Chapter - I

INTRODUCTION
Organic reagents have an established position in Inorganic analysis. Their use greatly increases the specificity and selectivity of the analytical reactions introducing a simplification and rationalisation of analytical methods particularly in microchemical analysis. Significant advances have been made in recent years towards elucidation of the relation between the structure of organic reagents and their analytical behaviour. Development in theoretical chemistry e.g. ligand field theory of metal ions and their complexes have laid to a greatly increased understanding of the factors which affect stability of metal complexes, nature of their absorption spectra and other factors of analytical interest.

Ligands that can bind with more than one donor atom to the same central metal ion or atom are called chelate ligands or chelators. Binding of a multidentate chelator to a metal ion results in an increased stability of the complexes as compared to monodentate analog (chelate effect) Organic chelating agents have great practical importance. Some of the most frequently used chelating agents include ethylene diamine tetracetic acid (EDTA), piconilic acid, oxalic acid, citric acid, dimethylglyoxime, 8-Hydroxyquinoline etc.

The critical parameters for the design of a new chelating agent are complex strength, solubility of the ligand and its complexes selectivity for particular metals or class of metals and the thermal stability of the chelate complexes. The relative importance of these parameters is determined by practical objective. For example for scale prevention in natural water stability and solubility of the
complex are often the key parameters. To complex a particular metal ion in a mixture of similar metal ion selectivity is the key characteristic. Metal complex stability and kinetics of dissociation are also very important. The most desirable characteristics are also shaped by the conditions under which the substance will be used. These design parameters apply equally to both water soluble chelating agents and to lyophilic chelating agents used as extractants.

Various instrumentation techniques have been used for detection and determination of metal ions. Colorimeter and pH meters are among the oldest instruments used for this purpose. The electrical methods including potentiometry, polarography, conductometry, coulometry etc. are also used. Now various sophisticated instruments like UV, IR, atomic absorption spectrophotometer, flame photometers, chromatography, HPLC, TLC are being often used for detection and determination of elements present in ppm or ppb level.

Among the various analytical techniques available spectrophotometry is still an important tool in trace elemental analysis. This is because of the fact that it is simple, sensitive, economical and less time consuming. By proper choice of organic chromagenic reagents and solvents, this technique can be made sensitive as well as selective. Spectrophotometric methods are based on the relationship between absorption of radiation by the solution and the concentration of the coloured species in it. In order to determine a species spectrophotometrically, it is usually converted into a coloured complex by the addition of complexing agent. A large number of elements can be determined spectrophotometrically.

Earlier complexing agents used were inorganic in nature. For example, ammonia was used for the determination of copper and thiocyanate for ferric
ion and cobalt. The first organic reagent to be used by Illinsky and Knorre\textsuperscript{13} was $\alpha$-nitroso-$\beta$ naphthol. In 1905 Tschugaef\textsuperscript{14} reported dimethylglyoxime as a precipitant for Nickel(II). Since then innumerable compounds have been proposed and studied resulting in many excellent analytical procedures. Low solubility and large molar mass of the chelate which an organic reagent forms favours its use in gravimetric analysis. Absorption technique because of their simplicity, reliability and low cost play an important and vast role in the determination of the elements in trace amounts, for a chelating agent to be of photometric value it must contain chromogenic or fluorogenic as well as chelating groups which may be same. Most chelating reagents of interest to analytical chemist are of the type $HL$ having replaceable hydrogen atom (Monobasic). Such groups are $\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OH}$, $N-\text{OH}=\text{NH}$ etc. and at the same time it must contain other functional grouping like $\text{>C}=\text{O}$, thiocarbonyl ($=\text{CS}$), primary amine ($-\text{NH}_2$), secondary amine ($\text{>NH}$), nitroso ($\text{NO}$), Azo ($N=N-$) etc; in such a position that it may saturate the residual valency of the metal ion giving rise to five or six membered ring. The stability of the chelate is related to acidity of the reagent. In general other factors remaining the same, a chelating reagent $HL$ with a small value of $K_a$ will complex metals more strongly than others with larger value of dissociation constants. Thus weaker the acidic nature of the reagent the stronger is the complexing ability but in acidic solution at fixed $\text{pH}$, the weak acidic ligand will give a lower concentration of $L^-$ and therefore its complexing ability will be low. The presence of high resonating structure in a chelate molecule gives rise to light absorption. Due to nonionic nature, these are usually soluble in non polar solvent hence can be separated from aqueous phase with immiscible organic liquids thus making separation and colorimetric estimation possible.
In general chelating reagents react not only with one or two metals but with a group of metals. The selectivity of the organic reagent and the mechanism of its reaction with metal ion depend on the presence of a functional analytical group. The analytical value of a reagent can be improved by suitable substitution into the molecule of the reagent. According to Kulberg substitution of an electronegative group increases the acidity and decreases the basicity of acid and basic group respectively. There is no known specific reagent, but by right choice of masking agents and judicious conditioning of the reaction environment, the reaction in which a reagent can participate can be made very selective or even specific. Moreover selectivity of reaction often increases as the functional groups which form chelates through two oxygen atoms are charged to those chelating through one oxygen and one nitrogen atom and further when chelation is through two nitrogen atoms. Even greater selectivity is expected when electronegativity of coordinating atom is increased. Such an electronegative atom can enhance acidity and thus make the reagent more selective as the complexes formed are less stable.

Reagents of poor selectivity can often be made to give selective reactions, by using masking agents for other metals. pH, adjustment of oxidation state of other metals, a combination of a selective photometric reaction and a selective separation may result in specific determination.

Chelate formation usually results in a marked change in visible or ultraviolet absorption of the reagent.

The colour intensity of the chelate can be increased by proper substitution in chelating molecule. The effect of substitution has been studied specially with 1, 10 phenanthroline and related compounds.
Sensitivity and selectivity of the methods are increased by the use of mixed ligand also. Complex compounds formed by central ion with two or more different ligands are known as mixed ligands or mixed complexes. Mixed ligand complexes are formed when one ligand does not occupy all the coordination places on central ion, then the second ligand can be incorporated to occupy some or all the remaining coordination places on the metal ion.

In some cases the association of the ions of the second ligand and the first binary complex results in the formation of coordinately saturated mixed complex, if all the valencies of inorganic ion are not compensated since these mixed ligand complexes are coordinately saturated and electrically neutral many of them are readily extracted by organic solvents, so that extraction photometric methods of analysis can be developed\(^{53-63}\).

A number of monobasic and bidentate chelating agents like oxine\(^{64},\) PBHA\(^{65-66},\) dithiozone\(^{67}\) etc. have been reported for extraction photometric determination of traces of various metal ions e.g. V(v), Mo (vi), Cu (II), Co (II), Fe (III) etc. in presence of SCN\(^{-}\) - COOH, etc. i.e. anion or other neutral ligands\(^{68-92}\).

The absorption spectra of these mixed ligand complexes differ from those of the corresponding single ligand complexes in both position and height of absorption maxima. This allows higher sensitivity of the determination to be achieved. In addition the formation of mixed ligand complex, leads to change in other properties of analytical importance such as solubility in water and organic solvents, extraction rate etc.

The increased interest in mixed ligand complex has stimulated development of new methods of analysis and on analytical applications and also on general problems relating to the conditions on the formation of mixed
ligand complexes. The third international symposium on coordination chemistry\textsuperscript{93} (Hungry, 1970) was devoted to research on complex with mixed ligands. The use of mixed ligand have several advantages viz.

1. The sensitivity and specificity of reactions are enhanced
2. The rate of extraction of metal is increased.
3. The hydrophilic nature of complex is minimised.
4. In some cases the hydrolysis of metal is prohibited.
5. The decrease in solubility of the mixed chelate increases the accuracy of gravimetric determination.

Thus an important line of approach in developing more sensitive and selective methods of determining ions is the use of mixed ligands besides the synthesis of new reagents with specific properties.

Geological samples, ores and alloys contain low to high concentration of transition metals. Iron, vanadium molybdenum, copper etc. are common elements and present in geological samples of earth crust. If concentration of transition element is low in ores and environmental compartments, their analysis requires analytical methods of high sensitivity, selectivity and the control of interference effects\textsuperscript{94}.

N- Hydroxyamidines are new type of organic reagents useful for the gravimetric and spectrophotometric determination of some metal ions.

\textbf{N- HYDROXYAMIDINES}

The reaction which involves the interaction of aromation amines (III) with N-aryl-benzimidoyl-chloride (II) resulting in high yield of amidines (IV) are quite general. The synthetic chemistry of the latter has been extensively studied by various researcher\textsuperscript{95-97}. 
This method is capable of extension to the preparation of hydroxyamidines. Ley and other\textsuperscript{98-99} reacted N-aryl-benzimidoyl chloride, II, with N-arylhydroxylamine, V, in absolute ether medium at low temperature and obtained the corresponding hydroxyamidine hydrochloride which on treatment of ammonia gave free base.

Hydroxiamidines have sometimes been confused with amidoxines\textsuperscript{100}.

These studies were principally concerned with the isomerism and reduction of hydroxyamidines. They showed that 1, 2 phenyl-3-p-tolyloxyamidine (VII) and 1 - p - tolyl-2, 3 phenyloxyamidine, VIII are not identical and melt at 175\textdegree{} and 191\textdegree{} respectively.
They further showed that the treatment of alcoholic solution of 1, 2 phenyl-3-p-tolyl-oxyamidine with sulphurdioxide yields the corresponding amidine. These authors also tried to study the hydrolysis of the hydrochloride salts of oxyamidine free bases with the help of conductometric experiments, but unfortunately the analytical potentialities of this group of reagents had remained unexplored.

In 1974, the analytical chemistry of this class of reagents have been discussed by K. Satyanarayana and R. K. Mishra\textsuperscript{101-103}. The study was further extended in our laboratory and more reagents have been prepared and applied for gravimetric and spectrophotometric determination of metal ions\textsuperscript{104-113}. It has been found that in presence of complexing agents like carboxylic acids, phenols, aldehyde, thiocyanate azide etc. bathochromic and hyperchromic effect in the absorption spectra occurs\textsuperscript{114-115}.

**Present Investigation**

It appears from review of the earlier work that not much attention has been paid on the synthesis and complexing properties of this group of compounds. As these compounds promise large field, both of theoretical nature and of analytical value, the synthesis and analytical applications of these reagents, especially in presence of other complexing agents was undertaken. The method developed on this basis were found suitable for determination of transition metal ions in geological materials.
In the present investigation the preparation and properties of five new hydroxiamidines have been reported. These compounds have been characterised in terms of elemental analysis, m.p., U.V. and IR spectra. Methods have been developed for the determination of vanadium (V) with a newly synthesised hydroxyamidine, N-Hydroxy N (4 methyl) Phenyl N' (4 fluoro) phenyl benzamidine hydrochloride and thiocyanate. The reliability of these methods have been tested in BCS steels.

Methods have also been developed for extraction spectrophotometric determination of iron (III) and Mo (V) with the same hydroxyamidines in presence of thiocyanate.

Gravimetric estimation of copper has been worked out with N-Hydroxy N (4 methyl) Phenyl N' (4 fluoro) phenyl benzamidine hydrochloride.

**SPECIAL FEATURE OF HYDROXYAMIDINES**

**AS ANALYTICAL REAGENTS**

The introduction of hydroxyamidine hydrochloride as new type of metal chelating agents, opens a new field, both of synthetic as well as of analytical interests. As compared to the established reagents such as oxine, cupferron, oximes, hydroxamic acid, hydroxytriazine and dithizone, the present compounds have wider scope as analytical reagents. The special feature of these reagents are -

1. The hydroxyamide functional grouping has three sites for substitution with various groups and a better understanding of the influence of substituents in the aromatic system of the reagents will help greatly in carrying out systematic investigations towards the improvement of this class of reagents.
2. The high molecular weight of these compounds favour their use in gravimetric determination of some metal ions.

3. These reagents form intensely coloured and easily extractable mixed complexes with various metal ions in presence of several complexing agents. These colour reaction have been found to be highly sensitive and selective for estimation of these ions.
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