PART 1
THEORETICAL
CHAPTER I

ORGANIC REAGENTS IN ANALYTICAL CHEMISTRY
Organic reagents are being used in ever increasing numbers ever since the introduction of dimethylglyoxime as an analytical reagent for the detection and determination of nickel by Tschugaeff in 1905. This reagent is highly sensitive and extremely specific for nickel. This gave an impetus to the systematic investigation of other organic compounds for use in inorganic analysis. Through their use many traditionally difficult separations have been simplified. Extreme sensitivities once possible only with a few elements are now commonplace.

There is voluminous literature on the use of organic analytical reagents and it is briefly surveyed in the following pages.

The reactions with organic reagents may be classified as follows:

(1) reactions not involving valence changes
(2) oxidation-reduction reactions, and
(3) reactions involving the formation of complex compounds

(1) Reactions not involving valence changes: The acid groups such as -COOH and -SH which react with metal ions to form simple salts can be included in this group. They are very useful as precipitants for thorium, the rare earths, zirconium and hafnium. Benzoic, diphenic and sebacic acids are employed for the estimation of thorium. But most of the organic acids used form complex compounds instead of simple salts.
The weak organic acids and bases are used as pH indicators. The phthaleins, the sulphophthalein, thiazo, the nitro and triphenyl methane dyes are some of the important classes of indicators that are used. Substitution reactions are sometimes employed in the determination of metals. Zinc dibenzyl-thiocarbonate\(^{10}\) is used as reagent for the estimation of copper in dilute acid solution.

(2) Oxidation and reduction reactions: Only a few organic reagents are used as oxidants in inorganic analysis. Chloramine-T was proposed by Noll\(^{11}\) as an oxidimetric titrant. It reacts like a hypochlorite solution.

\[
p - \text{CH}_3 \text{C}_6 \text{H}_4 \text{SO}_2 \text{N} \xrightarrow{\text{NaCl}} + \text{H}_2\text{O} \rightarrow \text{CH}_3 \text{C}_6 \text{H}_4 \text{SO}_2 \text{NH}_2 + \text{NaOCl}
\]

It is used for the determination of As(III), Sb(III) and Sn(II) and as a substituent for iodine in titrimetry.\(^{12}\)

Examples of organic reducing agents are more numerous. Oxalic acid and its sodium salt are primary standards. Hydroquinone\(^{13,14}\) precipitates gold from 1.2 N HCl, separating it from platinum, palladium, selenium and tellurium. Thionalide metal complexes are being volumetrically determined with iodine, the thionalide being oxidized to dithionalide. Ascorbic acid\(^{15}\) is used for the direct titration of ferric iron.

Mention may be made of the redox indicators\(^{16,17}\).
(3) **Reactions involving formation of complex compounds:** Werner complex compounds (chelates) contain a central atom or ion, usually a metal around which are grouped or co-ordinated a number of attached atoms or groups (ligands). The co-ordinating groups can be either charged atoms or radicals (generally negative) or whole molecules. Ligands are unidentate or polydentate, depending on whether they have one or more than one co-ordination atom. When a polydentate group combines with a metal, one or more rings may be formed giving rise to chelate compounds.

The types of analytical applications may be broadly classified as follows: (1) Spot tests, (2) Masking, (3) Solvent extraction, (4) Colorimetric methods, (5) Titrimetry and (6) Gravimetric methods.

(1) **Spot tests:** Feigl\(^{18}\) recorded a large number of organic reagents suitable for spot test analysis. Such reagents are characterised by high sensitivity and selectivity. In some cases they are also highly specific. The sensitivity of a test is composed of two factors viz., (a) limit of identification and (b) limit of dilution.

The identification limit is the minimum quantity of a substance which could be detected by a particular technique. The following simple relation between identification and dilution limits was suggested by Feigl:
Dilution limit = 1 : \[ \frac{\text{vol. test soln. (in ml.)} \times 10^6}{\text{limit of identification (in micrograms)}} \]

The term selectivity deals with the magnitude of interference from other ions present in the solution, when this is a minimum the reagent is said to be specific.

(2) **Masking:** Dimethylglyoxime precipitates nickel in ammonia medium. Iron and aluminium if present precipitate as hydroxides. To prevent this tartaric acid is used which combines with iron and aluminium forming complexes. Citric acid, tartaric acid, higher alcohols, glycerol and mannitol have been used as masking agents. These agents increase the selectivity of reagents. Citrate prevents many metals being precipitated by dithizone.

Ethylenediamine tetraacetic acid is a well known masking agent. It forms stable water soluble complexes with most of the metals, with alkaline earth metals and to some extent with alkali metals.

(3) **Solvent Extraction:** The inner complexes containing no acidic or basic groups are generally soluble in non-polar solvents. These solvents are immiscible with water and therefore extraction procedures are possible with the complexes.

Sandell\(^{19}\) has derived the equation for the extractability of complexes as a function of acidity and reagent concentration. If the cation \(\text{Me}^{+n}\) reacts with reagent HL to give the extractable
compound. \(MeL_n\) then

\[
(MeL_n)_\text{org}/(Me^{+n})_\text{water} = K (HL)_\text{org}/(H^+)_\text{water}
\]

Where \(K\) is the extraction constant.

Dithizone is a typical example. The theory of dithizone extractions has been developed by Kolthoff and Sandell\(^{20}\) and by Irving and Williams.\(^{21}\) The extraction coefficient for zinc dithizionate is \(E = K \ (H_2D_2)_0^2 / a(H)_W^2\).

(4) **Colorimetric methods:** A wide variety and large number of organic compounds are in use for colorimetric analysis. The intense colors of many inner complexes of metals make these complexes exceptionally useful for colorimetric and spectrophotometric determinations. The more sensitive reagent permits the determination of about 0.1\(\gamma\) of a metal or about 0.1 p.p.m.

The water soluble complexes can readily be determined colorimetrically directly in the reaction solution whereas the water insoluble complexes are extracted with organic solvents in which these complexes are soluble.

(5) **Titrimetry:** In volumetric analysis the principal application of organic reagents is as indicators. These may be classified as (a) acid-base, (b) oxidation-reduction and (c) adsorption precipitation titrations (Kolthoff and Stenger).\(^{22,23}\)

Volumetric methods have been developed for some metal complexes wherein the complex, after having been washed free
of excess reagent is dissolved and then determined by an appropriate titration reaction involving the organic ligand. A familiar example is the bromometric titration of 8-quinolinol complexes. Estimation of aluminium, magnesium and zinc is carried out by Hahn\textsuperscript{24} by this method.

When a complex is formed the hydrogen ions are liberated; numerous volumetric methods are used for the direct determination by acid-base titrations particularly with 8-quinolinol complexes.

Direct and indirect volumetric procedures have been developed with EDTA and the end point is detected by a metal indicator.

Amperometric titrations can be used when the element being determined, the reagent, or both produce well defined cathodic or anodic polarographic waves.

(6) \textbf{Gravimetric Methods:} Organic reagents in gravimetric analysis may be classified as follows:

(a) \textbf{Hydrolytic Reagents:} Urea, urotropine and phenylhydrazine have been used to precipitate metal ions. (By the hydrolysis of urea the pH is increased). The advantages of this homogeneous precipitation are: (1) it permits the addition of a precipitant at a nearly ideal rate sought but rarely attained in a direct precipitation process carried out in the usual manner, (2) concentration effects are eliminated,
(3) the precipitate formed is dense and readily filterable and (4) coprecipitation is lesser. Aluminium, calcium, copper and gallium\(^{25}\) were estimated using urea. Gallium could be determined and separated from zinc, manganese and calcium.\(^{26}\)

(b) **Adsorption reagents:** Tannin with cinchonine or antipyrine have been used as adsorption reagents for precipitation of metals. The precipitate is of indefinite composition and hence it is ignited to the oxide and weighed. A detailed description of these reagents is given by Scholler and Powell.\(^{27}\) It has been employed for the precipitation of titanium and tungsten. Tannin has also been used for the precipitation and separation of niobium and tantalum from other metals.

(c) **Chelating agents:** Probably the largest number of recorded cases of precipitation by organic compounds involves the formation of unionised chelate complexes. There are three main types of compounds: (1) addition compounds, (2) penetration compounds and (3) chelates (inner complexes).

(1) **Addition compounds:** A typical example of this group is CrCl\(_3\)Py. In aqueous solution this compound is not an electrolyte - a fact that is expressed by co-ordination formula

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{Cr} \\
\text{Py} \\
\text{Py}
\end{array}
\]

Py = Pyridine

consequently, the nature of addition compounds is such that the bond between the central atom Cr and the anionic constituent Cl
is not broken. It is so quickly stabilised by entrance of further ligands that it becomes non-ionic.

(2) Penetration Compounds: Ligands enter between the anionic constituent and the cationic constituent (central atom) and loosen the bond between anion and cation. Tetra ammine cupric sulphate is an example:

\[
\text{CuSO}_44\text{NH}_3 \rightarrow \left[\begin{array}{c}
\text{H}_3\text{N} \\
\text{H}_3\text{N}
\end{array}\right]^{++} \text{Cu} \left[\begin{array}{c}
\text{NH}_3 \\
\text{NH}_3
\end{array}\right] \text{SO}_4''
\]

In this, only the ammonia molecule but not the $\text{SO}_4''$ ions are bound to the copper by auxiliary valences.

In certain compounds ring systems are formed through the action of auxiliary valences. Usually organic compounds of higher molecular weight are the attached groups in these molecules. Thus ethylenediamine forms complex ions; for example

\[
\left[\begin{array}{c}
\text{CH}_2\text{-NH}_2 \\
\text{CH}_2\text{-NH}_2
\end{array}\right]^{++} \text{Cd} \left[\begin{array}{c}
\text{NH}_2\text{-CH}_2 \\
\text{NH}_2\text{-CH}_2
\end{array}\right]
\]

The cadmium is thus bound completely to the two $\text{NH}_2$ groups of each diamine molecule with the formation of stable five membered rings and consequently one molecule of diamine occupies two co-ordination positions.

(3) Chelates (Inner Complexes): Ley\textsuperscript{28} defined an inner complex salt as one in which a metal atom manifested auxiliary valence towards certain atoms of the acid radicle.
Sidgwick\textsuperscript{29} classified chelating agents according to the relative number of acidic and coordinating groups. Diehl\textsuperscript{30} divided the chelating agents into classes based on the number of reactive groups (unidentate and bidentate etc.) and then within each class, by the distribution of the groups between acidic and coordinating types.

The important acid groups are the carboxyl, sulphonic, enolic hydroxyl, phosphonic, oxime and the primary and secondary amino groups.

The donor or coordinating groups of organic chelating reagents contain oxygen, nitrogen and sulphur atoms. The most common donors are the oxime, imino and substituted imino, thioether, keto, thiketo, alcoholic hydroxyl and primary, secondary and tertiary amino groups. In the following description Diehl's classification\textsuperscript{30} is followed.

(1) $\Theta$-Dithiol Group

The $\Theta$-dithiol (dimercapto) compounds containing the group $-C(SH)-C(SH)-$ were first investigated as analytical reagents by Clark.\textsuperscript{31-34} Metal ions readily replace the hydrogen of aromatic $-SH$ groups. These compounds resemble hydrogen sulphide ($H_2S$) in their reactions. The reaction with metal ions involves the formation of five membered rings.
The first dithiol proposed by Clark was 4-C1-1-2-dimercapto-
benzene which is very unstable and has been superceded by the
more stable Toluene-3,4-dithiol, commonly known as dithiol.

Dithiol is mainly used for the estimation of tin,
molybdenum and tungsten. The red turbidity produced by the
reaction of tin with dithiol is measured photometrically.35,36
Tungsten and molybdenum37,38,39 form extractable complexes with
dithiol. By control of acidity and temperature it is possible
to determine either element in the presence of each other.

(2) Diketones and related compounds

The 1-3 diketones are characterised by the grouping -C-C-C-
and they function as versatile reagents because of the ease
with which they enolise. Acetyl acetone and thenoyl trifluoroacetone
(T.T.A) are the two important compounds of this group.

Acetylacetone reacts with more than 60 metals. Most of
the chelates formed are soluble in excess reagent or in solvents
such as carbontetrachloride. Procedures have been described
using E.D.T.A as a masking agent for the selective extraction
of beryllium and of uranium.40

Among the metals reacting with T.T.A are the actinides,
lanthanides, zirconium, hafnium, thallium, iron and lead. The
principal application of T.T.A is in the isolation of zirconium
and the actinide metals41 for subsequent radiochemical measurement.

The various hydroxy anthraquinones are compounds of different
character. 1,2-dihydroxyanthraquinone42(alizarin) forms an inner
complex with aluminium forming a six membered ring.

Quinizarin (1,4-dihydroxyanthraquinone), 1-amino-4-hydroxyanthraquinone and purpurin (1,2,4-trihydroxyanthraquinone) are some of the important quinones used. 1-amino-4-hydroxyanthraquinone gives intense fluorescence with thorium in acid medium and with beryllium in alkaline solution. These reactions were studied by Sandell.\textsuperscript{19}

The related flavones such as Morin and Quercetin are especially interesting, not only because of the intense colors of their products with some metals but also because of the frequent fluorescence exhibited. Morin is used as a sensitive test for aluminium.\textsuperscript{44}

It has been shown that various 2,3,7-trihydroxy-6-fluorone derivatives when substituted in the 9-position give intense colours with Sn(IV) and Sb(III).\textsuperscript{43}

(3) 8-Quinolinol and its derivatives

Hahn\textsuperscript{24} introduced the reagent for the gravimetric determination of aluminium, zinc and magnesium. Despite its lack of
selectivity, useful separations and determinations are possible by pH control, the use of masking agents, solvent extractions and prior separations.

The chemistry and analytical applications of 8-quinolinol and its derivatives are surveyed completely by Hollingshead and also by Welcher. Extraction procedures are treated by Morrison and Freiser.

The structure of chelate compound with metal ions is shown below.

\[ \text{(4) } \alpha\text{-Acyloin oxime group} \]

\[ \alpha\text{-acyloin group} = C(\text{OH})-C(=\text{NOH}) \text{- is highly selective for copper, forming green water insoluble complexes. The reaction of acyloin oximes were studied extensively by Feigl and co-workers.} \]

\[ \alpha\text{-benzoin oxime is the only one of the } \alpha\text{-acyloin oximes that is used as an analytical reagent. Feigl gives the following structure for its copper complex:} \]
It also precipitates molybdenum quantitatively from mineral acid solution (Knowles).

(5) 6-hydroxylaldoximes and ketoximes

Bphraim found that the salt formed with copper and salicylaldoxime was insoluble in dilute acetic acid and hydrochloric acid. The reagent acts as a monobasic acid. It was confirmed by methylation studies of Feigl and Bondi that the hydrogen of the OH group is replaced by copper and therefore the nitrogen atom of the oxime group coordinates with it. Bphraim later confirmed this by the reactions carried out with copper and other aldoximes.

Feigl and Bondi (loc.cit) showed that aliphatic hydroximes, such as chloral acetophenoneoxime CCl₃-CH(OH)-CH₂-C(=NOH)-C₆H₅ and methyl acetonyl carbinoloxime CH₃-CH(OH)-CH₂-C(=NOH)-did not give colours or coloured precipitates with copper acetate. This shows conclusively that the presence of the acidic phenolic hydroxyl is necessary to provide the replaceable hydrogen.

The yellow colour of the silver salicylaldoxime does not change with the introduction of chlorine in 5-position whereas NO₂ group in the same position changes its colour to red. Another interesting observation made by Flagg and Purman was about the colours of the substituted salicylaldoxime with ferric
salts. Ferric salicylaldoxime was red, chlorine compound was blue, while the nitro-derivative was violet.

(6) o-Nitrosophenol group

The o-nitrosophenols contain the reactive group = C(NO)-C(OH) = which forms chelate complexes with a number of metals among which cobalt and palladium are important.

o-Nitrosophenol, α-nitroso-β-naphthol, nitroso-R-salt
(2-hydroxy-1-nitrosonaphthalene-3, 6-disulphonate) and
β-nitroso-α'-naphthol are some of the important nitrosophenols. According to Feigl, the reactive form is the tautomeric isonitroso oxime with metal replacing the oxime hydrogen.

\[
\begin{align*}
\text{NO} & \quad \text{OH} \\
\text{N} & \quad \text{OH} \\
\text{O} & \quad \text{Me}_n
\end{align*}
\]

α'-Nitroso-β-naphthol was first prepared in 1884 by Ilinski and its application to the determination of cobalt was described by Ilinski and Knorre. Although cobalt, iron, copper, palladium, vanadium, zirconium and rhenium are all precipitated by this reagent, it has been applied most often to cobalt determination.
(7) **Thionalide (Thioglycollic Acid β-Aminonaphthalide)**

The reactive group -NHOCH\(_2\)SH is present in both thioglycollic acid anilide and in the homologous compound thionalide \(\text{C}_{10}^7\text{NHCOCH}_2\text{SH}\). Of the two compounds thionalide is decidedly a more important analytical reagent. Thionalide reacts with most of the metals of hydrogen sulphide and ammonium sulphide groups in acetic acid medium.\(^{57-59}\) The metal complexes may have one of the three following structures:

\[
\begin{align*}
\text{C}_{10}^7\text{NH} & \quad \text{C}_{10}^7\text{N} \\
\downarrow \text{CH}_2 & \quad \downarrow \text{CH}_2 \\
\text{S} & \quad \text{S}
\end{align*}
\]

Thionalide is the only quantitative organic precipitant for ruthenium.\(^{60}\)

(8) **Dithiocarbamate and Xanthate Groups**

Sodium diethyldithio carbamate the most widely used reagent of this group was introduced by Delepine\(^{61}\) as a reagent for copper. The structure of copper complex is shown below.

\[
\begin{array}{c}
\text{S} \\
\text{Cu} \\
\text{S} \\
\text{S} \\
\text{C} \quad \text{O} \quad \text{CH}_3
\end{array}
\]

Several xanthates have been used as reagents for some of the metals particularly of copper, with which yellow colours are produced. Potassium ethyl xanthate \(\text{C}_2\text{H}_5\text{OSSK}\), is the most widely used reagent of this group. Scott and Derby\(^{72}\) introduced
it as a reagent for copper. Molybdenum\(^7\) can be separated from tungsten by extraction of the ethyl xanthate complex with chloroform.

(9) Mercaptobenzothiazole

Mercaptobenzothiazole, \((C_7H_5NS_2)\) gives precipitates with all the metals precipitated by hydrogen sulphide in acid medium, except for members of the arsenic and molybdenum groups.

Thallium(I)\(^{54b,62}\) is the only ion quantitatively precipitated. The salt structures are given below (Feigl).\(^{54b}\)

![Chemical structures](attachment:image)

(10) Dithiooxamide (Rubesanic acid)

According to Feigl and Kapulitz\(^63\) the tautomeric forms of dithiooxamide are

\[
S = C-\text{NH}_2 \quad \longleftrightarrow \quad HS-C = \text{NH} \quad \longleftrightarrow \quad \left[\text{S-C = NH}\right]^{-2} + 2\text{H}^+ \\
S = C-\text{NH}_2 \quad \longleftrightarrow \quad HS-C = \text{NH} \quad \longleftrightarrow \quad \left[\text{S-C = NH}\right]
\]

Yaffe and Voigt\(^64\) found that it behaved like a monobasic acid. It forms insoluble coloured complexes with copper, cobalt, nickel, iron, silver, bismuth, mercury, palladium and platinum.
The following structure is given for the complexes of copper, nickel and cobalt:

\[
\begin{align*}
\text{HN} & = \text{C} - \text{C} = \text{NH} \\
\text{S} & \quad \text{S} \\
\downarrow & \\
\text{M} & \\
\end{align*}
\]

(11) Dithizone

Dithizone, \(C_6H_5N\text{H}_2\text{NCSNH}_2\text{C}_6H_5\), was first prepared and studied by Emil Fischer\textsuperscript{65} and latter it was applied to metal analysis by Hellmut Fischer. Dithizone exists in two tautomeric forms.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH} & \begin{array}{c} \equiv \text{N} \\ \text{C} - \text{SR} \end{array} \\
\text{C}_6\text{H}_5\text{N} = \text{N} & \end{align*}
\]

Enol

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH} & \equiv \text{NH} \\
\text{C} & = \text{S} \\
\text{C}_6\text{H}_5\text{N} = \text{N} & \end{align*}
\]

Keto

Fischer\textsuperscript{66} formulated the following structures for monovalent and bivalent metals:

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 \\
\text{NH} & \equiv \text{N} \\
\text{N} & \equiv \text{N} \\
\text{S} & = \text{C} \\
\text{N} & = \text{N} \\
\text{C}_6\text{H}_5 & \\
\text{Me} & \equiv \text{C} \\
\text{N} & \equiv \text{N} \\
\text{Me} & \equiv \text{C} \\
\end{align*}
\]
Dithizone is the only known acidic organic reagent which under the conditions of its practical analytical applications can function towards a given metal as either mono or a dibasic acid. This reagent has been reviewed extensively by Sandell,19 Wichman67 and Fischer.66

(12) *Cupferron and related compounds*

Baudisch68 in 1909 reported that cupferron (I) quantitatively precipitated iron and copper from mineral acid solution.

This reagent finds several analytical applications (Prodinger).5 Baudisch and Holmes reported the reactions of neocupferron (II) and found that the uranium, neodymium and cadmium salts were soluble in organic liquids whereas the precipitates obtained with cupferron were not soluble. The precipitates obtained by these reagents were not of definite composition and the estimations
were completed by ignition to the respective metal oxides.

The reactive group is \(-N-N = 0\) which permits the formation of typical five membered chelate.

(13) **Dioximes**

The dioximes containing the grouping \(-C(\text{\text{\text{-}}NOH})-C(\text{-NOH})-\) were among the first organic reagents to be applied (Dimethylglyoxime by Tschugaeff)\(^6^9\) to inorganic analysis. They are excellent reagents for nickel, palladium and a few other elements.\(^7^0\) The structure for Ni(Pd) dimethylglyoxime is:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \text{N} & \quad \text{N} & \quad \text{O} \\
\text{H} & \quad \text{O} & \quad \text{N} & \quad \text{N} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{CH}_3
\end{align*}
\]

\(^\alpha\)-Puril dioxime: The compound was first recommended by Soule\(^7^1\) as a reagent for nickel. Using this reagent nickel and palladium can be separated by controlling the pH of the medium. It is also applied for the estimation of nickel in steel.\(^7^0\)
REFERENCES


   and Volumetric Analysis", Interscience, N.Y., (1948).

5. Prodinger, W., "Organic Reagents used in Quantitative Inorga-

   Chemistry", Part I, 2, 835-916, Interscience, N.Y.,
   (1961).


    (1952).


    373, (1937).
33. Clark, R.E.D., Analyst, 82, 177, (1957).
34. Clark, R.E.D., Analyst, 82, 182, (1957).
51. Feigl, F., and A. Bondi, Ber., 64, 2819, (1931).
52. Ephraim, F., Ber., 64, 1210, (1937).
55. Ilinski, M., Ber., 17, 2581, (1884).
60. Beamish, F.E., Talanta, 1, 3, (1958).

70. Diehl, H., "The Applications of the Dioximes to Analytical Chemistry," G.F. Smith, Columbus, Ohio, 1940, (a) pp. 35-46, (b) p. 53.

