CHAPTER - 1

INTRODUCTION
Organic reagents reacting with a metal ion can be classified into two groups, those which form heteropolar or electrovalent salts and others forming a chelate. The small solubility and large molecular weight of the chelate which they form favour their use in gravimetric analysis. The high intensities of the coloration of the numerous chelates of different metal ions with organic reagents make the latter suitable for the detection and determination of trace quantities of metals by the photometric methods. These complexes due to their nonionic character are usually soluble in non-polar solvents and can be extracted from aqueous phase with immiscible liquids thus making separation and solvent extraction possible. Illinski and Knorre in 1885 suggested 1-Nitroso-2-Nepthol as the first synthetic organic reagent. This reagent was applied for the gravimetric determination of cobalt, before the understanding of the nature and properties of organic compounds was established most of the applications were empirical. The real development in the field of organic reagents started only in 1905. When Tschugaeff reported dimethyl glyoxime as a selective precipitant of Nickel(II), Jaudish and others developed new methods
of analysis using organic compound. Since then several monographs, papers and books\textsuperscript{7-30} have been published on the application of organic reagents in Inorganic analysis.

Organic reagents react with metal ions and form co-ordinate compounds. The area of co-ordination chemistry has been widely developed in the last three decades. Complexes are playing increasingly important roles in industry ranging from anti-corrosion agents and soil treatment agents to medicinal agents which certainly testify for their importance in contemporary life.

The phenomenon of complex formation is really a general one but it is markedly noted during transition metal ions. The formation of a complex is the result of Lewis Acid-Base type of interaction in which one atom with a vacant orbital (generally a metal) attracts the electron pair of another atom generally a non-metal. The metal must possess vacant orbitals and these orbitals must be symmetrically correct, stearically available and of reasonably low energy, so that binding may occur as a result of interaction with donor atom transition elements meet these requirements best hence they form complexes readily.

A metal complex is formed when a number of ions or molecules combine with a central metal atom or ion to form an entity in which the number of atoms directly attached to the central atom exceeds the normal valency (oxidation state) of this atom. Metal complexes may be
neutral (no charge) cationic, (positively charged) or anionic (negatively charged). The groups bonded to central metal atom are called ligands. A ligand may be attached to the central metal atom by more than one donor atom, thus forming a heterocyclic ring, in which case the ligand is called a chelating agent and the resulting complex, a metal chelate. The ligands characterised as mono, bi, tri, or multidentate ligands depending on the number of donor sites (atoms) present in the ligands. Living stone has discussed the particular features of ligands in two excellent reviews\textsuperscript{31,32}.

The structure and stereo-chemistry of complexes are governed by Werner's co-ordination theory and Bayer's strain theory. Crystal field theory and Ligand field theory offer the most practical modern approach to bonding in co-ordination chemistry.

The specificity of an organic reagent and the mechanism of its reaction with metal ion depend on the presence of a functional analytical group, the analytical value of this reagent can be increased by suitable substitution. The introduction of such substituents which Kulberg\textsuperscript{33} calls analytically active group widens the possibility of investigating reagents with more suitable chelating properties. The type of organic reagent used for the determination must be given importance more precisely its specificity and sensitivity should be taken into consideration during the determination of the metal ions.
Suitable adjustment of the conditions of experiment such as temperature, pH, reagent concentration, presence of masking agents, etc. modify the selectivity of the reagent. Extraction with organic solvent is widely used to overcome interferences from foreign ions and to increase the sensitivity of photometric methods of analysis. In modern chemistry solvent extraction plays a great role in colorimetry. An organic reagent when used as an extractant separates the undesirable constituents. Selectivity and sensitivity of the method can be increased by the use of mixed ligand complexes. The complex formed by a metal ion with two or more different ligands is known as ternary or mixed ligand complex. When one ligand does not occupy all the co-ordinating places on the central ion the second ligand can then be incorporated to occupy some or all the remaining co-ordinating places on the metal ion. In some cases association of the ions of the second ligand (charged) and the first binary complex, result in the formation of co-ordinately saturated mixed ligand complex, when all the valencies of the inorganic ions are not compensated. As a result of the fact that the complex formed are co-ordinately saturated and electrically neutral, many of them are readily extracted by organic solvents \(^{34-40}\), so that extraction photometric methods can be developed. Generally bathochromic and hyperchromic shift is observed during the formation of these coloured mixed ligand
complexes \( ^{41-45} \) . A number of monobasic and bidentate chelating agents like oxine, PBHA, Dithiozone, etc. have been reported for extraction photometric determination of traces of various metal ions e.g. \( V(V) \), \( H.O(V) \), \( Fe(III) \), etc. in presence of other anions or neutral ligands \( ^{49-75} \).

In extraction chemistry new methods have been developed which are based on the formation of mixed ligand complexes. Interesting work has appeared on synergistic effects during the extraction of metals with chelating agents and also interesting example of research on the extraction of anionic or cationic chelates \( ^{76-81} \).

Studies have been carried out on the extraction chemistry of compounds of ionic associate type. When mixed ligands are used the selectivity and specificity of reactions are enhanced, the extraction of metal increases in some cases hydrolysis of metal is prevented. Thus the accuracy of the determination is increased.

**HYDROXYAMIDINES AS NEW ORGANIC REAGENTS**

Hydroxyamidines are new type of organic reagents having the functional grouping –

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{N}
\end{array}
\]
The synthetic chemistry of hydroxyamidines has been extensively studied by various researchers. Ley and Holzwasings synthesized seven aromatic hydroxyamidines. Their study was mainly concerned with kinetics of hydrolysis of hydroxyamidine hydrochloride, its isomerism, reduction and analytical potentialities of this reagent remained unexplored.

Recently the analytical chemistry of this class of reagents have been discussed by Mishra et al.\textsuperscript{93-100}. It has been found that these reagents react with metal ions in presence of various complexing agents like carboxylic acids, thiocyanate, azide, etc. giving coloured mixed complexes which have been useful for extraction spectrophotometric determination of these metals\textsuperscript{101-104}.

**Present Investigation**

The literature survey reveals that only few investigations regarding synthesis and analytical potentialities of hydroxyamidines have been carried out. Hence it was thought worthwhile to undertake the study regarding systematic synthesis and analytical applications of these reagents. Five new hydroxyamidines have been synthesised and characterised by elemental analysis and spectral measurements. Their analytical applications have been investigated.
The thesis consist of seven chapters. The first Chapter gives a general introduction relevant to the literature on the topic of the research.

The second Chapter describes the preparation and characterisation of five new hydroxymididine hydrochloride. New hydroxymididine hydrochloride have been synthesised by condensation of N-arylbenzamidoyl chlorides with N-(o-chloro)phenyl hydroxylamine in absolute ether medium at low temperature. These compounds have been characterised in terms of elemental analysis, M.P., UV and I.R. spectra.

The third Chapter describes the reactions of newly synthesised hydroxymidine hydrochloride with metal ions. Hydroxymidine reacts with copper(II), Ni(II) and Mo(VI), and form complexes, which are heavy granule water insoluble and of definite composition and can be used for gravimetric determination of these metal ions. The coloured binary complexes of iron(II) and iron(III) are soluble in ethanol and can be used for spectrophotometric determination of metal ions. Vanadium(V), iron(III) and molybdenum(V) form coloured mixed complexes in presence of SCN, I, which are extractable into various organic solvents and are suitable for extraction spectrophotometric determination of these metal ions.

The fourth Chapter describes the gravimetric determination of copper(II) using N-Hydroxy-N-(o-chloro)phenyl-N'-(2-methyl)phenyl benzamidine hydrochloride. The
reagent has been found to be an excellent precipitant for copper(II) at pH 3.5 - 10.2. The chelate \((C_{20}H_{16}N_{2}OCl)_2Cu\) is stable upto 205°C. The low conversion factor (0.0866) is favourable for determining small quantities of copper accurately. The method is free from interferences of most of the common ions. The complex has been characterised on the basis of elemental analysis, M.P., I.R. and magnetic property. It is paramagnetic. Thermogravimetric and differential thermal analysis of the copper complex have been carried out in order to determine its thermal stability.

The fifth Chapter describes the extraction spectrophotometric determination of vanadium(v). N-Hydroxy-N-(o-chloro)phenyl-N'-(2-methyl)phenyl benzamidine hydrochloride reacts with vanadium(v) in presence of thiocyanate and azide, forming intensely coloured complex which can be extracted in chloroform. Interference due to copper(II) and iron(III) can be eliminated by masking with thiourea and trisodium phosphate respectively. Many common ions including Cr(III), Mn(II), etc. do not interfere. Method has been successfully applied for the determination of vanadium(v) in alloys.

The sixth Chapter presents the new method for the micro determination of iron(III) using N-Hydroxy-N-(o-chloro)phenyl N'-(2-methyl)phenyl benzamidine hydrochloride in presence of thiocyanate. The orange red complex developed on interaction with iron(III) and HCPMBH can be extracted quantitatively, into benzene at .25 -.70 M HCl. On this
A selective, sensitive and rapid method has been developed. The method is free from strict control of analytical variables such as volume of aqueous phase, time of standing, etc. Most of the common ions do not interfere with the determination of iron(III).

The seventh Chapter describes the extraction spectrophotometric determination of molybdenum(V) in presence of SCN⁻. The orange red complex is extractable into benzene. The extraction is quantitative at pH 1.8 - 4.2 in HCl. The method is free from interferences of diverse ions including Fe(III), and vanadium(V). The method is applicable to analysis of alloy and steels.
3. L. A. Tschugaeff, Ber., 36, 2520 (1905); Z. anorg. chem., 46, 144, (1905).
4. O. Baudish et al., Ber., 42, 1164 (1912); 48, 1565 (1915); 49, 180, 191, 203 (1916).
7. F. Feigl, Ber., 56, 2033 (1923).
15. K. Fischer, Angew. Chem., 47, 585 (1934); 52, 312 (1937).


34. G. Irving, "Extraction Chemistry" (Russian translation) Atomizdat, Moscow, p. 64, (1971).


42. V.P. Shmidt, "Extraction with minerals" (In Russian), Atomizdat, Moscow (1970).


44. I.A. Silyum, "Extraction Photometric Methods of Analysis by means of Basic Dyes" (In Russian), Nauka Moscow (1970).


83. C. Mallach, Ber., 9, 1244 (1876).


91. H. Le, Ber., 24, 2622 (1901).

