CHAPTER - I

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Chemically based analyses rely heavily on complex formation, the aim being to provide reagents which give maximum sensitivity and selectivity. Organic reagents have an established position in inorganic analysis. The specificity, selectivity, sensitivity of their reactions with inorganic ions and the solubility and stability of the products of their reactions, are some of the factors which are taken into account in the evolution of analytical methods involving organic reagents.

Ever since Pliny's 1 observation about the use of gall nut tannin for producing a blue colour with iron and preparation of fast dyes from natural dyes with other chemicals 2 the use of organic compounds as reagents has developed as a chemical science itself.

Ilinski and Van Knorre suggested \( \alpha \)-nitroso-\( \beta \)-naphthol as a first synthetic organic reagent 3 for gravimetric determination of cobalt but the systematic research in the field of organic reagents started only in 1905 when Tschugeff 4 reported dimethylglyoxime as a selective precipitant for nickel. Since then several thousand
papers and a large number of reviews and monographs have been published on the use of organic reagents in inorganic analysis\textsuperscript{5-32}. Most important organic reagents are those which form metal chelates in which the metal ion is bound to the ligand via at least two donor atoms. The ligand must possess at least one acid group with a replaceable hydrogen atom and a basic co-ordinating donor group.

The phenomenon of complex formation is a very general one but it is markedly noted among the transition metal ions. The formation of a complex is the result of the Lewis-acid base type of interaction in which one atom with a vacant orbital (generally the metal) attracts the electron pair on another atom generally a non-metal. For bonding to occur the metal must possess vacant orbitals and these orbitals must be symmetrically correct, sterically available and of reasonably low energy. Since transition elements meet these requirements best they form complexes so readily. The groups bonded to central metal atom are called ligands. Ligands are characterised as mono, bi, tri or multidentate ligands depending on number of donor sites present in the ligands. Livingstone\textsuperscript{33} has discussed the particular features of these ligands in detail in two excellent reviews\textsuperscript{34,35} on metal complexes of the reagents containing sulphur, nitrogen, selenium, tellurium or oxygen as donor atoms.
The specificity of an organic reagent and the mechanism of its reactions with metal ion depend on the presence of analytically active group. The analytical value of these reagents can be increased by suitable substituents into the molecule of the reagent beyond the limit of the functional group. There is no known specific reagent. The selectivity of reactions often increases as the functional groups which form chelate through two oxygen atoms are changed 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 the electronegativity of the co-ordinating atoms is increased. Also such an electronegative group may enhance the acidity and thus make the reagent more selective as the complex formed are less stable. Steric factors also govern the selectivity of the reactions.

Temperature, pH, reagent concentration, presence of masking agents, oxidation reduction, etc. are some factors which often modify the selectivity of the reagent. Extraction of the coloured reaction product into an immiscible organic solvent is very often used to increase the sensitivity and to overcome interferences from foreign ions.

Sensitivity and selectivity of the method can be achieved by the use of mixed ligand complexes. Complex
compounds formed by the central ion with two or more different ligands are known as ternary or mixed complexes or different ligand complexes. There are two types of reactions leading to the formation of different ligand complexes, which are very wide spread in the practice of chemical analysis. In the first case different ligand complex is formed when one ligand does not occupy all the co-ordination places on the central ion, the second ligand can then be incorporated to occupy some or all the remaining co-ordination places on the metal ion. In the second case, the metal forms a co-ordinately saturated complex but in the process all the valencies of inorganic ions are not compensated. Thus the mixed ligand complex is formed as a result of the association of the ions of the second charged ligand and the first binary complex. Studies have also been carried out on reactions leading to the formation of different metal complexes where one ligand reacts with two different metals$^{40-53}$.

Formation of a complex between one central ion and two or more different ligands increases the selectivity of the reaction, since the probability of other ions reacting to form similar compounds is reduced. The absorption spectra of these complexes differ from the respective similar ligand complexes, both with respect to position and value of the maximum wavelength. This makes it possible to increase the sensitivity of the determination.
In addition, the formation of mixed ligand complexes leads to changes in other properties of analytical importance viz. solubility in water and in organic solvents, extraction rate, etc. Thus the transition from complexes with a similar co-ordination sphere to different ligand complexes is an effective technique for increasing the selectivity and sensitivity of analytical reactions. The fact that mixed ligand complexes are co-ordinately saturated and electrically neutral many of them are readily extractable by organic solvents, so that extraction photometric methods of analysis can be developed. Increasing work has appeared on synergistic effects during the extraction of metals with mixed chelating agents forming co-ordinately saturated compounds. A number of monobasic and bidentate chelating agents like oxime, P3HA, Dithiozone, 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 other anions or neutral ligands.

As the sensitivity and selectivity of the reactions are enhanced when mixed ligand complexes are formed, the degree of extraction of metal is increased, the hydrophilic nature of the complex is minimised, extraction is quantitative, the complex formed is more stable, new methods should be developed for the determination of ions using mixed ligands besides the synthesis of new reagents.
Present Investigation

Ley and Holzweissig\textsuperscript{96, 97} reported synthesis of seven hydroxyamidines (I). They studied hydrolysis and reduction of this class of compounds but their analytical potentialities remained untouched. Mishra et al.\textsuperscript{98-100} synthesised several new hydroxyamidines and studied their analytical properties.

\[ \text{Ar}^1 - C = N - \text{Ar} \]
\[ \text{Ar}^1 \rightarrow \text{N} - \text{O} - \text{H} \]

The salt forming group $N - OH$ and donor group $= N - \text{Ar}$ (substituted imino), are capable of forming five membered ring. The analytical value of these reagents can be improved by suitable substituents into the molecule of the reagent. The introduction of such substituents which Kulberg\textsuperscript{101} calls analytically active group widens the possibility of investigating reagents with more suitable chelating properties. Hydroxyamidines promise large field, both of theoretical nature and of analytical value, therefore synthesis and analytical applications of these reagents was undertaken.
The thesis consists of five 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 properties of five new hydroxyamidines. The newly synthesised compounds have been characterised on the basis of elemental analysis, m.p., U.V. and I.R. spectra. The reactions of the newly synthesised compounds with several metal ions have been studied with a view to find out analytical usefulness of these reagents in the estimation of metal ions in presence of various complexing agents like carboxylic acids, phenols, aldehydes, azide, thiocyanate, etc.

The third chapter describes the preparation and properties of copper complex. The solid binary complex formed has been characterised on the basis of m.p., elemental analysis, I.R., magnetic measurement and thermal studies. N-Hydroxy-N-(o-chloro)phenyl-N'- (2,6-dimethyl)phenyl benzamidine hydrochloride has been described as a new reagent for convenient gravimetric determination of copper(II).

The fourth chapter describes the colour reactions of N_Hydroxy-N-(o-chloro)phenyl-N'- (p-anisyl)benzamidine hydrochloride with Fe(III) at different pH. Spectrophotometric methods have been developed for the formation of
alcohol soluble coloured complexes. The methods are not selective. However, selective extraction-spectrophotometric determination of Fe(III) using N-Hydroxy-N-(o-chloro)phenyl-N'-(p-anisyl)benzamidine hydrochloride,\textsuperscript{acidi}

The method has been successfully applied for the determination of iron content in ores and biological samples.

The fifth chapter describes the extraction spectrophotometric determination of vanadium using N-Hydroxy-N-(o-chloro)phenyl-N'-(p-anisyl)benzamidine hydrochloride in acetic acid. The validity of the method has been tested for the determination of vanadium content in BCS steel samples.
REFERENCES


7. F. Feigl, Ber., B. 56, 2083 (1923).


9. O. Baudish et al., Ber., 45, 1164 (1912); 48, 1665 (1915); 49, 180, 191, 203 (1916).


42. V.S. Shmidt, Extraction with amines (In Russian), Atomizdat, Moscow (1970).

43. I.A. Blyum and N.N. Pavlova, Zavod. Lab., 29, 1407 (1953).


96. H. Ley, Ber., 34, 2620 (1901).

97. H. Ley and E. Holzweissig, Ber., 36, 18 (1903).


