₃, L₁ ZnCl₄</td>
<td>Methanol, dioxane, nitrobenzene, methanol (1+4),</td>
<td>Ascending technique; run 8⁻⁴ C,</td>
<td>155</td>
</tr>
<tr>
<td>CH₂Cl₆, CH₂Cl₂, CHCl₃</td>
<td>separation and identification of some metal complexes</td>
<td>-</td>
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</tr>
<tr>
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<td>CH₂Cl₆, tetrahydrofuran</td>
<td>Run 8 cm; qualitative analysis of metal chelates of 1-hydroxy-2-pyridinethione</td>
<td>157</td>
</tr>
<tr>
<td>Mixed organic solvent systems containing benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu, Cd, Hg, Se, Pt, Au, Fe, C, Ni and Zn acetamido chelates</td>
<td>Microcrystalline cellulose, various concentrations of Water, 10⁻² M HCl and Sephadex G-10 and G-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal / Complex Type</td>
<td>Sorbent</td>
<td>Solvent / Solvent Mixture</td>
<td>Additional Details</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Mn, Co, Ni, Zn, Rh, Pd, Pt chelates of dithioacetetylacetone</td>
<td>Silica gel</td>
<td>CCl₄, 1,1,1-trichloroethane</td>
<td>Run 10 cm; detection by natural colour of complexes which disappeared during development</td>
</tr>
<tr>
<td>α and β - Napthlylanils of methyleneglyoxal of Ti, UO₂, Au and Hg</td>
<td>Silica gel - starch (19:1)</td>
<td>Various organic solvents</td>
<td>Layer thickness 1mm; temperature 35°C. butanol-hexane - CHCl₃ (1+2+1) was most suitable mobile phase for the separation</td>
</tr>
<tr>
<td>Cis and trans isomers of Co(III) complexes with 1,3- dianimopropane, 1,2-diaminoethane, 1,2-diaminopropane, glycine and β - alanine</td>
<td>Silica gel</td>
<td>Distilled water, various organic solvents</td>
<td>Qualitative separations</td>
</tr>
<tr>
<td>Cu and Hg chelates with quinoline 2-aldehyde thiosemicarbazone</td>
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<td>Different solvent mixtures</td>
<td>The results of separation and analysis of some standard samples</td>
</tr>
<tr>
<td>Transition metal benzoylecetonates and thiobenzoyl acetonates</td>
<td>Alumina, silica gel, cellulose</td>
<td></td>
<td>Among the sorbents studied hydroxylated silica gel gave best results</td>
</tr>
<tr>
<td>Substance Description</td>
<td>Column Material</td>
<td>Mobile Phase</td>
<td>Separation Notes</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------</td>
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<td>-----------------</td>
</tr>
<tr>
<td>Diamminedichloroplatinum (II)</td>
<td>Alumina G, Silica gel G</td>
<td>Iso-butanol-methanol-CCl₄ 0.15M NaCl (9+6+4+1)</td>
<td>Separation of cis, trans 163 diamminedichloroplatinum and their hydrolysis products.</td>
</tr>
<tr>
<td>Seventeen metal diethyldithiocarbamate (DEDTC)</td>
<td>Silica gel</td>
<td>Dichloromethane, benzene</td>
<td>Separation of various 164 isomers</td>
</tr>
<tr>
<td>Cis and trans isomers of tetrahedral and trigonal planar isomers of Hg, square planar and tetrahedral isomers of Zn with p-diethylaminoanil of anthraceneglyoxal and thiourea</td>
<td>Silica gel - starch (19:1)</td>
<td>n-butanol-benzene (1+1), n-butanol, acetic acid</td>
<td>Separation of various 165 isomers</td>
</tr>
<tr>
<td>Ti, Mn, Fe, Co, Cu, Zn complexes with the p-diethylaminoanil of anthracene glyoxal alone and along with thiourea</td>
<td>Silica gel - starch (19:1)</td>
<td>Acetone, n-butanol-benzene</td>
<td>Cations of complexes were identified by means of migration rates and spectroscopic correlations 166</td>
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<tr>
<td>Piperidine -1- carbodithioates of Ni, Cu, Zn, Co, Cr, Mn, Fe.</td>
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<td>Qualitative separations 167</td>
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<td>Highly polar amines</td>
<td>The effect of the mobile phase on the migration behaviour of the chelates 168</td>
</tr>
<tr>
<td>Compound/Complex</td>
<td>Adsorbent/Mobile Phase</td>
<td>Solvents/Conditions</td>
<td>Separation Technique</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>------------------------</td>
<td>----------------------------------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>Sn, Mn, Fe, Co, Ni, Cu, Zr, Y, La, Pr, Sm, Nd, Gd, Dy as their ions and as their complexes with the <em>p</em>-dimethylaminoanil of 3-benzoylmethyl glyoxal (DMABG)</td>
<td>Silica gel G-starch (24:1)</td>
<td>CH₂Cl₂, CHCl₃, CCl₄, C₆H₆, butanol, C₆H₆ - butanol (1+1, 2+1, 1+2)</td>
<td>Ascending technique: layer thickness 1mm, temperature 30±2°C, qualitative separations</td>
</tr>
<tr>
<td>Isomeric complexes of Co(II) and Cu (II) with anil and thiourea</td>
<td>Alumina with plaster of Paris binder</td>
<td>Acetone</td>
<td>Quantitative separations</td>
</tr>
<tr>
<td>Trivalent metal complexes with β-diketones</td>
<td>Silica gel</td>
<td>CHCl₃ and i-Pr₂O</td>
<td>The chromatographic properties depend on ligand structure</td>
</tr>
<tr>
<td><em>d</em>-Block cations complexed with anils</td>
<td>Silica gel G</td>
<td></td>
<td>Spectroscopic detection and identification; quantitative analysis</td>
</tr>
<tr>
<td>Square planar complexes of Pt and Pd with pyridine, hydroxylamine, triphenyl phosphine. SCN⁻, Cl⁻ and NH₃</td>
<td>Silica gel G and H</td>
<td>Single component and multi component organic and aqueous - organic solvent systems</td>
<td>Separation of <em>cis</em> and <em>trans</em> isomers</td>
</tr>
<tr>
<td>Phenyl hydrazine-N-DTC complexes of Ru, Rh, Pd, Fe</td>
<td></td>
<td>CHCl₃, C₆H₆ or ACOEt - CCl₄ (1+4); MeCN - CCl₄</td>
<td>Some of the metal complexes are soluble in Me₂CO</td>
</tr>
</tbody>
</table>
Co, Ni, Ir, Pt. (1+4) whereas others are not; the coloured complexes are visible in daylight

DMSO - metal ion complexes EtOAc media Specific separation of Hg (II) from other metal ion complexes

Metal -8- hydroxyquinolines Mass transfer conc. is equated in terms of separate spot areas for quantification of the concentration of each constituent

Complexes of Ru sulphates Silica gel Acid solutions containing 0.5 -2.0 mL H₂SO₄ The Rₓ values and UV-Vis absorption spectra were measured for five different complexes of Ru sulphates.

Co (II) and Co (III) Silica gel, alumina acetylacetonates Several solvent systems consisting of ketones, esters, alcohols, aqueous butanol, butanol- acetic acid (1+1, 1+2, 2+1) aqueous butanol - acetic acid - CHCl₃ (5+5+1, 5+5+2, 5+5+3) The differential migration behaviours of the compounds of different valencies is discussed; quantitation by spectrophotometry
<table>
<thead>
<tr>
<th>Complex System</th>
<th>Support Material</th>
<th>Method/Extraction</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris (alkylxanthato) Co (II) complexes</td>
<td>Silica gel</td>
<td></td>
<td>The $R_f$ values of the complexes increase with increasing number of alkyl groups; for homologous series there is a linear relationship between the numbers of carbon atoms and the $R_m$ value.</td>
</tr>
<tr>
<td>Transition metal complexes of monothio $\beta$ - diketones</td>
<td></td>
<td>Single and binary solvent systems</td>
<td>Separation pattern discussed in terms of choice of solvent systems and magnitude of $R_f$ values.</td>
</tr>
<tr>
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<td>Mobile Phase</td>
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and Zn (II) containing ligands such as ethylene diamine -N, N-diaceoto - N, N-di - 3 - propionate, ethylene propionate ; 2,4 - pentanedionate; 1- phenyl - 1,3 - butadionate or α - dipyridyl

<p>| Thiocyanate complexes of Re, Mo, V and W | Alumina | HCl solutions containing different amounts of ammonium thiocyanate and SnCl₂ | Qualitative separations, TLC data can be used to determine the optimum concentrations for promoting effective complex formation in solution |
| Metal chelates | Silica gel | | The dependence of Rₜ values is explained on the basis of ion-exchange of metal chelate for the H atom of the silanol groups and the dissociation of the chelates in the stationary phase |
| Seven pairs of cationic complexes and three pairs of neutral cobalt cis, trans isomeric complexes | Polyacrylonitrile | Water aqueous solutions (0.1-1%) of KClO₄ and HClO₄ | The trans isomers have higher Rₜ values than the cis isomers |</p>
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Influence of solvent systems on the $R_f$ values of the complexes and the dependence of the $R_f$ values on the number of carbon atoms in the hydrophobic moiety
Detection limit 4 µg; qualitative separation and identification
Best separation was on silica gel with an eluent of solvent strength 0.45; eluent of higher polarity caused spreading of the spots
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<td>Acetonitrile - xylene (70+30)</td>
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</table>

STTA = 1, 1, 1- Trifluoro -4- (2-thienyl ) - 4 - mercapto - 3 - butene - 2 - one; en = Ethylenediamine; dip - Dipylicdial; Ophen = o - Phenanthroline; OX = Oxyquinoline; \(A = p\) - dimethylaminoanil of 3 - benzoymethyl glyoxal; \(B = p\) - diethylaminoanil of 3 - benzolmethylglyoxal; gly = Glycine; phen = Phenanthroline; bpy = Bipyridine; L = Ligand; DTC = Dithiocarbamate; ala = Alanine; Val = Valine; bzac = 1- phenyl - 1,3 - butanedione ion
Figure 1.6 - Number of publications appearing during 1973 - 1996 in important chromatographic and analytical journals

- $J_1$ J. Chromatography
- $J_2$ J. Liquid chromatography
- $J_3$ J. Planar chromatography
- $J_4$ Chromatographia
- $J_5$ J. Chromatographic science
- $J_6$ Microchim. Acta
- $J_7$ Bunseki Kagaku
- $J_8$ Fresenius J. Anal. Chemistry
- $J_9$ Zh. Anal. Khim
1.10 CONCLUSION

It is apparent from above description that there is always a necessity of developing new application-oriented TLC methods for rapid analysis of inorganic and organometallics. The present work was therefore, taken up and various aspects of the analysis of transition metal and rare earth chlorosulphates using TLC were examined. Aqueous and non-aqueous solvents were used so that the separation potential of this technique may be fully exploited. An effort has also been made to examine the quantitative aspects of some separations. As a result, some very simple, reliable and efficient separations of metal and rare earth chlorosulphates were achieved for the first time.

Quantitative recovery of the metals as their chlorosulphates has been done using titrimetry, spectrophotometry and atomic absorption spectrophotometry (AAS) with preliminary TLC separation. Some important physical parameters, e.g. ionic radii, magnetic moment and number of ‘d’ electrons of central metal atom have been successfully correlated with $R_p$ values.

Chromatographic behaviour of rare earth benzoates (an intermediate compound prepared during the synthesis of rare earth chlorosulphate) have also been investigated. Sorbent layers prepared in our laboratory from mixtures of chicken egg shell and silica gel or cellulose have been utilized for the separation of rare earth chlorosulphates. It is an attempt to develop inexpensive sorbent layer materials for their better utilization in chromatography. The complete work carried out during last five years has been described in the following five chapters.
REFERENCES

59. N.A. Izmailov and M.S. Schraiber, *Farmatsiya*, 3 (1038) 1.
73. C.F. Poole, *J. Planar Chromatogr.*, 1 (1988) 373


141. K.N. Johri and H.C. Mehra, *Chromatographia*, 8 (1975) 244.


