CHAPTER - 1

INTRODUCTION
INTRODUCTION

Organic reagents are used in inorganic analysis from the earliest times, but a systematic study of these reagents was not done and no theoretical basis was provided for the methods used. In the last 70 years a thorough investigation has led to better understanding of the reactions that take place between various metal ions and organic reagents and this has put these methods on a firm footing. Many analytical investigations have been carried out for the development of new organic reagents, in exploring the important applications in micro-analysis, gravimetry, titrimetry, colorimetry, spot tests etc.

Many organic compounds having convenient preparations and reactivity have been recognised as reagents only within the few years. Many organic compounds are used as solvent extraction media, flotation reagents, wash materials, protective colloids, indicators, primary standards in titrimetry etc. but are not designated as organic reagents. Not the reactivity, but the analytical aids which are admitted by the reagents are important, and such a substance finds its place in organic reagents.
The chemical principles which divide whether organic compounds can be regarded as analytical reagents are discussed below from the point of view of the different functional groups they contain. The principle functions of analytical reagents are (1) to isolate a species (2) to react with other species so that the reaction product can be detected or measured (3) to provide an indicator (4) to provide proper chemical environment during the analysis.

A specific reagent is one which under certain test conditions is unambiguous for one component but a selective reagent will react with a small number of components. If the product of a reaction has a measurable property, such as colour and has a reproducible composition, the reagent may serve for analytical purposes. The usefulness of a reagent may depend upon, such as availability of other reagents, selectivity or specificity, the nature of the test and the product, and the sensitivity i.e. the lowest concentration of the species that can be detected through the use of the reagent under specified conditions. This is similar to identification limit described by Feigl. The usefulness of a reagent may be enhanced enormously by masking and unmasking phenomenon. In general, masking consists of removal of an ion by formation of an insoluble nonionized product or a complex ion. Presence of phosphate in the usual scheme of qualitative analysis of cations is
an example of masking. Masking when deliberate may be of use in improving selectivity of a reaction. Presence of organic substances which contain groups like -OH, -COOH, may alter the course of reaction. E.D.T.A. is a known masking agent. It forms anionic complexes, which in conjunction with solvent extraction permit many separations. Demasking may be used to improve selectivity of a reaction. Most obvious example of "unmasking" is the precipitation by pH adjustment.

Masking and Demasking agents i.e. addition agents may not only alter the solubility and the dissociation of complexes but may influence other respects such as purity. Solvent extraction is useful in separations. Solvent characteristics can be changed greatly by pH control, salting out agents, and addition of miscible solvents as alcohols.

Analytically useful reagents may be classified as follows:—

(1) precipitation (2) volatilization (3) extraction
(4) ion exchange (5) chromatography (6) complex formation
(7) oxidation and reduction (8) formation of coloured species (9) transformation into compounds with chromophoric groups.

Precipitation reaction may be considered analytically useful if

1) Solubility of the desired product is less than $10^{-5}$ moles/litre.

2) Stoichiometry is perfectly reproducible.

3) Error due to coprecipitation is negligible or correctible.

4) The product or its ignited or dried form is weighable.

Volatileization technique has been widely used for estimation of many inorganic substances, examples are the decomposition of substances with acids and measurement of the carbon dioxide liberated from the decomposition and distillation under reduced pressure for separations. Formation of complexes of organic reagents with metal ions has proved very useful in analytical chemistry. Extraction technique has provided a very powerful separation tool in conjunction to ion exchange and chromatographic separations.

The concentration of an ion in solution may be altered by the formation of a complex. Complexes play an important role in analytical processes.
Redox reactions are useful when oxidation potential of half cell reactions differ by 0.2 V. It is possible to alter the potential of a couple by complexation. If the difference in the oxidation potentials is large it is possible to determine two or more substances (oxidizing or reducing) present in the same solution. The situation is analogous to the titration of mixture of strong acid and a weak base.

It is frequently possible to convert a colourless or slightly coloured species to a highly coloured one, so that a colorimetric determination can be made. This method includes absorptions in the infra-red and ultra violet regions of the spectrum. Reactions of this type may be either direct or indirect. If the colour formation is direct, the desired element is made part of the coloured species being measured. An indirect reaction is one in which a stoichiometric relationship is established between the ion desired and some reagent, though ion itself does not enter in the coloured species e.g., p-phenetidine is oxidized by Cerium(IV) to yield a purple colour.

Lake formation accounts for colour reaction of a different type e.g., red lakes between aluminium and surinetricarboxylic acid. The type of reaction tends to be very pH sensitive.
Coupling reactions are examples of the conversion of colourless compounds to coloured species that respond analytically in some other way. Phenols give azodyes which can be determined colorimetrically. Amines and many heterocyclic compounds containing nitrogen react similarly. Presence of nitro group can be detected with a benzene solution of rhodamine-B. These type of conversions are not generally stoichiometric. Organic reagents are used in inorganic analysis in ever increasing number. Their use has simplified many separations and offered sensitivity to many of the reactions. Analytical reactions of organic reagents can be classified as:

(1) reactions not involving valence changes
(2) oxidation reduction reactions
(3) reactions involving the formation of a complex

Compounds containing acid groups like COOH, SH may react with ions to form simple salts. Use of oxalic and benzoic acids in titrations with bases and of benzoic acid for precipitation of thorium are examples. Kolthoff in discussion of acid base indicators has defined indicators as weak acids and bases of which the inorganic form possesses a colour and constitution different from the

colour and structure of the pseudo or normal form. Important classes of pH indicators include phthaleins, sulfo phthaleins, azo indicators, nitro indicators, and the triphenyl methane dyes. These substances are used as pH indicators.

Methylene Blue may be used as oxidizing titrant. The reagent serves as its own detector. Methods have been described for determination of titanium, tin and other metals, but the reagent is not widely used, only a few organic oxidants, are used in inorganic analysis, but organic reducing agents are numerous. Pyroquinone precipitates gold from 1.2 N HCl, thus separating it from platinum, palladium, selenium and tellurium.

Ascorbic acid is oxidized to dehydroascorbic acid and has been applied to the direct titration of Ferric ion. Redox indicators are compounds that change colour when oxidized or reduced.

The coordination compounds contain a central ion, around which are coordinated a number of attached ligands. Ligands are either unidentate, or polydentate depending on whether they have one or more than one

coordinating atom. Werner’s coordination theory presented a stereo chemical interpretation of coordination compounds. Inner complexes are stable compounds insoluble in water, but are soluble in nonpolar solvents and are often coloured. Chelating agents contain groups like carboxy, sulfonic, enolic hydroxyl, phosphonic, oxime and primary and secondary amino groups.

Tendency to form chelates is greatest among transition elements. All chelating agents are weak acids or bases and hence pH of the solution exerts an important effect on the formation of the complex and the solubility of the reagent. The more stable is a particular complex the lower the pH at which it can be precipitated. Thus reagents like E.C.T.A., dithizone, &quinolinol which react with many metals in alkaline solution, become increasingly selective as the acidity is increased. Depending upon analytical procedure, we have differing solubility requirements for reagents and for metal complexes. Many of the inner complexes are sufficiently insoluble to enable the quantitative precipitation of a metal from solution; these compounds can be dried to a compound with stoichiometrically definite composition. Nickel-dimethyl glyoxime complex and aluminium complex of &quinolinol can be used for gravimetric determination of the metals.

Use of hydroxy acids such as tartaric and citric and higher alcohols like glycerol and mannitol
are well known masking agents. In the precipitation of nickel by dimethylglyoxime in presence of tartaric acid prevents the precipitation of metals like iron and aluminium by ammonia. Masking agents increase the selectivity of a reagent. Amino carboxylic acids like E.D.T.A. can be used for masking metal ions as they form water soluble stable complexes with metals.

The intense colour of inner complexes makes them useful for colorimetric determination. Sandell has estimated that organic reagents are superior to inorganic reagents because of either better sensitivity or selectivity. The more sensitive reagents permit the determination of about 0.1 μg of a metal or about 0.1 p.p.m. in a gram sample.

Coloured complexes can be readily determined colorimetrically in reaction solution. The main problem in such cases is to distinguish between the colour of the metal complex from that of the reagent (if any) and from that of other possible metal complexes. Most of the important organic reagents for metals are chelating agents. They can be classified according to either Sidgwick or Diehl. Sidgwick's classification is based on the types of bonds forming the ring and the number of atoms in the

ring and Diehl's classification is based on the number of bonds, unidentate, bidentate etc. and the nature of the bonds.

The group reactivity of organic reagents is well known. The main groups which give reaction products of analytical importance are discussed here following mainly Diehl's system.

**DITHIOLS**

Dithiol compounds consisting a grouping - C S H - C S H - were first investigated as reagents by Clark\(^{11-14}\). Metal ions readily replace the hydrogen of aromatic -SH groups. These resemble H\(_2\)S in precipitating from acid solutions sulphides of metals having a 5 membered ring structure. Cobalt, nickel, tungsten, molybdenum are precipitated with this reagent.

\[
\begin{array}{c}
\text{Me (II)} \\
\text{S} \\
\text{S}
\end{array}
\]

Dibenzyldithiol gives complex with palladium.

Diacetyl dithiol forms complexes with palladium (II), rhenium (II) tellurium (IV) and selenium (IV).

---

12. ibid *Analyst* 62 661 (1937).
13. ibid *Analyst* 62 177 (1957).
DIKETONES AND RELATED COMPOUNDS :

The 1:3 diketones are characterized by the grouping
\[ \text{CH}_3 - \text{C} - \text{C} = \text{C} - \text{C}_3 \text{H}_3 \]
They tend to be versatile reagents because of the ease with which they enolize. Most important of this class are acetyl acetone and theonyl trifluoroacetone (T.T.A.). Stability resulting from chelation causes the disappearance of the ketoform. Observation on a group of complexes supports this view\(^\text{15}\). In acetyl acetone chelation occurs with the enol form and a representative structure is

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

Compounds like benzoyl acetone, acetone dicarboxylic esters, salicylaldehyde, hydroxyalizarin come in this group and give similar type of ring structured chelates with metals in proper conditions.

8-QUINOLINOL AND ITS DERIVATIVES :

8-Quinolinol is 8-hydroxyquinoline or oxine. Chelation with metals results in the formation of a 5-membered ring

---

The mechanism of the complex formation is discussed by Feigl. Fifteen membered ring of the metal chelate results in stable structures. Precipitation of aluminium oxinate from dilute acid solution is a good method of separating aluminium from beryllium. Precipitation of magnesium from ammonical solution is a rapid method for magnesium estimation than the phosphate method. Vanadium can be separated and spectrophotometrically determined with oxine. The 2-methyl derivative does not chelate with aluminium. This is attributed to the steric factor. Halogen derivatives are of analytical interest. Yoe introduced 7-Iodo-8-Quinoline-5-Sulfonic acid (ferron) as a colorimetric reagent for iron. Other derivatives of oxine are also useful as reagents.

O-Acylcinioxime Group

Compounds containing = C OH C(N OH) - come in this group. These are highly selective for copper and form green chelates. Reactions of acylcinioximes were studied by Feigl and coworkers. The N-OH groups strengthens the acidity of the alcoholic OH group so that

\(\alpha\)-acyloinoximes act as dibasic acids towards copper. The formation of five membered ring is indicated in case of copper complex.

\[
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{N}\to\text{O} \\
\text{Cu}
\end{array}
\]

Compounds such as methyl acetonylecarbinol and chloral acetophenone in which the OH and N OH groups are separated by a methylene group can not form five membered rings and do not form water insoluble copper salts.

\(\alpha\)-Benzoin oxime belongs to this group and is used as an analytical reagent. This reagent is useful for spot test\(^\text{22}\) and also for gravimetric estimation of copper\(^\text{23}\).

\[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{O} \\
\text{N}\to\text{O} \\
\text{Cu}
\end{array}
\]

**O-NITROSOPHENOL GROUP:**

O-Nitrosophenols contain the reactive group

\[\text{C} (\text{NO}) - \text{C} (\text{OH})\] which forms chelates with a number

---

23. Feigl F. Ber 2083 (1923).
of metals. Cobalt and palladium complexes are of analytical interest. The reacting form is the 0-nitrosoxime $^{24}$,

$$\text{NO} \quad \text{OH} \quad \text{O} \quad \text{N}$$

the metal replacing the oxime hydrogen. α-Nitroso-β-naphthal was introduced by Blandisch and coworkers $^{25, 26}$. It forms highly coloured complexes with several metals. Cobalt can be colorimetrically estimated with this reagent at pH $^{47}$, the interference of iron is being overcome by the addition of citrate. Iron can be determined as water soluble complex at pH 5.1 to 5.5.

Nitroso-R-Salt (Salt of 2-hydroxy 1-nitrozonaphthalene $^{36}$ disulfonic acid) is used to estimate cobalt even in presence of metals such as copper (II) and iron (II)$^{28}$. The isomer 2-nitroso-1-naphthol is also used for spectrophotometric determination of cobalt $^{30}$.

---

27. Illinski M. et al Ber 18 679 (1885).
THIONALIDE GROUP :-

The reactive group -NH CO CH₂ SH - is present in thioglycollic acid anilide and in the homologous compound thionalide. Feigl has offered evidence that more than one structure is present in various complexes.

The salt formation is due to the SH group rather than NH group. Thus N-methyl derivative also form, similar metal complexes.

Dithiocarbamate and Xanthate group. Dithiocarbamate and Xanthate give coloured chelates with metals. The formula of copper complex is illustrative of the structure of these compounds.

\[ 
\text{CH}_3\text{O} - \overset{\equiv}{\text{S}} - \text{Cu} - \overset{\equiv}{\text{S}} - \text{C} - \overset{\equiv}{\text{O}} - \text{CH}_3
\]

Diethyl dithiocarbamate \((\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na}\) is the most widely used reagent of this group; its important use is determination of copper in concentrations as low as 0.02 p.p.m. where a brown colloidal suspension is formed with the reagent\(^3\). Diethyl ammonium diethyl dithiocarbamate is another reagent of this group and is used for determination of traces of lead and zinc \((\text{C}_2\text{H}_5)_2\text{N CO SS NH}_2(\text{C}_2\text{H}_5)_2\).

Xanthates are prepared by the interaction of alcohols with carbon disulphide in presence of alkali, have a formula ROCSSK. Molybdate is separated from tungsten by the extraction of the ethyl carbamate complex with chloroform\textsuperscript{32}. Mercapto benzothiazole and p-dimethyl aminobenzylidene rhodamine belong to compounds containing sulphur. The latter was pointed out to be a reagent for silver by Feigl\textsuperscript{33}.

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{C} \\
\text{S} & \quad \text{C} = \text{CH} \quad \left\langle \text{N} \left(\text{CH}_{3}\right)_{2}\right. \\
\text{S} & \quad \text{C} = \text{C} \quad \left.\langle\text{N} \left(\text{CH}_{3}\right)_{2}\right)
\end{align*}
\]

Mercapto-benzothiazole has the acidic properties of a mercaptan and also has a coordinating centre in the ring nitrogen. Salt structures of the type shown below have been accepted for many of the metals.

\[
\begin{align*}
\text{S} & \quad \text{S} \quad \text{C} \quad \text{S} \quad \text{M} \quad \text{S} \quad \text{C} \\
\text{N} & \quad \text{N} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{N}
\end{align*}
\]

The imino group in rhodamines imparts reactivity for silver, mercury, copper(I), gold and platinium. Salt formation in the acid solution with the reacting metal

\textsuperscript{32} Hall D. J. A. C. S. 44 1482 (1922).
\textsuperscript{33} Feigl F. Z. anal. chem. 74 380 (1926).
replacing the labile hydrogen of the imino group takes place during the reaction. The sulphur in the adjacent side chain is essential for activity, although the ring sulphur can be replaced without a similar loss of activity.

\[
\text{\textbf{b-dimethyl-amo}no benzylidine rhodamine}
\]

**DITHIOOXAMIDE (RUBEAINCE ACID):**

Dithiooxamide \( \text{H}_2\text{NCSCS NH}_2 \) is more acidic than oxygen analog oxamide \( \text{H}_2\text{NCO.CO.NH}_2 \). It forms insoluble coloured complexes with copper, cobalt, nickel, iron, silver, bismuth, mercury, palladium and platinum. In strong mineral acid solution, soluble coloured complexes are given by Osmium and ruthenium. The reagent is also used as a spot test reagent for copper, cobalt and nickel whose complexes have the structure.

\[
\text{Structure of bridged polymer consisting of 5-membered rings has been proposed for metal-chelates}^{34,35}
\]

---

34. Ray P. Z anal chem 79 94 (1929-30).
A number of methods for copper determination have been described\textsuperscript{36,37,38}.

**DITHIZONE**:

Diphenylthiocarbazone was applied to metal analysis by Fischer\textsuperscript{39}. (The ketoform of dithizone is monotropic, the labile hydrogen is supplied by the imidohydrogen adjacent to the benzene structure, because of the latter's nucleophilic nature. Enolization would result in diprotic compounds owing to the formation of the acidithiol group.) As dithionates are soluble in organic liquids, the reagent is useful for colorimetric determination also. The theory of dithizone extractions has been developed by Kolthoff and Sandell\textsuperscript{40} and Irving and Williams\textsuperscript{41}.

**Cupferron and analogous compounds**:

Ammonium salt of nitrosophenyl hydroxylamine was assigned the name cupferron by Baudisch\textsuperscript{42}. He precipitated copper and iron from

\textsuperscript{39} Fischer H., Pharm. Chem., 47, 685 (1934).
\textsuperscript{40} Kolthoff I.M., Sandell E.B., J. A. C. S., 63, 1906 (1941).
\textsuperscript{42} Baudisch C., Chemiker Ztg., 33, 1298 (1909).
dilute acid solutions. The reasons for activity of cupferron and like reagents is not easily understood. The reactive group is \(-N-N=O\) which permits the formation of a five membered ring chelate. Metals coordinate through oxygen rather than the nitrogen of the nitroso group.

It is a selective precipitant for niobium, tantalum, tungsten, mercury(I), iron(III), and zirconium in strongly acid solutions\(^4\).\(^3\)

Besides other separations, of vanadium (V) from uranium (VI) is possible by the use of cupferron. Cupferrates are of uncertain composition and are unstable and therefore direct gravimetric techniques are not possible. Ignition to the oxide is the usual practice is such cases.

Extractibility of cupferrates by organic solvents is studied by Furman et al.\(^{loc.cit}\). Quantitative extraction of copper, iron, tin, uranium etc. is possible by the use of cupferron.

Cupferron shows increased selectivity in precipitation reactions in presence of E.D.T.A.\(^4\).\(^4\)\(^5\).

---

43. Furman N.H., Mason W.B., Pekola J.S. Z anal. chem. 119 60 (1940).
Neo-cupferron, \( \text{C}_{10} \text{H}_{7} \text{N(NO)} \text{ONH}_4 \) is ammonium salt of naphthyl hydroxylamine, has reactions similar to cupferron. Because of greater molecular weight, complexes are less stable; but is useful in determination of iron in water without preliminary concentration.

**DIOXIME GROUP:**

Dioximes containing a grouping \( \text{C}:(\text{NOH})-\text{C}:(\text{NOH}) \) were the first organic reagents applied in inorganic analysis. They are excellent reagents for nickel and palladium. They are also of interest for many structural studies made on their metal compounds. The form of the dioximes (Dimethyl glyoxime) gives a red precipitate with nickel having the structure as given below:

\[
\begin{array}{c}
\text{R} - \text{C} & \text{C} - \text{R} \\
\text{H} & \text{N} \\
\text{N} & \text{CH}
\end{array}
\]

The reactivity of the dioxime group is influenced by the structure of the remainder of the molecule; Benzene ring destroys the reactivity with nickel; an example is 1:2 naphthoquinone dioxime. Saturated ring compounds as

47. Diehl H. The Application of Dioximes to analytical chemistry G.F. Smith Columbus Ohio, 1940 (p. 35-46).
cyclohexanedione dioxime$^4$ (nioxime) do give the nickel reaction. The specimen of this group is $\text{dimethyl glyoxime}$; under proper conditions it may be considered to be specific for nickel and palladium. A monograph giving uses of dioximes has been published by Dick (loc. cit) $\text{L-\text{diulidioxime}, } C_4H_7O \text{C(NO)} \text{H} \text{C(NO)} \text{H}_2 \text{O}, \text{is used for determination of nickel in steel}^5 \text{ and chrome ores}^6$.

CUPROINE GROUP :-

Compounds of this class contain a grouping,

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{C}
\end{array}
\]

They have structures similar to ferroin reagents except for substituent groups on the carbon atom adjacent to the ring nitrogen atoms.

Cuproine reagents are specific colorimetric reagents for copper (II) and do not give any reaction with iron. The difference in behaviour between the ferroin and cuproine reagent is due mainly to steric effects resulting from substitution.

Cuproine is 2-2'-Biquinoline.

FERROIN GROUP:

Ferroin group reagents have a grouping =N-b-':-N= in a cyclic structure. Dark red 1:10 phenanthroline ferroin complex is known as ferroin. The use of ferroin as redox indicator was demonstrated by Walden, Hemmett and Chapman. Most studied ferroin reagents are complexes with 2-2'L-dipyridine, 1-10 phenanthroline, 2-2'-2"-tripyridine and their derivatives in which one or more of ring hydrogen atoms may be replaced by radicals such as CH₃, Br, Cl, NO₂, OH, OCH₃, COOH. Substitutions on carbon atoms adjacent to the ring nitrogen results in compounds which do not give ferroin reaction. Ferroin complexes are more stable than ferric complexes. The ferroin reagents are most often used as sensitive colorimetric reagents for iron(II) and as redox indicators.

Complexones are amino-carboxylic acids. The specimens may be mentioned as nitrilotriacetic acid (NTA·H₂X) and ethylene diamine tetra acetic acid (E.D.T.A·H₂Y). E.D.T.A. is a strong complexing agent than N.T.A. and the complexing reactions are well known. Some of E.D.T.A. complexes are highly coloured and can be used in spectrophotometric determination as examples may be mentioned Bi·EDTA, Co·EDTA and Cr·EDTA.

SALT FORMING AND MISCELLANEOUS REAGENTS

Besides chelating reagents there are some reagents like salt forming acids, lake forming compounds, reagents forming addition or penetration compounds, oxidizing and reducing reagents and organic solvents. A few of these are discussed here.

The arsonic acids RAs (OH)₂O precipitate zirconium from acid solutions. Alkyl arsonic acids, phenyl arsonic acids, and substituted phenyl arsonic acids are effective precipitants for zirconium. The introduction of azo group result in compounds that form coloured salts with zirconium. Suitable for colorimetric determination.

Tannin, C₆H₁₀O₉ XH₂O, is a very useful precipitant for metals. It is especially useful in precipitation of niobium, tantalum and tungsten⁵³.

Compounds containing thiourea group = NCSN = form precipitates and coloured compounds with many metals. Yoe and Overholser⁵⁴, could find no definite corelation between structure and reactivity. Thio-urea forms amine type penetration complexes with many metal ions in acid solution.

Thio-urea is used to mask copper(II), mercury(II), and silver in the estimation of zinc or cadmium with sodium-quinolate$^{55}$ formation of soluble yellow complex of thio-urea with bismuth can be used for determination of bismuth in tin base alloys$^{56}$. Thio-urea is used for colorimetric determination of osmium$^{57}$. Thio-urea is a reducing agent, reduces acid solutions of selenites to colloidal red selenium. Oxidation of thio-urea to disulphide,$(\text{NH}_2\text{NH})_2 \text{S}_2$, by strong oxidizing agents, e.g., chlorates, bromates and chromates and used for their determination$^{58}$.

Different groups which are responsible for the activity of the compounds as reagents have been discussed above. These groups do not include the sulfonamido ($\text{SO}_2\text{NH}^-$) group, $p$-Toluene-sulfonamido-o-(aniline), a compound containing ($\text{SO}_2\text{NH}^-$) group, was reported by Bilman et al., in 1960 as a reagent for gravimetric determination of copper$^{59}$.

Toluene-sulfonamido-o-anilines is also used for amperometric titrations of copper(II)$^{60}$.

The use of T-sulfonamidine as spectrophotometric reagent for copper(II)\textsuperscript{61} and cerium(IV)\textsuperscript{62} was also reported.

The present work was undertaken with a view to investigate the effect of substitution of halogens in the reagent in place of CH$_3$ group situated in para position with respect to SO$_2$NH$^-$ group. With this in view p-chloro-sulfonamido-o-aniline, p-bromo-sulfonamido-o-aniline and p-iodo-sulfonamido-o-aniline were synthesized and their uses as the spectrophotometric precipitation and spot test reagent were studied.

The use of p-halo-sulfonamido-o-aniline i.e. p-halo-sulfonamidines as indicators in cerate titrimetry was also investigated.