

# **Executive Summary**

## **of the**

# **Minor Research Project**

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The work of Werner may be taken as a landmark between the conscious and unconscious applications of complexes. Werner set forth the foundation of co-ordination chemistry. His proposals, however, did not lead to immediate analytical consequence. The work of Werner in the field of co-ordination chemistry which was expanded & extended during the last few decades has been exploited to the maximum by analytical chemists.

The formation of co-ordination compounds by organic reagents with metal ions has been extensively used in analytical chemistry. For quantitative determination of the metal ions, the organic reagents are used as gravimetric reagents, as a spectrophotometric reagent and in solvent extraction. The perusal of the literature shows that an organic reagent which forms a chelate with a metal ion is superior to the rest in the analytical work. It has been found that the reagents capable of forming chelates with metals are often specific or highly selective in their action and hence offer attractive potentialities as analytical reagents.

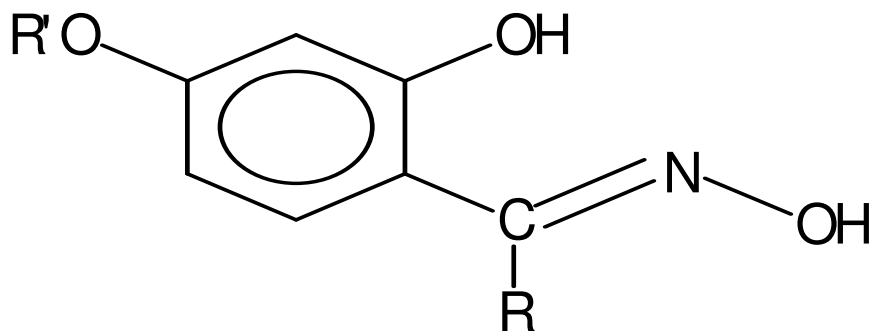
Organic chelating ligands containing oxime functional groups have been extensively used in analytical chemistry for the determination of metal ions. Most of oximes are colourless and with the presence of –OH group in ortho position, can form very stable metal complexes. These complexes of transition metal ions are coloured and hence reagents can be used for spectrophotometric determination of metal ions. In some cases the complex can be extracted in organic solvent and interference can be easily avoided.

The chemistry of chelates has received much attention and such compounds have been extensively studied in recent years. The o-hydroxy oximino chelates occupy a unique position in the development of co-ordination chemistry because of the complexity of structures.

The use of organic chelating reagents has become inevitable because these compounds possess reactive groups which enable them to form a ring structure, containing a metal atom which is known as a chelate. Many organic reagents have been investigated as gravimetric and spectrophotometric reagents for a variety of metal ions. Among the many systems used, the chelating systems found in o-hydroxy aldoximes and ketoximes require special mention due to the situation of groups in suitable position to form stable metal chelates. Oximes are selective and sensitive reagents for the gravimetric and spectrophotometric determination of metal ions.

The chelates formed are highly stable, intense coloured, have high molecular weights and in many cases can be readily extracted in organic solvents due to their neutral character.

The moiety which has been widely used are 2,4-dihydroxy aromatic ketones and their oximes. Besides these, alkoxy substituted ketoximes, are also much studied. Along with this, the reagent has the following general moiety:

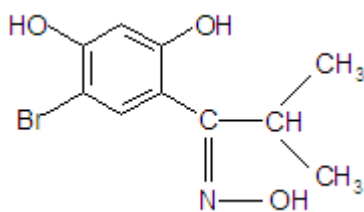


[Where R = alkyl or aryl group

R' = H or alkyl group]

Generally o-hydroxy aldoximes and ketoximes have been very much used to study the complexation behavior for a variety of transition metal ions. Therefore it was found interesting to study the complexation behaviour of metal ions with following reagent.

**2,4 - Dihydroxy-5-bromo[2'-methyl]propiophenone oxime**



The elemental analysis, UV-visible spectra, IR spectra,  $^1\text{H}$ -NMR spectra and  $^{13}\text{C}$ -NMR spectra have been used to confirm the structure of the reagent. It also contains the preparation of the solutions and their standardization, the instruments and conditions used in present study.

Project work contains the study of complexes of DHBMPPO formed with Cu(II), Co(II), Pd(II) and U(VI) metal ions. The reagent have been used for the gravimetric determination

Cu(II), Co(II) and Pd(II) ions. U(VI) ion was studied spectrophotometrically. The effect of pH on the quantitative precipitation has been studied.

Spectrophotometric study of Cu(II), Co(II), Pd(II) and U(VI) complexes were done after extracting the complexes in  $\text{CHCl}_3$ . Absorption spectrum of all above complexes were taken. The obedience of the Beer law at the wavelength of maximum absorbance, were checked. The composition have been determined spectrophotometrically using Job's method of continuous variation and Yoe and Jone's mole ratio method using two different sets of concentration. The Cu(II), Co(II), Pd(II) and U(VI) complexes have 1:2[M:L] stoichiometry. The data of mole ratio method and Job's method have been used to determine the stability constant of metal complexes. The molar absorptivity, Sandell's sensitivity and standard Gibb's free energy change for complexes are also calculated.

Thermogravimetric analysis data has been used to check the thermal stability of the complexes. From TGA studies, the M:L (metal:ligand) ratio was determined and activation energy( $E_a$ ) also calculated.

The reagent DHBMPO has been successfully applied for the determination of copper in drain micro etch solution, % cobalt in pure metal sample, palladium in palladised charcoal and uranium ion concentration in synthetic sample.

The results obtained at the end of the analysis are tabulated below:

**i). DETERMINATION OF COPPER IN DRAINED MICRO ETCH SOLUTION:**

Cu(II) taken in ml	Absorbance	ppm found	ppm taken	% Found	% Error
2.5	0.492	11.65	11.755	2.3300	-0.89
3.5	0.696	16.35	16.457	2.3357	-0.65

**ii). DETERMINATION OF PERCENTAGE PURITY OF COBALT FROM COBALT METAL SAMPLE:**

**RESULTS:**

% of Cobalt in cobalt metal sample=99.50%

Co(II) taken in ml	Absorbance	ppm found	ppm taken	% found	% Error
1.0	0.196	5.50	5.52	99.14	-0.36
1.5	0.290	8.24	8.28	99.02	-0.48

**iii). DETERMINATION OF PALLADIUM IN PALLADISED CARBON:**

**Reported percentage of Pd(II) in palladised carbon sample=5.01 %**

<b>Pd(II) taken in ml</b>	<b>Absorbance</b>	<b>Ppm found</b>	<b>ppm taken</b>	<b>% found</b>	<b>% Error</b>
3.0	0.074	4.75	4.8	4.9579	-1.04
5.0	0.124	7.95	8.0	4.9784	-0.63

**iv). DETERMINATION OF URANIUM IN SYNTHETIC SAMPLE:**

<b>U(VI) taken in ml</b>	<b>Absorbance</b>	<b>ppm found</b>	<b>ppm taken</b>	<b>% Error</b>
7.5	0.118	5.65	5.71	-1.05
11.5	0.180	8.70	8.76	-0.68

The reagent studied in the present work offer quite a good number of advantages listed below:

1. Reagent is solid and can be prepared in pure form with good yield.
2. Reagent is easily soluble in aqueous ethanol. The solutions are stable and can be stored for a long time without any decomposition.
3. Reagent has high molecular weight and due to higher conversion factor, small quantity of metal ion can be determined with more accuracy in gravimetric analysis.
4. TGA studies indicates that the complexes have good thermal stability and hence they can be dried without fear of decomposition.
5. The complexes formed with the reagents are found to have good stability. The stability of the complexes may be attributed to the presence of electron donating -OH group in position 4 to the ketoximes group. It may also be due to the presence of -OH group in position 2 which facilitate the formation of six membered heterocyclic ring in the metal chelate.
6. Many cations and anions do not interfere in the spectrophotometric determination and gravimetric determination of metal ions using these reagents.

7. The complexes formed with these reagent, except U(VI)-DHBMPPO, are insoluble in aqueous ethanol in which the ligands are soluble and hence in gravimetric determination of these metal ions, the excess ligand could be easily washed out by washing the precipitate finally with aqueous ethanol.

8. All metal complexes can also be extracted in organic solvents. This enabled us to do spectrophotometric determination of these metal ions avoiding interference of some metal ions. Molar absorptivity of complexes are also high to offer sensitivity.

9. Reagent is suitable for determining the metal content in some alloys, catalyst, industrial and synthetic samples giving fairly accurate results.

Thus overall the reagent DHBMPPO is suitable reagent for gravimetric and spectrophotometric determination of metal ions.