SUMMARY

The analytical application of organic chelating reagents has become more or less inevitable. Several organic chelating reagents have been found for variety of common and rare metal ions. The application of salicylaldoxime as an analytical reagent for Cu$^{2+}$, Ni$^{2+}$ and Fe$^{2+}$ indicated the effectiveness of chelating system HO-C=C-O=N-OH. Several o-hydroxyketoximes, o-hydroxy anilides and anils have been indicated for the analytical applications of transition metal ions. The precipitation of corresponding chelates has been studied and constitution of resulting chelates has been established by spectrophotometric and magnetic methods in many cases.

The o-hydroxyketoximes are expected to be selective for Cu$^{2+}$, Ni$^{2+}$ due to presence of the HO-C=C-O=N-OH system (1-3). On these considerations several workers (4-12) studied the effectiveness of the above system. Joshi (13) studied 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$^{2+}$, Ni$^{2+}$, Ti$^{3+}$, Ti$^{4+}$, Fe$^{2+}$ and Pt$^{2+}$ at definite pH range.

The present work deals with the investigation of oximes derived from 2-hydroxy-4-n-propoxyacetophenone, 2-hydroxy-4-n-propoxypropiophenone and 2-hydroxy-4-n-propoxyvalerophenone. The chelates with Cu$^{2+}$, Ni$^{2+}$ and Pt$^{2+}$ with the above
Ketoximes have been prepared and purified by usual methods.

\[ R = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_4\text{H}_9 \]

The thesis has been divided into two parts. Part I deals with the analytical application of the above mentioned ketoximes and part II with the composition and constitution of chelates obtained from the above ketoximes.

**PART I**

2-HYDROXY-4-n-PROPOXYACETOPHENONE, 2-HYDROXY-4-n-PROPOXYPROPIOPHENONE AND 2-HYDROXY-4-n-PROPOXYVALEROPHENONE OXIMES AS ANALYTICAL REAGENTS:

Bhatki and Kabadi (5) and Singh, Gupta and Malik (14) have investigated resacetophenone and resvalerophenone oximes respectively as an analytical reagents. It was thought interesting to study the effect of \(-\text{OC}_3\text{H}_7\) group in meta position and para to \(-\text{C}==\text{N}-\text{OH}\). 2-Hydroxy-4-n-propoxyacetophenone was prepared using 2-propyl bromide, resacetophenone and
anhydrous potassium carbonate in acetone. 2-Hydroxy-4-n-propoxypropiophenone and 2-hydroxy-4-n-propoxyvalerophenone were also prepared by the above method from respropiophenone and resvalerophenone respectively.

The oximes of above propoxy ketones were prepared by the reaction between ketone and hydroxylamine hydrochloride. These ketoximes have been studied for qualitative and quantitative analysis for the transition metal ions.

It has been observed that Cu$^{+2}$, Ni$^{+2}$, Pd$^{+2}$, Co$^{+2}$, Fe$^{+2}$, Fe$^{+3}$ and Ti$^{+4}$ can be detected with these reagents qualitatively in amounts up to $10^{-5}$ ppm at a suitable pH in the presence of non interfering radicals. The ions like Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ have been determined quantitatively. The precipitation is complete and sharp at a suitable concentration and pH condition. The ions like Pb$^{+2}$, Cd$^{+2}$, Al$^{+3}$, Cr$^{+3}$, Zn$^{+2}$, Mn$^{+2}$, Ba$^{+2}$, Be$^{+2}$, Mg$^{+2}$, Na$^{+}$, K$^{+}$, Cl$^{-}$, NO$_3^{-}$ and SO$_4^{2-}$ have been found non interfering. Suitable sequestering methods are also investigated and adequate pH range has been established for the quantitative determination of Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ in presence of interfering metal ions.

An attempt has been made to study the quantitative determination of Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ at different dilutions with these reagents.

The ketoximes are fairly soluble in 40% ethanol. The chelates of Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ prepared with these reagents
are insoluble in 80 % ethanol. This enabled to remove contamination of excess reagent from the chelate.

The specificity, selectivity and accuracy of these reagents for Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ made possible their quantitative determination in binary mixtures of (i) Cu$^{+2}$ and Ni$^{+2}$ and (ii) Pd$^{+2}$ and Ni$^{+2}$.

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$^{+2}$ and Ni$^{+2}$ have been purified and their known weights have been burnt to metal oxides which were gravimetrically determined. Alternatively the known weights of chelates were digested with concentrated nitric acid and sulphuric acid. The resulting chelates were analysed by standard analytical methods for corresponding metal ions. The chelates of palladium with these reagents have been purified and their known weights have been ignited strongly in air to jewelry metal which was gravimetrically determined.

The chelates of Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ were investigated for colorimetric methods of analysis. As the chelates obey Beer's law, it is possible to follow the Job's method of continuous variation for determination of the metal ligand ratio. The experimental results for Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$ indicate the
metal-ligand ratio 1:2.

The metal ions Cu$^{+2}$ and Ni$^{+2}$ being the members of the transition series are expected to have unpaired electrons in 3d orbital. Hence the measurement of magnetic susceptibility and studies in absorption spectra are expected to valuable in establishing the constitution. The structures of the 1:2 (metal-ligand) chelates have been confirmed by spectrophotometric, I.R. and U.V. spectral studies. The magnetic susceptibility was determined at room temperature on a Gouy balance. Coplanar structures have been assigned on the basis of magnetic studies and absorption spectra.

The chelates of Cu$^{+2}$ with above ketoximes are paramagnetic. The chelates of Ni$^{+2}$ and Rh$^{+2}$ with above ketoximes are diamagnetic.