SUMMARY

Presence of HO - C = C - C = N - OH system in o-hydroxy ketoximes indicated their use for Ca(II), Ni(II) (1-3). On these considerations several workers (4-15) studied the effectiveness of the above system. Joshi (16) examined the effect of aryl group attached to the chelating nitrogen atom. They have reported fairly high sensitivity, selectivity and specificity of o-hydroxy ketoximes for Cu(II), Ni(II), Ti(III), Ti(IV), Fe(II), Pd(II) at definite pH range.

The present work deals with the investigations of oximes derived from (1) 2-hydroxy-4-benzyl oxyacetophenone (2) 2-hydroxy-4-benzyl oxypropiophenone (3) 2-hydroxy-3-chloro-5-methylacetophenone (4) 2-hydroxy-3-chloro-5-methylpropiophenone and (5) 2-hydroxy-3-chloro-5-methylbenzophenone as chelating agent.

(A)  
(B)
(A) (i) \( R = \text{CH}_3 \), 2-hydroxy-4-benzyloxyacetophenone oxime
(ii) \( R = \text{C}_2\text{H}_5 \), 2-hydroxy-4-benzyloxypropiophenone oxime

(B) (iii) \( R = \text{CH}_3 \), 2-hydroxy-3-chloro-5-methylacetophenone oxime
(iv) \( R = \text{C}_2\text{H}_5 \), 2-hydroxy-3-chloro-5-methylpropiophenone oxime
(v) \( R = \text{C}_6\text{H}_5 \), 2-hydroxy-3-chloro-5-methylbenzophenone oxime

The thesis has been divided into two parts. Part - I deals with the analytical applications of these ketoximes and Part - II with the composition and constitution of Cu(II), Ni(II), Pd(II) chelates obtained from 2-hydroxy-4-benzyloxy ketoximes and of Pd(II) chelates obtained from 2-hydroxy-3-chloro-5-methylketoximes. Part - I has been divided in two sections:

Part - I : Section - I :

2-HYDROXY-4-BENZYL OXYAC E T OPH ENONE AND PROPI OPH ENONE OX IMES AS ANALYTICAL REAGENTS

Bhatki and Kabadi (5) have investigated resacetophenone oxime and Singh, Gupta and Malik (12) have investigated resvalerophenone oxime as analytical reagents. Patel and Naik (13), Desai, Naik and Naik (14) studied the effect of allioxy group in meta position to OH. It was thought interesting to study the effect of introducing benzyloxy
group in meta position to -OH group and para to -C = N - OH group.

2-Hydroxy-4-benzyloxyacetophenone was prepared by refluxing benzylchloride, resacetophenone and anhydrous potassium carbonate in acetone. 2-Hydroxy-4-benzyloxypropio- phenone was prepared using similar method from respropiophenone.

The ketones obtained thus were converted to their oximes by condensing them with hydroxylamine hydrochloride in alcoholic solution. These ketoximes have been studied for qualitative and quantitative analysis of transitional metal ions.

It has been observed that Cu(II), Ni(II), Pd(II), Co(II), Fe(II), Fe(III), Ti(IV) can be detected with these reagents qualitatively in amount up to $10^{-5}$ ppm at a suitable pH in the presence of non-interfering radicals. The ions like Cu(III), Ni(II) and Pd(II) have been determined quantitatively. The applicability has been established by carrying out the determinations at different pH conditions, with different aliquots of metal ions and in presence of other cations. The ions like Pd(II), Al(III), Cd(II), Zn(II), Ca(II), Sr(II), Mg(II), Ba(II), chloride, nitrate and sulphate have been found non interfering. Estimations in presence of Fe(II) and Fe(III) were carried out by masking them with potassium citrate and Rochelle salt. In every estimation the contamination of the ligand from the complex was removed by washing the complex with
80 per cent ethanol because the complex does not dissolve in 80 per cent ethanol.

The specificity, selectivity and accuracy of these reagents for Cu(II), Ni(II) and Pd(II) made possible their quantitative determination in binary mixtures of (1) Cu(II) and Ni(II) (2) Pd(II) and Ni(II).

**Part I : Section II :**

2-HYDROXY-3-CHLORO-5-METHYLACETOPHENONE, PROPIO PHENONE AND BENZO PHENONE OXIMES AS ANALYTICAL REAGENTS

In continuation of the analytical work on (i) 2-hydroxy-3-chloro-5-methylacetophenone oxime (ii) 2-hydroxy-3-chloro propiophenone oxime and (iii) 2-hydroxy-3-chlorobenzophenone oximes in this laboratory, the ligands were investigated for palladium(II).

2-Hydroxy-3-chloro-5-methylacetophenone was prepared from 2-chloroparacresol by preparing the ester followed by the Frie's migration. The other two ketones were prepared by the same method using 2-chloro-paracresol and propionic anhydride and benzoylchloride respectively.

The above o-hydroxyaryl ketones were converted into the corresponding oximes using hydroxylaminehydrochloride and sodium acetate in ethanol. These ketoximes have been studied for qualitative and quantitative analysis of Pd(II).
It has been observed that Pd(II) can be detected with these reagents qualitatively in amount up to $10^{-5}$ ppm at a suitable pH in the presence of noninterfering radicals. The Pd(II) ion has been determined quantitatively. The applicability has been established by carrying out the determinations at different pH conditions, with different aliquots of metal ion and in presence of other cations. The ions like Pb(II), Al(III), Cd(II), Zn(II), Ca(II), Sr(II), Mg(II), Ba(II), chloride nitrate and sulfate have been found non interfering. Estimations in presence of Fe(II) and Fe(III) were carried out by masking them with potassium citrate and Rochelle salt. In every estimation the contamination of the ligand from the complex was removed by washing the complex with 80 per cent ethanol because the complex does not dissolve in 80 per cent ethanol.

The specificity, selectivity and accuracy of these reagents for Pd(II) made possible its quantitative determination in binary mixture of Pd(II) and Ni(II).

Part - II:

STUDIES ON COMPOSITION AND CONSTITUTION OF METAL CHELATES

This part of the thesis deals with the determination of composition and constitution of metal chelates. The chelates with Cu(II), Ni(II) have been purified and known weights of Cu(II), Ni(II) chelates have been burnt to metal oxides which
were gravimetrically determined. Alternatively known weights of chelates were digested with concentrated nitric acid and sulphuric acid. The resulting solutions were analysed by standard analytical methods for corresponding metal ions.

The Cu(II), Ni(II) and Pd(II) chelates were found to obey Beer's law and hence the metal ligand ratio in a chelate was determined using Job's method of continuous variation.

Infrared spectra of chelates were compared with similar spectra of ligands. This helped in establishing the structure of chelates.

The metal ions Cu(II), Ni(II) being the members of transitional series are expected to have unpaired electrons in 3rd orbital. Hence the magnetic susceptibilities were measured to throw light on the structure of chelates. Absorption spectra of chelates were also studied to confirm the structures of chelates. All the chelates have been assigned coplanar structure.

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\text{(A)} \quad R = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_6\text{H}_5; \\
\text{M} = \text{Cu(II), Ni(II), Pd(II)}
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\text{(B)} \quad R = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_6\text{H}_5.
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