CHAPTER I
INTRODUCTION

After the introduction of dimethylglyoxime for the detection and determination of nickel by Tschugaef\textsuperscript{1} use of complexing agents in inorganic analysis has become prominent. An enormous number of organic reagents were used as complexing agents in inorganic analysis for both qualitative and quantitative determinations. Publication of a large number of monographs, reviews and books\textsuperscript{2-21} and increase in their number from time to time is a clear indication of the interest shown in this field.

The word Chelate (Chele = Claw) was first coined by Morgan and Drew\textsuperscript{22}. The reactivity of the organic reagents was explained by Werner\textsuperscript{23} in his "Theory of Complex Compounds" in 1891. Using the electronic theory of valency, the trial and error methods previously employed for the prediction of chelates were eliminated.

The coordination of a metal ion and a reagent molecule can be compared with a reaction between a Lewis acid and a Lewis base i.e., metal being in the center and number of coordinating groups surrounding it. These groups could be either charged or neutral molecules containing atoms with one or more lone pairs of electrons. The coordinating
ligands may be unidentates or polydentates. When a ring is formed keeping the metal ion as a part of the complex, such complexes are called chelate compounds. The atoms like oxygen, nitrogen and sulphur of the coordinating groups with lone pairs of electrons forms the complexes more favorably. Some of the important coordinating groups (ligand) were given below.

**Carboxyl**
\[ -\text{C} = \text{O} \]

**Sulphonic**
\[ -\text{S} = \text{O} \]

**Arsonic**
\[ -\text{As} = \text{O} \]

**Enolic**
\[ -\text{C} = \text{C}_2 - \text{C} \quad \Leftrightarrow \quad -\text{C} = \text{C}_1 - \text{C}_1 \]

**Phenolic**
\[ -\text{C} = \text{O} \]

**Thiophenolic**
\[ -\text{C} - \text{S} \]

**Oxime**
\[ =\text{N} - \text{O} \quad \Leftrightarrow \quad \text{N} - \text{H} \]

**Semicarbazone**
\[ =\text{N} - \text{N} \quad \text{CO} \quad \text{NH}_2 \]

**Thiosemicarbazone**
\[ =\text{N} - \text{N} \quad \text{CS} \quad \text{NH}_2 \]

**Hydrazone**
\[ =\text{N} - \text{NH}_2 \]

**Phenylhydrazone**
\[ =\text{N} - \text{NH} \quad \text{C}_6 \quad \text{H}_5 \]

2-Hydroxy-1-Acetonaphthone oxime is used in the present investigations which is a derivative of 2-hydroxy-1-acetonaphthone. A brief review of the use of O-hydroxy carbonyl compounds and oximes as analytical reagents is presented here.
0-Hydroxy carbonyl compounds

These compounds are an important group of organic reagents which form a stable six membered ring with the metal ions. Many types of compounds of this group, like hydroxylaldehydes, hydroxyketones, o-hydroxy quinones derived from anthracene, benzene or naphthalene, 5-hydroxy-2-pyrones have been introduced as analytical reagents. In these compounds generally the phenolic hydrogen is substituted and the oxygen of the carboxyl group takes part in the coordination.

0-Hydroxy aldehydes

Ettling has introduced salicylaldehyde for the qualitative and quantitative analysis of copper and nickel. Duke has reported that the compound and its 5-nitro, 5-bromo and 3,5-dibromo derivatives react with different metal ions in aqueous and nonaqueous solutions giving stable metal complexes. Conducometric, turbidimetric and spectrophotometric methods for the analysis of various ions have been reported.

Nee and Rao reported that boric acid forms complexes with salicylaldehyde, P-resorcylicaldehyde, 4-methoxy-2-hydroxy benzaldehyde and benzoyl phloroglucinaldehyde. P-Resorcylic aldehyde was used for copper and nickel and 2-hydroxy-1-naphthaldehyde for the gravimetric
determination of copper which gave coloured complexes. 2-Hydroxy-1-naphtaldehyde was used for trace analysis of magnesium\textsuperscript{37} and beryllium\textsuperscript{38}. Chelate compounds of boron and o-hydroxy carbonyl compounds\textsuperscript{39} were also reported by Shibazaki.

**O-Hydroxy ketones**

Like aldehydes, ketones have also been used for inorganic analysis: Nenki and Sieber\textsuperscript{40} used 2,4-dihydroxy acetophenone for the determination of ferric iron. The same reagent was used by Ramanujan\textsuperscript{41,42} for the gravimetric and volumetric determination of copper. Germanium was analysed by Raju and Rao\textsuperscript{43} using the same reagent by fluorimetry. Neelakantam and Rao reported several reagents such as 2,4-dihydroxy acetophenone, 2,6-dihydroxy acetophenone, L-methoxy-2,4-dihydroxy acetophenone and 2-methoxy-3,6-dihydroxy acetophenone for the determination of boric acid\textsuperscript{34}. O-hydroxy acetophenone was used for the determination of copper and nickel\textsuperscript{44}. Nickel and titanium\textsuperscript{45} were also determined by the reagent Perrin\textsuperscript{44}, Patel and Patel\textsuperscript{46} reported stability constants of the above complexes. Various metal ions were determined by 2,4-dihydroxy propiophenone, butyrophenone\textsuperscript{47} and 2-hydroxy-3-methyl acetophenone -4-methyl\textsuperscript{48} and 5-methyl acetophenone\textsuperscript{49} 2,3,4-trihydroxy acetophenone were found useful for the gravimetric determination of tantalum\textsuperscript{50}. Dhar and Jain\textsuperscript{51} has reported the
composition of the U (vi), V (v) and Fe (iii) complexes of the reagent, 5, 6-dibromo gallalacetophenone was used by Sane\textsuperscript{52} et al for the spectro photometric determination of Ti (iv) and V (v).

\textbf{O-Hydroxy acids}

Salicylic acid\textsuperscript{53-61} was used for the determination of many metals. Holleck\textsuperscript{62} has studied its europium complex for its polarographic behaviour. Salicylic acid\textsuperscript{63} was also used for the separation of titanium from niobium and tantalum. It was also used in the separation of Th (iv) from U (vi)\textsuperscript{64}. Stability constants of these complexes were reported by several workers\textsuperscript{65-67}.

Iron complexes of substituted salicylic acids were studied by Park\textsuperscript{68}. Crystalline precipitates of potassium, magnesium and ammonium\textsuperscript{69} were prepared by using 1-hydroxy-2-naphthoic acid. Thorium and zirconium\textsuperscript{70} were also determined by using the same reagent by Agarwal and Mehrotra. P-resorcylic acid\textsuperscript{71} has been used for the determination of uranium and zirconium and separation of thorium\textsuperscript{72} from zirconium and uranium. Same reagent was used for the gravimetric\textsuperscript{73} determination of mercury(II) and spectrophotometric determination\textsuperscript{74} of iron and aluminum\textsuperscript{75}. Fluorescent colour reactions were studied using salicylic acid and its derivatives. Fluorimetric determination of some other metals
were carried out by Rao and Neelakantam\textsuperscript{76} using these reagents. Azodye derivatives\textsuperscript{77} of O-hydroxy acids were examined for the detection of beryllium and aluminium.

**O-Hydroxyquinones**

5-Hydroxy-1,4-naphthaquinone was used for the gravimetric and potentiometric determination of copper\textsuperscript{78}. 5,8-Dihydroxy-1,4-naphthaquinone\textsuperscript{79} was used for the determination of aluminium and beryllium\textsuperscript{80-82}.

**O-Hydroxy anthraquinones**

Characteristic colour reactions of alizarin sulphonic acid with hafnium and zirconium\textsuperscript{83} was used for their estimation. Zirconium\textsuperscript{84} was determined using 1,2,4,5,8-Penta hydroxy anthraquinone and purpurin\textsuperscript{85}. Orthohydroxy quinone derivatives were utilised for the indirect estimation of fluoride by bleaching their coloured complexes. Beryllium-quinizarin was estimated by spectrophotometric and fluorometric techniques by White et al\textsuperscript{86}. Babko\textsuperscript{87} studied the composition of the complex with quinizarin by colorimetry. Colour reactions of hydroxy anthroquinone with aluminium and gallium\textsuperscript{88,89}, indium and scandium\textsuperscript{90} were also reported.

**O-Hydroxy-γ-pyrones.**

Morin has been used for the detection\textsuperscript{91} and determination\textsuperscript{92} of aluminium. Aluminium was masked in the titration of gallium and indium with complexone(III). Morin has also been
used in the detection of Ti(iv)$^{93}$ and U(vi)$^{94}$ and colourimetric determination of Mo(vi)$^{95}$ and U(VI)$^{96}$. An isomer of morin i.e., quercetine was used for the detection by spotttest of uranium and iron. It was also used for the determination of gallium and indium$^{97}$, thorium$^{98}$, iron$^{99}$ and titanium$^{100}$. Kojicacid was used for the determination of iron(III)$^{101}$, germanium$^{102}$, zirconium and iron, thorium and molybdenum$^{103}$ were determined using purpurgallin. Dutt and Singh$^{104}$ have used this reagent for the determination of thorium, cerium, zirconium, molybdenum, lead(II) and a number of elements gravimetrically.

O-Hydroxy carbonyl compound derivatives were found to be more reactive and sensitive of the reagents. Oximes, semicarbazones and thiosemicarbazones are some of the important derivatives which increase reactivity and sensitivity.

A brief review of the analytical methods reported with the oximes was presented below.

**Oximes as analytical reagents**

O-Hydroxvoximes usually form chelates with the metals by replacement of the hydrogen atom of the −OH group and by coordination of the nitrogen atom of the oxime group. oximes can be broadly classified into four categories:
1. orthodioximes
2. orthohydroxy aromatic oximes
3. acyloinoximes
4. monoximes of diketones

1. Orthodioximes

Some of the dioximes extensively used as analytical reagents were given below.

a) Dimethyglyoxime:

This was discovered by Tschugaeff in 1905 and was used by Brunk\textsuperscript{105-109} for the determination of nickel. Dioximes in general react with nickel to form red precipitate. They will react generally in three ways

1. Through the coordination of \(-\text{NOH}\) groups by the nitrogen atoms present in the neutral conditions

2. Through salt formation using one \(-\text{NOH}\) group and through coordinate linkage with the other \(-\text{NOH}\) group, i.e., as mono basic acid.

3. Through salt formation using both \(-\text{NOH}\) groups either with or without coordination of their Nitrogen atoms i.e., as dibasic acid.

b) L-Benzil dioxime:

This was first used by Tschugaeff\textsuperscript{1} for the detection of nickel. The compound was used for the confirmatory tests
for Nickel in several analysis.\textsuperscript{110-111} This was used as a gravimatic reagent for nickel by Attack\textsuperscript{112-114} and many others. Fairhall\textsuperscript{115} has determined nickel in biological samples with this reagent.

c. Nioxime:
This is a cyclic analogue of Dimethyl glyoxime prepared by Wallach\textsuperscript{116-118} for the determination of palladium. Nickel and palladium were gravimetrically determined by Votar, Banks and Diehl\textsuperscript{119}.

d. Alpha-furildioxide:
This reagent was proposed by Macnair\textsuperscript{120} and used by Soul\textsuperscript{121} for the gravimetric determination of nickel. It formed a red precipitate with nickel in ammoniacal medium. Ogburn\textsuperscript{122} has used the reagent for the separation and determination of platinum metals. Reed and Banks\textsuperscript{123} have used the reagent for the gravimetric determination of palladium.

e. Benzoylmethylglyoxime:
This is a potential reagent for the determination of palladium. Durdik\textsuperscript{124} determined palladium in jewelry metals. Grissolett and Servigin\textsuperscript{125} used it for the gravimetric determination of palladium in hydrochloric acid medium. Holzer\textsuperscript{126} stated that this is a more useful reagent than dimethylglyoxime for the determination of palladium.
f. Oxalene diamidoxime:
Nickel\textsuperscript{127-129}, was detected and determined by using this reagent. Palladium was determined by Dasgupta\textsuperscript{130} gravimetrically.

2. Orthothyroxy aromatic oximes.
a. Salicylaldoxime: This oxime acts as a monobasic acid where the phenolic hydrogen will be replaced. Ephraim\textsuperscript{131} has detected copper and determined it gravimetrically using this reagent. The mechanism of reaction was confirmed by the absence of similar reaction with isomeric methylesters of salicylaldoxime by Fiegl. Bandi\textsuperscript{132} used this reagent for the determination of copper,\textsuperscript{133,134} nickel,\textsuperscript{135} palladium,\textsuperscript{136,137} bismuth\textsuperscript{138} and iron\textsuperscript{139}. Tougarinoff\textsuperscript{140} has developed an indirect titrimetric method for the determination of copper. Furman and Flagg\textsuperscript{141}, developed a bromate-arsenite method for the determination of copper.

b. Resorcylicaldoxime
This reagent was first introduced by Chain\textsuperscript{142} for the detection and colorimetric determination of iron. Mukharjee\textsuperscript{143} used it as a a gravimetric reagent for copper and nickel.

c. \textit{L}-Furfuraldoximes: Formation of an yellow precipitate of palladium with the reagent was used for the gravimetric determination of the metal by Hayes and Hayes and
d. Resaacetophenoneoxime: Neelakantam and Sitaraman\textsuperscript{145} have used this reagent for the colorimetric determination of Ferric Iron at pH 3.6 to 7.0. It was also used for the photometric and colorimetric determination of iron and uranium respectively\textsuperscript{146,147}. This was also employed for the determination of many metals\textsuperscript{148-151}. Seshagiri\textsuperscript{152} reported physico-chemical studies on copper, nickel and palladium complexes with this reagent. Halder and Trivedi\textsuperscript{153} has utilised 5-nitro resaacetophenoneoxime for the complex study of nickel and copper.

e. Gallacetophenone oxime: Various metal Ions were determined by gravimetric, amperometric, spectrophotometric methods by Adinara-yana Reddy\textsuperscript{154}.

f. 2-Hydroxy-1-naphthaldoxime: Endo and Mashima\textsuperscript{155} determined copper, nickel and cobalt gravimetrically in acid medium. Rajareddy\textsuperscript{156} used this as a photometric reagent for the determination of uranium, palladium and titanium. SeshadriNaidu and Raghava Naidu\textsuperscript{157,158} utilised this reagent for the determination of palladium and titanium. Physico-chemical aspects of the oxime and several of its metal chelates were also studied\textsuperscript{159,160}.
g. Salicylamidoxime: Copper, nickel and palladium were determined by Bandhopadhyay and Ray\textsuperscript{161} using this reagent.

h. 0-Hydroxy acetophenoneoxime: Copper, nickel and titanium were determined by Poddar\textsuperscript{162} gravimetrically by using this reagent. Ingle and Khanolkar\textsuperscript{163,164} studied the complexes of this oxime and its substituted derivatives. This was used as an indicator for the direct titration of ferric iron\textsuperscript{165}.

i. Respropiophenoneoxime: Nickel was determined by Dave and Patel\textsuperscript{166} using this reagent.

j. 2-Hydroxy-5-methylpropiophenoneoxime: Prakash Dutt and Singh\textsuperscript{167,168} employed this reagent for the determination of copper, nickel, cobalt and titanium.

k. 2-propionyl-l-naphthaldoxime: Tambat and Merchant\textsuperscript{169} used this compound for the determination of copper.

l. O-vanillinoxime: Goel et al\textsuperscript{170} used this reagent for the gravimetric determination of copper and nickel.

m. Peonoloxime: Vanadium, palladium, copper, titanium and nickel were determined by Raja Reddy\textsuperscript{171} using this reagent. He also developed an indirect volumetric method using this reagent for the determination of copper, nickel, titanium and iron III. Copper, nickel and palladium were also determined by amperometry. Physico chemical studies of the oxime and
its metal chelates was reported by Suresh Babu et al.\textsuperscript{172,173}

n. 2-hydroxy-3-chloro-5-methylacetophenone oxime: Naik et al.\textsuperscript{174} used this reagent for the determination of copper.

3. Acyloinoximes: The functional groups of these compounds is (OH)-C(OH)-C(NOH)-. They form green water soluble complexes with cupric salts. Feigl\textsuperscript{175} studied a number of oximes and found that the above group is specific for copper, irrespective of the R and R' radicals. Out of many acyloinoximes only L-benzoinoxime is the most important from analytical point of view.

Molybdate\textsuperscript{176} and tungstate\textsuperscript{177} ions were determined gravimetrically in acidic solutions. Hoenes and Stones\textsuperscript{178} found that this reagent gave an yellow precipitate with vanadium of composition 1:2. The precipitate was always contaminated with excess of the reagent and therefore the complex was extracted with chloroform and determined colorimetrically.

IV. Monoximes of diketones: These compounds possess the characteristic functional group -CO-C(NOH)- and have an ability to form inner complexes of blue colour with metal ions. The group is also found in many other compounds like \textit{L-nitroso-β-naphthol} and \textit{o-nitrosophenol} in which the two carbon atoms are a part of the ring.
a) **Iso nitroso-3-phenylpyrozolone**: Hovorka\textsuperscript{179} used this reagent for the determination of copper.

b) \textit{\textalpha}-Isonitroso-\textbeta-oximido acetoacitanilide:} Dave and Talati\textsuperscript{180} used this reagent for the determination of copper, nickel and palladium gravimetrically.

c. **Methyl Phenyl Pyrazoloneoxime**: Popa et al\textsuperscript{181} has used this reagent for the determination of copper gravimetrically.

d. **Oximidobenzotetronic acid**: Manku et al\textsuperscript{182} had separated and determine palladium and cobalt using the reagent.

e. **N-\textbeta-naphthylooxamic acid**: Tandon, Gupta and Omprakash\textsuperscript{168} determined copper with this reagent.

f. **Benzimidazol-2-carboxylic acid**: Ray, Kanakendu and Poddar\textsuperscript{183} used this reagent for the determination of copper and palladium.
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