CHAPTER - I

ORGANIC REAGENTS USED IN INORGANIC ANALYSIS

C H A P T E R - I

ORGANIC REAGENTS IN INORGANIC ANALYSIS

The principle of chemical analysis lies in chemical reaction of a substance to be determined with an auxiliary substance, the reagent being added (from Latin reagens). The reagents may be of organic or inorganic origin. However, organic reagents are preferred over inorganic reagents in chemical analysis because they possess many advantages. The identification and determination of substances with organic reagents can often be performed with higher sensitivity and selectivity. The separations are also more effective if organic reagents are employed. Therefore, the scope and number of their applications in analytical practice continue to increase. Organic reagents are also attractive for the simple reason that a large number of them is known and therefore a better choice can be made. It is also possible to synthesise a new "Made to measure " reagent possessing more advantageous properties for a given analytical problem. The reactions of organic reagents with inorganic ions in solution can yield products of various properties. They can exhibit a change in colour, luminiscence, solubility and volatility. The reaction products may be complex compounds, or the other forms of the reagent or an altogether a new organic substance. Besides these types, organic reagents in solution can be

absorbed on a precipitate of inorganic substance, the adsorption

being accompanied by a colour change of the reagent (adsorption

indicators). Solid organic reagents which are insoluble in a

given solvent find applications as ion exchange resins and

chromatographic stationary phases. The formation of a product

which is insoluble in a given solvent can be employed for the

gravimetric determination of metal ions. The same principle

leads to separation of ions if there is preferential precipi-

tation. If the reaction product is less soluble in water than

in organic solvent immiscible with water, the reaction can be

used for solvent extraction of any of its parent constituents.

In many reactions of organic reagents a conspicuous colour

or fluorescenee is developed or conversely a coloured compound

in solution is decolourised during the reaction, or its fluore-

scence is quenched. Such reactions can be applied both for

qualitative test and for spectrophotometeric determinations.

This type of reaction is also employed for end point indication

in acid - base, oxidation - reduction or complexometric titra-

tions, Amongst the most common applications described above,

organic reagents have found wide applications in spectrophoto-

metric analysis mainly for determination of trace amounts

of nearly all common and most rare elements in great variety

of natural materials and industrial products. Now a days ,

spectrophotometric methods are more commonly used because of

general availability of sensitive and high precision modern

spectrophotometers in most academic and industril laboratories.

Furthermore applications of differential techniques with modern spectrophotometer now ensures that sufficiently high precision can be obtained for much smaller amounts of material. This attitude is undoubtely reflected in the great volume of recent literature on spectrophotometric methods of analysis.

Historical Development of Applications of Organic Reagents:

In the 6th century A.D. Varahmihira in India reported the preparation of fast dyes from madder with alum and other chemicals while Pliny noticed the blue colur formed by gallnut tannin with iron. In the 17th century Boyle reported the use of litmus, a vegetable extracts as an acid - base indicator. In the 18th century many more applications of organic reagents were reported. The iron was detected in the form of a prussian blue (Diesbach 1709). Tartaric, oxalic and succinic acids were used for masking of iron (Wenzel 1777). Whereas calcium was precipitated with oxalic acid (Wieglieb 1779). In 19th Century the colorimetric determination of iron (iii) with thiocyanate was worked out (Herapah 1852) and titrimetric determination of silver using same reagent was described (Volhard 1877). Glycerol was advocated for the titration of boric acid (Thomson 1893). 1 - Nitroso - 2 - naphthol was reported as precipitant for cobalt (Ilinski, Von Knorre 1885). The systematic study of the reactivity of organic reagents with the inorganic ions began after the development of Werner's theory of complex compounds in 1891 and Brunek's observation in 1907 that diacetyl dioxime acts as a specific reagent for

nickel which gives deep red weighable precipitate. The develop-
ment of the theory of reactivity of organic reagents and the
investigation of numerous applications in spot tests are due
to Feigl.

The following some selected families of organic reagents
have found general applications.

1. **Ligands with donor atoms O, O.**

This family includes poly phenols and aromatic hydroxy
acids, such as 5 - sulphosalicylic acid, chromotropic acid and
tiron. These organic reagents form colored chelates with
transitionmetals like titanium (IV), iron (III), Vanddium (V)
etc.

2. **Ligands with donor atoms N, N and O, N**

Aromatic nitrogen contdining bases such as 1,10 - phe-
nonthroline, 2 2' - bipyridyl and their derivatives are
mainly used for determination of iron and copper. 8 - Hydro-
xyquinoline and its derivatives containing N, O donors fowm
metal complexes that are not ionic in nature. PAN, PAR and
Arsenazo form with a number of metal ions intensely colored
complexes.

3. **Ligand with donor atoms S, S and S, N.**

These reagents contain thionic and thiolic groups as
exemplified by dithiocarbamates, dithizone, dithiols, 8 -
mercaptoquinoline or xanthates. They form highly coloured
complexes with heavy metals . The metal chelates are usually

soluble in organic solvents and are useful in extraction photometric determinations.

Desirable Properties of Organic Reagents.

Organic reagents used in colorimetric reactions should be sufficiently stable and resistant to aerial oxidation or to light. The same should hold for the reaction product. The product should exhibit a characterstic intense absorption band well separated from that of the reagent and the substance being determined.

The reagents for which the characterstic absorption bands coincide with that of the product are not suitable for spectrophotometry but can be used when absorption coefficents differ by a factor of at least 2. Products forming homogenous solutions in a given solvent are more suitable for photometoric measurements than those giving colloidal dispersions, or even turbid solutions. The formation of stable metal complex requires the presence of acidic or basic analytical functional groups in the molecule of the reagent preferably in those positions which allow the formation of 5 or 6 membered chelate ring.

In these groupings the most common donor atoms are O, N and S. When both donors are sulphur atoms, the formation of stable four membered ring is also possible. The colorimetric complexes are formed only when organic reagent has π electron chromophoric groups in the molecules. The cyclo group should

also form a part of π electron system and no insulation

group is permitted between the aci group and the congugated

system of the molecule. The complex forming properties of

organic reagents can be influenced by introducing suitable

substituents into their molecules. The stability of the complex

is usually increased by higher basicity of the ligand. This

can be achieved when electron donor substituents are present

in position meta or para to the active grouping. When a bulky

substituent is close to the functional grouping, the reactivity

of the reagent may be decreased or even lost owing to the

steric effect. In this manner it is sometimes possible to

increase the selectivity of the reagent. The replacement of

oxygen by sulphur as a donor atom often leads to higher

selectivity and sometimes even to higher intensity of colour.

Though some reagents form sufficiently stable complexes, they

do not possess properties desirable for spectrophotometry.

A more suitable derivative can sometimes be obtained by intro-

ducing chromophoric groups into the molecule or increasing

the number of aromatic or hetrocyclic rings. In this way the

greater delocalisation of electrons can be achieved which

brings about bathochromic shift in the absorption spectra

of metal complexes. The selectivity can often be increased by

extraction of reaction product, thus it is possible to separate

the component to be determined from other interfering substances.

Selectivity can also be increased by pH adjustment or by masking.

The masking reagent should be colourless and should not form

any complex with the metal being determined or react with

the colorimetric reagent. It is sometimes important to choose

the right order of adding the masking agent and colorimetric

reagent. In some cases the interferences can be suppressed by

changing the oxidation number of the interfering ion.