CHAPTER- 1

1.1 Introduction:

Modern sciences and technology place tremendous demands upon analytical chemist. These demands in recent times have become more meaningful and justifiable in view of the spectacular breakthrough in the area of material sciences. Trace compounds, presence of which was hitherto considered insignificant or not even suspected, pose a great challenge for the analytical chemists in terms of their detection and determination. In the analysis of complex materials,speed has become a factor of considerable significance in recent times and therefore the desire to automate the analysis and to introduce newer and specific reagent presents tremendous challenges in the field of analytical chemistry. The precision and accuracy of the determinations are not only the requirements of modern analysis since analytical chemistry has extended its boundaries into the area of population and development of is materials .In the area of analysis ,organic reagents occupy an important place in the list of analytical reagents.

A good number of Colorimetric methods based on the formation of colored products (soluble or insoluble) through redox reactions rather than the complex formation reactions have been reported. But the complex forming methods still occupy predominant place in chemical analysis. The complex forming reagents are required to possess the functional groups capable of metal complexes.

It is found that compounds containing –OH,-SH and –NO serve as good organic reagents. Some typical compounds reported in the literature are presented, for example. 1-nitroso-2-naphthol-3,6-disodiumsulfonate, o-nitrosophenol, ammonium salt of nitrosophenylhydroxylamine, 4-chloro-1,2-dimercaptobenzene, thionalide, 4-hydroxybenzothiazole, pyrogallol, methoxy salicylaldoxime, mercaptobenzothiazole etc.

A careful analysis of the different reports made in the literature on the use of organic compounds as inorganic analytical reagents suggest that, certain groups are specific for specific metals or groups of metals. These are [=C(OH)-CO-] for germanium, [-CO-CH_2-CO-] for thallium and [-CHOH-COOH] for zirconium etc.

The facts mentioned above indicates that the presence of a coordinating group (>C=N-) together with the acidic groupings (-OH,-SH) seems to favor the reactivity of the compounds with metals such as copper,cobalt,nickel,vanadium,molybdenum,uranium,thorium,ruthenium,palladium,and

zirconium etc. Among the compounds possessing these characteristics, hydrazones or azomethines characterized by the presence of atomic group (>C=N-N<) seems to offer advantageous over others. A large number of such hydrazones find application as spectrophotometric analytical reagents. Since schiff bases also posses similar atomic grouping as present in the hydrazones, a brief account of schiff bases presents in Chapter 2, Table No. 2.1.

1.2 Schiff base

Schiff bases, the derivatives of carbonyl compounds formed in the reaction with amino compounds constitute an important class of organic analytical reagents [1-8].

The compounds containing the azomethine group (>C=N-) possess basic properties by the virtue of the presence of lone pair of the electrons on the nitrogen atom and of the general electron donating character of the double bond. They accept a proton from a Bronsted –Lowry acid to form the conjugate cation. They react with hydroxylic compounds to yield hydrogen bonded complexes in aprotic solvents. The most characteristic feature relating to this basic character of the compounds lies in the formation of complexes with metals. However, the basic strength of the >C=N-group is insufficient by itself to permit the formation of stable complexes by simple coordination of the lone pair to metal ions. Therefore it is essential that, another functional group with a replaceable hydrogen atom, preferably a hydroxyl group shall be present in the molecule of the schiff base near enough to >C=N-group to permit the formation of five membered or six membered ring by chelation with the metal ion. Some of them have been listed by Holm, Everett, chakravarthy and sacconi [9, 10]. The coordination complexes formed with divalent metal ion and also on the nature of the substituent on the nitrogen atom, the substituent if any on the aromatic ring.

Beside the utility of azomethines as complex formers in the analytical field, they are used widely in agriculture and medicine as fungicides and drugs respectively. among the azomethines, hydrazones and semicarbazones are found useful as Anti-convulsants [11].The semicarbazones are also found to possess Anti-tubercular, Anti leprotic, Anti-rheumatic activities. These activities are related to their complex forming abilities with the metal ions [12-15].

In the view of the great complex forming abilities of the azomethines and their metal complexes being used as drugs, the author has synthesized 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) and Diacetylmonoxime-3 amino-4-

hydroxyBenzoylHydrazone(DMAHBH) and studied their spectrophotometric behavior under different pH conditions.

Analytical methods play a vital role in checking the composition of the raw material and finished products in controlling various steps in the metallurgical processes and in the analysis of environmental pollutants. The research in analytical chemistry envisages the development of new methods of estimation that are simple, cheap, rapid, sensitive, accurate and amenable to automation.

Among the several instrumental methods of analysis, spectrophotometer is widely used by analytical chemist for the determination of metal ions, organic compounds and also for the investigation of the behavior of organic compounds under different pH conditions. Investigation of spectrophotometric methods using new reagents has been still in progress in academic institutions and some other research laboratories.