

**SCAVENGING OXYGEN DISSOLVED IN
WATER FOR MINIMIZING CORROSION IN
METALS**

BY

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INDIA

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**SCAVENGING OXYGEN DISSOLVED IN
WATER FOR MINIMIZING CORROSION IN
METALS**

**A Thesis Submitted
In Partial fulfillment of the requirements
For the Degree of**

**DOCTOR OF PHILOSOPHY
IN CHEMISTRY**

By

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Research Guide**

JANUARY 2011

T-546

STATEMENT

I hereby declare that the matter embodied in this thesis entitled, “*Scavenging Oxygen dissolved in water for minimizing corrosion in metals*” is the result of the investigations carried out by me in the Department of Chemistry, Goa University, Goa, India, under the supervision of Prof. K. S. Rane.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Declaration

The candidate's thesis work has been partly compiled for filing the Indian Provisional Patent Application with Indian Patent Office on 21-01-2011 for which a serial number has been assigned: 192/MUM/2011; CBR No 609. The title of the same is "Metal Complexes for enhancing the Oxygen Scavenging action of Hydrazine." Within one year of its filing the claims of this Provisional Patent Application need to be fine tuned everything claimed thereby. The candidate is, hence, pursuing the work for fine tuning it. Further, though the candidate has mainly indicated catalytic effect of several cobalt complexes, those prepared from cobalt source, cobalt chloride, for the enhancement of the oxygen scavenging action of hydrazine, the present thesis also presents the synthesis and characterization of the cobalt complexes from cobalt acetate source. However, their catalytic action in enhancing the oxygen scavenging action of hydrazine has not been discussed in the present thesis. The candidate plans to pursue this study in future. Moreover, the candidate also plans to prepare single crystals of some of the cobalt complexes, especially the hydrazine complexes, those prepared for the first time, to establish the structure and see whether better catalytic action can be achieved. The candidate has also collected several X-ray photoelectron spectroscopic data, X-ray powder diffraction data, electron spin resonance data on the cobalt complexes, which will be useful once the candidate goes for single crystal studies of the complexes to establish structure of the complexes. Plausible structure information is given in the present thesis. The candidate has also done the X-ray powder diffraction studies on the thermal products of the cobalt complexes. A systematic study is the future scope for preparing technological important cobalt oxides. All these data have been placed in the Appendix at the end of the thesis, for the benefit of the future workers in the area. Once final patenting takes place the candidate may be able to publish many of the cobalt complex systems.

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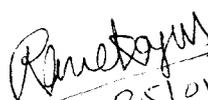
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CERTIFICATE

This is to certify that the work entitled, "*Scavenging Oxygen dissolved in water for minimizing corrosion in metals*" presented in this thesis has been carried out by Mrs.Sifali Santosh Bاندodkar under my supervision and the same has not been submitted elsewhere for the award of a degree.


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Chapter I

Introduction

Background

Hostile Oxygen

Metals are prone to deterioration or destruction or simply to corrosion in the environment consisting of air or oxygen. While normal corrosion is expected in metals used in variety of engineering equipments exposed to ordinary atmosphere, the real threat for further rampant corrosion can come from the purpose for which they are being used. For example, the metal parts of drilling machines used for boring oil and gas wells get corroded if the drilling fluids contain dissolved oxygen (DO). The water used in flooding the brine employed in the secondary recovery of petroleum if contains DO that will corrode metals used in the systems. In steam generating systems the boiler material corrosion is uncontrollable if DO concentration in the boiler feed water is even 0.003 to 0.005 mL per liter (3-5 parts per million). For that matter any system that is exposed to dissolved oxygen is under threat. Hence it is essential to know this threat well in advance and accordingly try to minimize, if not completely, the exposure to such aggressive environment. In order to control the dissolved oxygen, there are several oxygen scavengers. To study such oxygen scavenging processes and efficiency of any scavenger in any solution medium in which a metal part is in touch, it is best to study in a simple water medium, so that one can easily understand the mechanism of oxygen scavenging without unnecessarily complicating by using solution medium; and the best system would be Boiler Feed Water that is used in the boilers. As boilers are an integral part of any industry; the information of oxygen

scavenging would be of significance because no industry can afford to shut down their plant for want of the repeated maintenance of their boiler due to corrosion.

Boiler feed Water

A boiler is a closed vessel in which water or other fluid is heated. The heated or vaporized fluid exits the boiler for use in various processes or heating applications. The pressure vessel in a boiler is usually made of steel or historically wrought iron. Copper or brass is also sometimes used for specific purposes. Boiler feed water is water used to supply (“feed”) a boiler to generate steam or hot water. At thermal power stations the feed water is usually stored, pre-heated and conditioned in feed water tank and forwarded into the boiler by a boiler feed water pump. The feed water is specially conditioned to avoid problems such as corrosion due to dissolved oxygen (DO) and CO₂ by employing mechanical de-aeration technique followed by chemical oxygen scavengers. The deposits/sediments/fouling in the boiler and downstream components are controlled by using de-mineralized water.

Chemical oxygen scavengers

Several oxygen scavengers such as sodium sulfite, Na₂SO₃, carbohydrazides (CO (NHNH₂)₂), methyl ethyl ketoxime (MEKO), diethyl hydroxyl amine (DEHA), hydroquinone (HQ), (C₆H₄ (OH)₂), hydrazine hydrate (HH), N₂H₄·H₂O, find use in such situations. There are advantages and disadvantages in using these oxygen scavengers, but important aspect of any scavenger is that it should not leave any solids behind in the feed water. Among several oxygen scavengers, hydrazine is

widely used as it reacts with oxygen, $\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, releasing environmentally friendly nitrogen gas and water vapor. Here hydrazine is defined as the generic name for hydrazine hydrate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. Hydrazine hydrate is a colorless liquid with a boiling point of 118-119°C and a vapor pressure of 1 kPa at 20°C. It is miscible in water and alcohols and has alkaline and reducing properties. Among the other liquid oxygen scavengers, carbohydrazide is a volatile oxygen scavenger that reacts readily with oxygen, at low temperatures and pressures, $\text{H}_6\text{N}_4\text{CO} + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$; producing apart from N_2 and H_2O the carbon dioxide whose condensate forms carbonic acid, H_2CO_3 , which is detrimental to the boiler materials. However, the advantageous part of carbohydrazide is that it breaks down to hydrazine above temperatures of 350°F (180°C) and the hydrazine thus produced *in situ* reacts more vigorously with oxygen [1]. Although Hydroquinone, $\text{C}_6\text{H}_4(\text{OH})_2$, is yet another oxygen scavenger, it is mentioned in the literature [2] as catalyst for enhancing the hydrazine reactivity with oxygen reaction. Hydrazine reaction with oxygen at low temperatures is otherwise sluggish.

Hydrazine: An oxygen scavenger

Hydrazine reacts with oxygen, $\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$; and brings down the DO level to few parts per billion (ppb) levels from 4-5 parts per million (ppm) that had been achieved through mechanical de-aeration of de-mineralized water. The theoretical requirement of hydrazine for scavenging oxygen is 1 part per part oxygen: $32 \text{ g N}_2\text{H}_4 / 32 \text{ g O}_2 = 1$. In boiler operation, normally a 100% excess of hydrazine is used in the feed water. Hydrazine does not contribute solids in the

boiler feed water, so boiler blow down, or the mechanical removal of solids from the after-boiler section as sludge, is avoided. Under such reduced level of oxygen the metal oxide scale formation from the metal part of the boiler, $3\text{Fe} + 6\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_2 + 3\text{H}_2$ and $3\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2$ is arrested. In addition to this, the hydrazine promotes the formation of the protective magnetite, Fe_3O_4 , through a reaction with metal oxide scale, if present, $6\text{Fe}_2\text{O}_3 + \text{N}_2\text{H}_4 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{N}_2 + 2\text{H}_2\text{O}$, thus converting the red iron dust, hematite, into a protective film of magnetite. The alkaline nature of hydrazine in water, in fact, supports this magnetite formation. The hydrazine can also form a protective cuprous oxide, Cu_2O , film in copper based boiler materials by reacting with the cupric oxide, CuO , that formed due to the corrosion of copper, $\text{N}_2\text{H}_4 + 4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{N}_2 + 2\text{H}_2\text{O}$. Hydrazine also reduces the formation of iron hydroxide, $\text{Fe}(\text{OH})_2$, by reacting, $4\text{Fe}(\text{OH})_3 + \text{N}_2\text{H}_4 \rightarrow 4\text{Fe}(\text{OH})_2 + \text{N}_2 + 4\text{H}_2\text{O}$. It is because of these passivation effects that an excess of the hydrazine to oxygen is required to be maintained in the boiler feed water. Hydrazine is not without limitations. It is not considered “volatile”, so it does not leave the boiler with the steam to scavenge oxygen and passivate metal throughout the system. In boilers operating above 400°F (205°C), it can degrade to ammonia, $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$, and volatilize with steam, and, in the presence of oxygen, can attack metals containing copper [3].

Catalyzed hydrazine oxygen scavenger:

Though hydrazine as an oxygen scavenger has many advantages as described above, it may not be a preferred one at low temperatures, as its reaction with

oxygen is sluggish. There are mentions in the literature (mostly in Patents) regarding the use of metal complexes as catalysts in enhancing the oxygen scavenging activity by increasing the rate of reaction of hydrazine with oxygen. The metal complexes are the reaction products of cobalt, manganese or copper (e.g., containing anions such as chloride, nitrate, bromide, iodide or sulfate) with certain organic ligands. The use of hydrazine compounds, a catalytic organometallic complex, and preferably a quinone compound for deoxygenating feed water is disclosed in one of the patents [4]. The use of cobalt maleic acid hydrazide with hydrazine for oxygen removal is also mentioned in one of the patents [5].

Numerous suggestions have been made in the patented documents to add catalytic or accelerating agents to the hydrazine compound or to otherwise use hydrazine systems to facilitate oxygen removal or scavenging in fluidic corrosive environments or to otherwise treat water systems. Certain compounds when used in combination with a hydrazine compound in corrosive environments significantly increase the rate of reaction of the hydrazine compound in removing oxygen and this is so to a surprisingly significant degree even at ambient or lower temperature [6]. It is found that the oxygen scavenging action of hydrazine can be enhanced by adding cobalt chloride and diamino toluene (DAT) [6, 7]. Though details of the enhancing action are not available with the use of such additives, the oxygen affinity of cobalt may be one of the reasons for such enhancement [8].

Cobalt (Co) compounds and complexes: catalyst**Autoxidation of hydrazine: adduct of Co complex and N₂H₄**

Scavenging of the dissolved oxygen (DO) in the boiler is due to hydrazine reaction with the molecular oxygen [9],

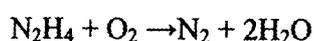


Since the autoxidation of hydrazine reaction is sluggish, metal complexes are used as catalyst to enhance the reactivity. In the literature, it was mentioned that to remove oxygen dissolved in water, say from the reservoir drinking water, use of cationic and anionic complexes of trivalent cobalt with inorganic ligand or the mixtures thereof are used as activators along with the hydrazine [10] such as $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$. In US Patent 4012195 a mention is made of catalyzing effect of organometallic complex, $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2$, where 3,4-TDA is 3,4-toluene diamine, in boiler feed water based on hydrazine, but the catalyzed hydrazine compound corrosion inhibiting composition is not clearly revealed. While studying the autoxidation of hydrazine, hydroxylamine and cystein by the Cobalt (II) chelate complex of 3,10,17,24-tetrasulphophthalocyanine (H₂tspc), the authors [11] found the complex, $[\text{Co}^{\text{II}}(\text{tspc})]$ to be an efficient catalyst for the oxidation of the target compounds in an aqueous solution by molecular oxygen. The oxidation of hydrazine and hydroxylamine involves the initial formation of a 1:1 adduct between $[\text{Co}^{\text{II}}(\text{tspc})]$ and the hydrazine/hydroxylamine, $[\text{Co}^{\text{II}}(\text{tspc})][(\text{N}_2\text{H}_4)]/\text{Hydroxylamine}$ and these adducts then react with molecular oxygen yielding oxidation products of hydrazine and hydroxylamine leaving intact $[\text{Co}^{\text{II}}(\text{tspc})]$. In the case of cystein the oxidation process involves an electron-

transfer reaction resulting in the formation of $[\text{Co}^{\text{I}}(\text{tspc})]^-$ and cystein. Simple oxygenation of $[\text{Co}^{\text{II}}(\text{tspc})]$, however, leads to oxygen adduct of the type $[\text{Co}^{\text{III}}(\text{tspc})(\text{O}_2)]$. But no ternary adduct formation with O_2 was observed when oxygen was bubbled through the binary adducts $[\text{Co}^{\text{II}}(\text{tspc})][(\text{N}_2\text{H}_4)]/\text{Hydroxylamine}$. Since the bubbling of the binary adduct $[\text{Co}^{\text{II}}(\text{tspc})][(\text{N}_2\text{H}_4)]$ with oxygen leads to oxidation products N_2 and H_2O , leaving intact $[\text{Co}^{\text{II}}(\text{tspc})]$, the role of the cobalt complex is to bring to its close proximity the hydrazine by way of forming an adduct which then effectively reacts with the hydrazine. Thus, the attack of oxygen to hydrazine is guided by the cobalt complex, as cobalt complex itself has affinity to oxygen. In the absence of the cobalt complex, hydrazine would have difficulty attacking oxygen as in water the dissolved oxygen is already in the ppm level. Thus, the cobalt complex plays a dual role of attaching hydrazine to itself and attracting oxygen to its close proximity. Once the hydrazine and oxygen have reacted, the cobalt complex remains intact, thereby, playing the role of a catalyst.

Studies of the reaction between hydrazine and oxygen at 25°C and 70°C in alkaline solution have shown that the observed rate is due to catalysis by traces of impurities [12]. It has been found that copper (II) and manganese (II) are the most active catalysts, and, under certain conditions, the copper (II)-catalyzed reaction appears to be homogeneous. Evidence is presented that catalysis occurs by redox reactions. The reaction was followed by measurement of the hydrazine concentration. The authors [12] did not make any attempt to measure the oxygen concentration during the reaction, owing to the great difficulty involved in the determination of oxygen in the presence of hydrazine when both are disappearing at an appreciable rate.

Therefore, in the kinetic experiments they arranged that dissolved oxygen should be in sufficient excess over the hydrazine so that changes in the concentration of oxygen during the reaction could be ignored. The practice of bubbling air through the solution to maintain a constant oxygen concentration during a reaction was open to objection. Not only would it involve assumptions on the rate of oxygen absorption but it might lead to the loss of hydrazine and /or ammonia from the solutions. In order that the stoichiometry of the reaction i.e. the number of molecules of hydrazine reacting with one molecule of oxygen might be determined, it was necessary to verify that the reaction was complete [12]. At 25 ° C and pH 9, in the presence of ammoniacal copper (II) catalyst, 8 ppm of dissolved oxygen completely oxidized 1 ppm of hydrazine or was completely reduced by 20 ppm of hydrazine. When hydrazine was in excess over oxygen, it was found that after all oxygen had disappeared, the excess hydrazine concentration remained constant, showing that there was no appreciable breakdown of hydrazine and also no interference by traces of oxygen in the blanketing nitrogen. When oxygen was readmitted, the hydrazine concentration began to fall again [12]. Within experimental error, the stoichiometry is 1 at 25 ° C and 70 ° C. This is consistent with the overall reaction;



Hence, little or no ammonia is formed at pH 9 in this temperature range. When hydrazine is in excess over oxygen, the catalyst will be in the form of Cu(I) at the end of the reaction. Therefore, the observed hydrazine consumption will include that used in reducing Cu (II) to Cu(I). With the amount of catalyst used by t

[12] the error involved in the determined stoichiometry is not greater than 0.25%.

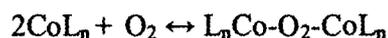
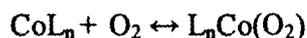
Hydrazine is oxidized by dissolved oxygen in aqueous solutions containing $[\text{Fe}(\text{CN})_5]^{3-}$, in slightly acidic or alkaline conditions. The reaction involves the oxidation of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{N}_2\text{H}_4)]^{3-}$ to $[\text{Fe}^{\text{III}}(\text{CN})_5(\text{N}_2\text{H}_4)]^{2-}$ as the first step, and kinetic features suggest that this is followed by dimerization to $[(\text{NC})_5\text{Fe}^{\text{III}}(\text{N}_2\text{H}_4)\text{---}\text{Fe}^{\text{II}}(\text{CN})_5]^{5-}$; $\text{Fe}^{\text{III}}\text{---}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{II}}\text{---}\text{Fe}^{\text{II}}$ dimers are then originated by fast electron-transfer. The first of these evolves to $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{N}_2\text{H}_2)\text{---}\text{Fe}^{\text{II}}(\text{CN})_5]^{6-}$; this diimide complex is very stable in alkaline solutions (pH 8) free of O_2 or H_2O_2 . In the presence of these [13], or in more acidic media it evolves further to $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-} + \text{N}_2$.

Since the activator effect of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [10] and catalytic effect of $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2$ [7] in enhancing the oxygen scavenging of hydrazine in the boiler feed water are not clearly indicated in the patents, it is difficult to comprehend how the effect takes place in the autoxidation of hydrazine. Though a hydrazine compound formation was mentioned in the case of $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2$, a clear composition or formula was not revealed.

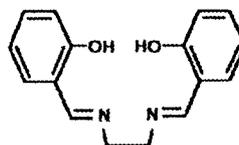
Oxygen uptake

There has been a continued interest in metal Schiff base complexes ever since the initial discovery of Tsumaki [14] that the complexes of cobalt (II) are oxygen (O_2) carriers [15] wherein the formation of one-to-one adduct of the type Co-O_2 has been invoked. Considerable effort has been made to determine the oxygen uptake ability of $\text{Co}(\text{L})\text{B}$ complexes, where L is quadridentate chelate group which occupies t

equatorial position in the complex and B is a unidentate ligand in the axial position. From Electron Spin Resonance (ESR) studies approximately 90% of the spin density of the unpaired electron on Co(II) is calculated to transfer to oxygen upon formation of the $\text{Co(L)B}\cdot\text{O}_2$ adduct. This suggests that the system can be viewed as a superoxide ion attached to Co(III), $\text{Co}^{\text{III}}\text{-O}_2^-$. On this basis, the reaction of Co(L)B with O_2 may be described as an electron transfer from Co(II) to the oxygen molecules, as found in the case of $[\text{Co}^{\text{II}}(\text{tspc})] \rightarrow [\text{Co}^{\text{III}}(\text{tspc})(\text{O}_2)]$ [11]. Ability of these complexes to react reversibly with oxygen also has been considered based on the redox potential of the system. Two types of bonding of dioxygen to cobalt (II) have been distinguished,



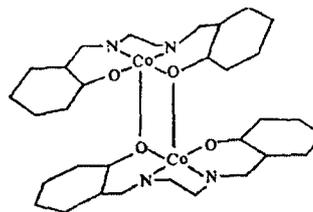
That is, the Co: O_2 may be 1:1 or 2:1, depending on the nature of the ligands, temperature, solvent etc. One of the best known cobalt(II) "oxygen carriers" is $\text{Co}(\text{salen})$, which forms when Co(II) links with salenH_2 , where salenH_2 represents N,N' -bis(salicylaldehyde)ethylenediimine (Structure I) [16]



I

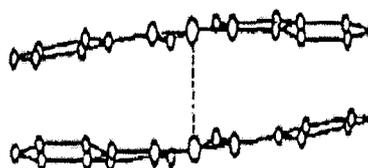
The cobalt complex, $\text{Co}(\text{salen})$ exists in two different solid forms, depending on the method of preparation: a brown active form towards oxygen absorption and a dark

inactive form. The inactive form consists of dimeric unit, in which the Co atom of one Co(salen) molecule interacts with an O-atom of the second.



Inactive

The active form also has dimeric units, but with one Co atom directly above the other and channels in this structure allow oxygen to enter easily.

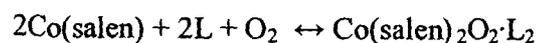


Active

The active form absorbs oxygen at room temperature and releases it at higher temperatures and this cycle may be repeated many times, although the activity of the compound towards oxygen uptake slowly decreases on continued cycling, owing to decomposition.

The O₂ uptake is favored by any event that brings electronic charge on the metal center [8], the more electron donating the ligand and/or solvent are, the higher the Co(II) complex dioxygen affinity will be. When Co(salen) is dissolved in donor solvents, L, such as dimethylsulfoxide, DMSO, dimethylformamide, DMF and

pyridine, in the presence of oxygen the adduct of the following type readily forms [17];



The L acts as ligand capable of occupying a co-ordination position around the metal. Unfortunately, auto-oxidative reversible processes often occur, and the complex undergoes rapid deactivation.

The oxygen uptake studies carried out on cobalt salen in our laboratory [18] on a setup [16], Figure 1.1

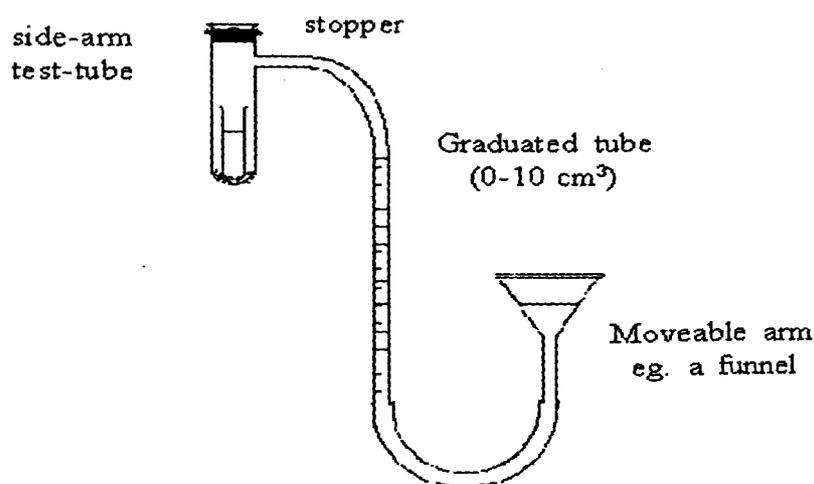


Figure 1.1: O₂ uptake set-up

indicates, 1mg of Co(salen) in DMSO takes up oxygen as a function of time up to 400 minutes of ~0.13 moles. Figure 1.2

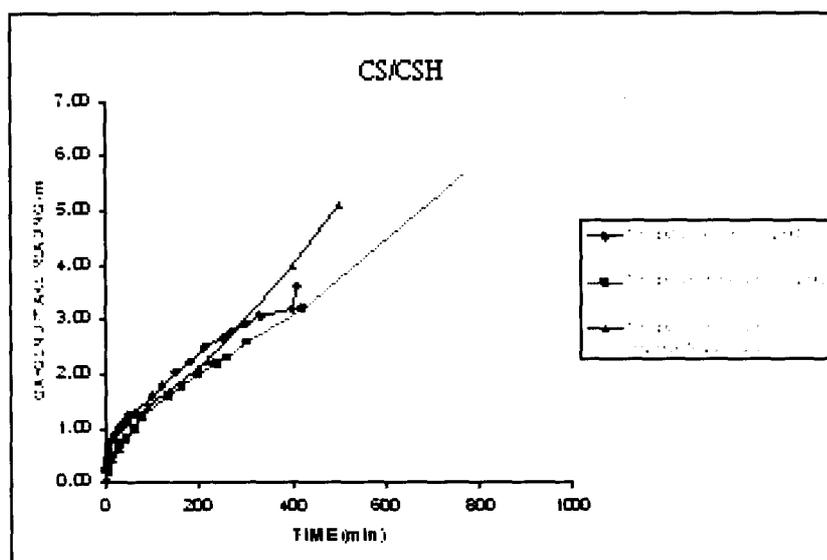
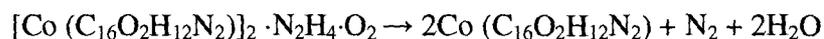


Figure 1.2: O₂ uptake versus time for cobalt salen (CS) and its hydrazinate (CSH)

On the other hand, the hydrazine complex of the cobalt salen, [Co (C₁₆O₂H₁₂N₂)] · N₂H₄ (CSH) too shows almost similar oxygen uptake of ~ 0.13 moles in 400 minutes and then continues upto 800 minutes linearly, while the CS shows a break ~ 400 minutes. Both the complexes do take up oxygen on reusing and in the Figure 1.2 it can be seen that the oxygen taken up in the reused cobalt salen hydrazine sample is slightly different than the virgin sample. In any case, both the complexes show the reversible oxygen uptake. In the autoxidation studies of N₂H₄ on [Co^{II}(tspc)], was considered a formation of an adduct [11] of the type [Co^{II}(tspc)] [(N₂H₄)] which on reaction with oxygen leaves behind the [Co^{II}(tspc)] producing the oxidation products of hydrazine, suggesting the catalytic effect of the cobalt complex [Co^{II}(tspc)] in the oxidation process, while the simple [Co^{II}(tspc)] on oxidation forms an adduct with oxygen → [Co^{III}(tspc) (O₂)], thereby, oxidizing the Co(II) to Co(III). In case of hydrazine complex of cobalt it may form an adduct

with O_2 , $[Co (C_{16}O_2H_{12}N_2)]_2 \cdot N_2H_4 \cdot O_2$ without Co(II) getting oxidized to Co(III). Then, hydrazine may get oxidized leaving behind unhydrazinated cobalt salen, $Co (C_{16}O_2H_{12}N_2)$.



Therefore, probably, the reused sample now seems to be simple cobalt salen and hence shows different oxygen uptake path which is more or less similar to the virgin Co(salen). Oxygen uptake studies carried out on hydrazine in the setup [16] by taking 0.1mL to 0.0001mL hydrazine hydrate in 1L of water, Figure 1.3, it clearly shows oxygen taken up by the hydrazine.

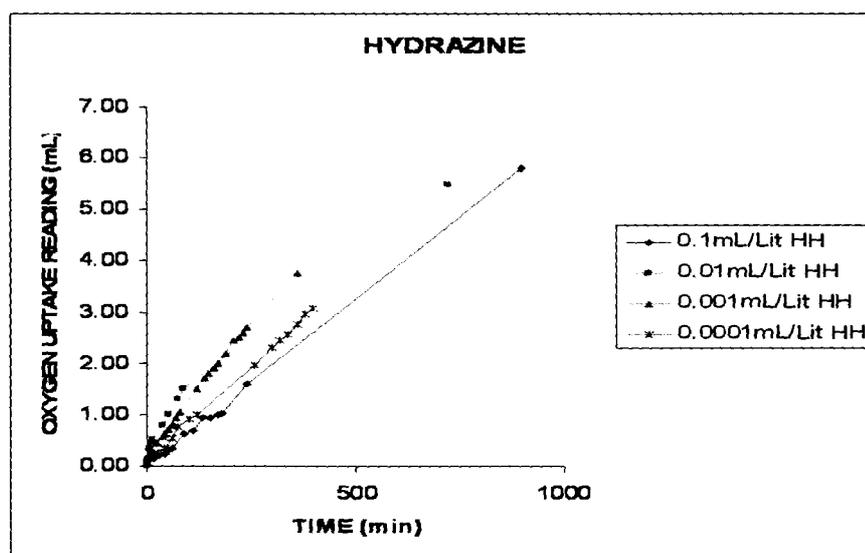


Figure 1.3: O_2 uptake versus time for Hydrazine Hydrate (HH)

In general the oxygen uptake takes place linearly with time. A maximum of 0.233 moles is taken up by 0.1mL hydrazine/L water in 900 minutes, while 0.01mL hydrazine/L water absorbed 0.225 moles in 700 minutes and 0.001mL hydrazine/L

water absorbed 0.151 moles in 400 minutes. When 0.1-0.0001mL hydrazine in 1L water is loaded in the oxygen uptake assembly and to it 1mg cobalt salen, CS, is added, the oxygen uptake of this shows a linear uptake of oxygen, Figure 1.4. The oxygen uptake at room temperature by CS +DMSO alone, Figure 2 is ~0.082 moles in 180 minutes, while the 1mg CS in 0.001mL hydrazine/1L water shows ~0.102 moles, Figure 1.4 and that only hydrazine (0.001mL/1L water) of 0.082 moles, suggesting a higher oxygen uptake by CS in hydrazine, indicating a catalytic effect of the cobalt complex in the autoxidation of hydrazine.

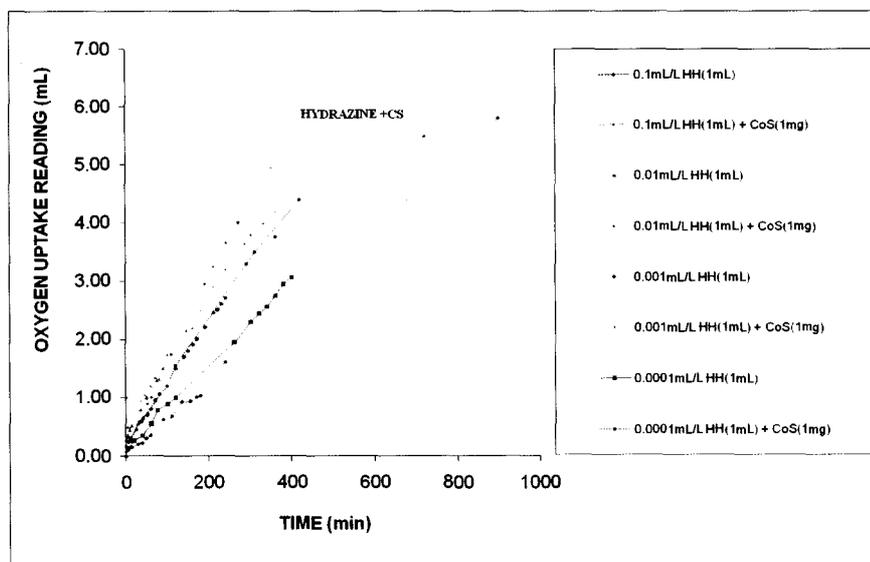
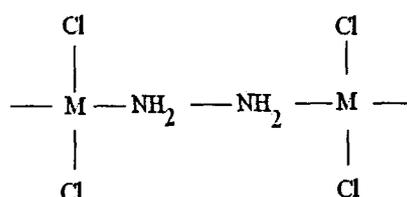


Figure 1.4: O_2 uptake versus time for Hydrazine Hydrate (HH) +Cobalt salen (CS)

These studies suggest that hydrazine may be acting as a donor ligand like DMSO helping the cobalt to get adducted with the O_2 .

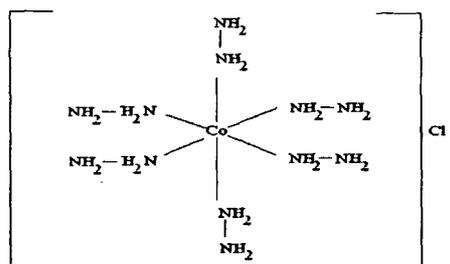
Metal hydrazine complexes

Hydrazine, $\text{H}_2\text{N}-\text{NH}_2$ coordinates to metal as a unidentate or a bridging bidentate ligand. No chelating (bidentate) hydrazines are known. For example, the hydrazine ligands $[\text{M}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, where $\text{M}(\text{II}) = \text{Mn}/\text{Fe}/\text{Co}/\text{Ni}/\text{Cu}/\text{Zn}/\text{Cd}$, are bridging bidentate (polymers). Structure II,



Structure II: The hydrazine ligands are bridging bidentate (polymers).

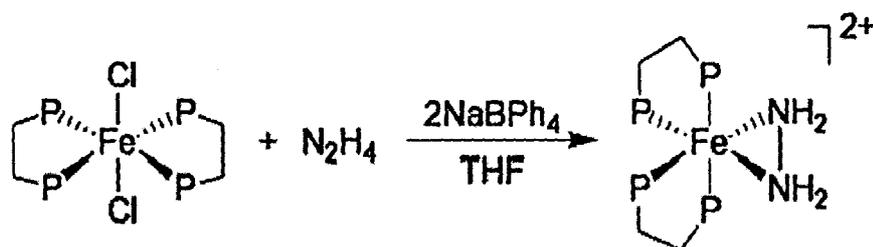
On the other hand, all hydrazine ligands in $[\text{Co}(\text{N}_2\text{H}_4)_6]\text{Cl}_2$ are coordinated to Co atoms as unidentate ligand.



Structure III: The hydrazine ligands in $[\text{Co}(\text{N}_2\text{H}_4)_6]\text{Cl}_2$ as unidentate ligand.

According to Nicholls and Swindells[19], the complexes of the former type (bidentate) exhibit the $\nu(\text{N}-\text{N})$ near 970 cm^{-1} , whereas those of the latter type (unidentate) show it near 930 cm^{-1} . The hydrazine complexes of $\text{M}(\text{II})$, where $\text{M} = \text{Ni}/\text{Co}/\text{Zn}/\text{Cd}/\text{Os}$ and $\text{Ln}(\text{III})$ ($\text{Ln} = \text{Pr}/\text{Nd}/\text{Sm}$) have also been reported to be

consisting of a unidentate or bridging bidentate ligand [20]. Metal hydrazine complexes, $[M(N_2H_4)_n]^{2+}$ ($M = Mn, Fe, Co, Ni, Zn$ and $Cd, n = 2$ or 3) with different anions like sulphate, sulphite, acetate, formate, oxalate, hydrazinocarboxylate, nitrate and perchlorate have also been synthesized[21]. Bis(hydrazine)complexes $[Fe(RNHNH_2)_2\{PPh(OEt)_2\}_4](BPh_4)_2$ ($R=H,CH_3$) 1, 2 were prepared by allowing nitrile complexes $[Fe(CH_3CN)_2\{PPh(OEt)_2\}_4](BPh_4)_2$ to react with hydrazine at $0^\circ C$. The monohydrazine $[Fe(NH_2NH_2)(CH_3CN)_2\{P(OEt)_3\}_3](BPh_4)_2$ derivative was also obtained. Treatment of bis(hydrazine) 1, 2 with $Pb(OAc)_4$ led to the acetate complex $[Fe(\kappa^2 O_2CCH_3)\{PPh(OEt)_2\}_4]BPh_4$ [22]. Mono and bis-(hydrazine)complexes of ruthenium have been reported [23].The iron phosphine complex *cis*- $[Fe(DMeOPrPE)_2(\eta^2-N_2H_4)][BPh_4]_2$ {DMeOPrPE = 1,2-bis[bis(methoxypropyl)phosphino]ethane} was synthesized and structurally characterized. The structure IV exhibits the first η^2 coordination of hydrazine to iron, which may be relevant to intermediates trapped during nitrogenase turnover [24].



Structure IV: The first η^2 coordination of hydrazine to iron

Several new polymeric complexes of general composition $MO_n(L)_4X_2$ (where $M = V, Zr$ and $U; n = 1$ or $2; X = Cl, Br, I, NO_3$ and NCS and $L = N_2H_4, PhNHNH_2$ and

Me_2NNH_2 have been synthesised [25]. The intercalation complex of a low-defect ("well-crystallized") kaolinite from Cornwall, England, with hydrazine was studied by high-temperature X-Ray diffraction (HTXRD), differential thermal analysis (DTA), and thermogravimetry (TG) which suggests a sort of adduct of hydrazine formation causing an increase in the basal spacing of the kaolinite. The X-Ray pattern at room temperature indicated that intercalation of hydrazine into kaolinite causes an increase of the basal spacing from 7.14 to 10.4 Å, as previously reported [26]. The preparation of moderately stable complexes of hydrazine with aluminum isopropoxide, titanium ethoxide, titanium isopropoxide, and zirconium isopropoxide are described [27].

Ultrafine cobalt ferrite has been prepared by the decomposition of cobalt oxalate-hydrazinate complex [28] which is used as precursor. The preparation and thermal decomposition of the precursor have been studied using chemical, thermal, and infrared techniques. The precursor decomposes at low temperatures with the effusion of large amounts of gases. The coordination compounds used as chemical precursors have to include, ligands, which generate, by decomposition, volatile products. Carboxylic acids are ligands, which correspond to this requirement. It is well known that the time required for thermal decomposition of oxalates can be considerably shortened if the precursors are heated in the presence of a reducing agent, such as hydrazine. The hydrazine together with cobalt cations have been incorporated in the structure of iron oxalate for yielding coordination compounds, chemical precursors for low temperature synthesis of the corresponding ferrite. For cobalt oxalate-hydrazinate, it was established the chemical composition, spectral

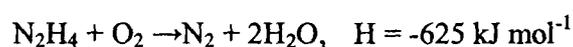
properties and thermal behavior to determine the conditions for ferrite powder synthesis. Chemical, infrared, and Mössbauer spectroscopy confirmed the formation of spinelic ferrite, at 500 °C [28]. The thermal decomposition of mixed-ligand complexes of cobalt, nickel and copper saccharinates with hydrazine and ethylenediamine were studied in static air atmosphere [29]. The reactions of nickel (II) chloride with hydrazine, methylhydrazine and 1, 1-dimethyl-hydrazine have been investigated [19]. As well as the hydrazine bridged complex $\text{Ni}(\text{N}_2\text{H}_4)_2\text{Cl}_2$, nickel (II) chloride forms $\text{Ni}(\text{N}_2\text{H}_4)_3\text{Cl}_2$ in which the nickel atom is surrounded by six nitrogen atoms as nearest neighbors. Methylhydrazine forms $\text{Ni}(\text{MeNHNH}_2)_2\text{Cl}_2$ and $\text{Ni}(\text{MeNHNH}_2)_6\text{Cl}_2$ while 1,1-dimethyl-hydrazine (DMH) forms $\text{NiCl}_2 \cdot 4\text{DMH}$, $\text{NiCl}_2 \cdot 2\text{DMH}$ and $\text{NiCl}_2 \cdot \text{DMH}$. The spectra and magnetic moments of all the complexes are consistent with octahedral (or tetragonal) stereochemistry [19].

The literature survey reveals the versatility of hydrazine ligand in forming metal complexes. In our own laboratories several metal hydrazine complexes have been synthesized and their potentiality in the synthesis of metal oxides has been realized [30-37]. The metal hydrazine complexes, such as $\text{FeC}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$, were synthesized [31] by two methods; first by the wet chemical method and second by equilibrating with hydrazine hydrate vapor in a dessicator. The resultant product was found to be an anhydrous ferrous oxalate hydrazinate. The decomposition end-products of these complexes were characterized and measurements were done. Ferrous oxalate dihydrate $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, yielded mainly $\gamma\text{-Fe}_2\text{O}_3$ upon controlling the atmosphere during decomposition. However, autocatalytic decomposition of hydrazinated complexes, $\text{FeC}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ formed a mixture of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. Efforts

were made to increase the γ -Fe₂O₃ content by controlling the atmosphere during decomposition of these complexes [31]. The hydrazine method as reported [32] gave iron (II) carboxylatohydrazinates of the iron (II) carboxylates: FeC₂O₄·2N₂H₄, FeC₄H₂O₄·2N₂H₄, FeC₄H₄O₄·2N₂H₄, FeC₃H₂O₄·1.5N₂H₄·H₂O, FeC₄H₄O₆·2N₂H₄·H₂O, FeC₄H₂O₄·2N₂H₄ and FeC₄H₄O₅·2N₂H₄ all decompose autocatalytically to mainly γ -Fe₂O₃ without controlling the water vapor atmosphere during the synthesis. The desired water atmosphere in the synthesis of γ -Fe₂O₃ from the hydrazinates of iron (II) carboxylates is provided by the reaction products. The N₂ + 2H₂O atmosphere helps in stabilizing γ -Fe₂O₃. γ -FeOOH topotactically dehydrates to γ -Fe₂O₃, while hydrazinated γ -FeOOH decomposes to γ -Fe₂O₃ via an Fe₃O₄ intermediate [32-34]. The iron oxides obtained as reported [35] were mainly α -Fe₂O₃ of hexagonal form with corundum structure. However, a novel hydrazine method used in the synthesis of iron oxides yielded mainly γ -Fe₂O₃ and the cubic spinel magnesium ferrite, MgFe₂O₄, prepared from synthetic iron oxide, γ -Fe₂O₃, showed superior magnetic and electrical properties as compared to the ferrite obtained from commercial grade α -Fe₂O₃ [35]. Hydrazine methods were adopted [36] because the hydrazinated complexes, in general, especially carboxylato-hydrazinates decompose explosively. Metal carboxylates are pyrophoric and the hydrazination further enhances their pyrophoric nature. FeC₂O₄·2H₂O in air decomposes [31] at 300-350°C to α -Fe₂O₃, while in an inert atmosphere of N₂ the decomposed product is black magnetite Fe₃O₄, a controlled atmosphere of moisture at ~310°C allows the formation of γ -Fe₂O₃. FeC₂O₄·2H₂O on hydrazination forms FeC₂O₄·2N₂H₄ which when brought near a burning splinter catches fire and a glow that spreads through the bulk

completing the decomposition autocatalytically to γ -Fe₂O₃. Thus, hydrazinated complexes are pyrophoric which allow the decomposition to take place easily at an ordinary temperature [36].

In general the hydrazine complexes decompose exothermically at much lower temperatures compared to the one without hydrazine. This may be due to the hydrazine leaving the structure reacts with the atmospheric oxygen [9],



liberating enormous energy which is sufficient to oxidatively decompose the complex. For example, FeC₂O₄·2N₂H₄ decomposes exothermically, while FeC₂O₄·2H₂O endothermically loses the water of crystallization followed by a broad exothermic reaction. Atmospheric oxygen plays an important role in the decomposition of hydrazine complexes as hydrazine has higher affinity for oxygen.

Aim and Objective

As mentioned earlier, to remove oxygen dissolved in water, say from the reservoir drinking water, use of cationic and anionic complexes of trivalent cobalt with inorganic ligand or the mixtures thereof are used as activators along with the hydrazine [10] such as [Co(NH₃)₅Cl]Cl₂ and Na₃[Co(NO₂)₆] and as catalyst the organometallic complex, [Co(3,4-TDA)₂]Cl₂ in boiler feed water based on hydrazine [7]. However, the exact mechanism of the activators or catalysts is not revealed. But, the autoxidation of hydrazine, hydroxylamine and cystein by the Cobalt (II) chelate complex of 3,10,17,24-tetrasulphophthalocyanine (H₂tspc), studies [11] do give a clue of probable formation of hydrazine adduct [Co^{II}(tspc)]

$[(N_2H_4)]$ which reacts with molecular oxygen producing reaction products of hydrazine, N_2 and H_2O leaving intact $[Co^{II}(tspc)]$, while only $[Co^{II}(tspc)]$ reacts with O_2 forming an oxygen adduct by getting oxidized to $Co(III)$, $[Co^{III}(tspc)(O_2)]$. The preliminary oxygen uptake studies carried out in our laboratories on cobalt salen and hydrazinated cobalt salen indicate reversible oxygen uptake by the complexes. The oxygen uptake enhancement is also seen when the cobalt salen is introduced in the aqueous hydrazine, suggesting likely formation of an adduct of hydrazine and O_2 with the cobalt salen, $[Co(C_{16}O_2H_{12}N_2)_2 \cdot N_2H_4 \cdot O_2]$. These preliminary studies give a clue of a likely formation of a hydrazine adduct with the cobalt toluene diamine complex $[Co(3,4-TDA)_2]Cl_2$ in the patented studies [6,7] and may react with the oxygen forming the hydrazine oxidation products leaving behind the complex $[Co(3,4-TDA)_2]Cl_2$, thereby, the complex acting as catalysts. Cobalt (II) halide tris(hydrazine hydrochloride) complexes of the formula, $[Co(II)(N_2H_4 \cdot HX)_3]X_2$ reported [38] suggest a likely formation *in situ* of $[Co(NH_3)_5 \cdot n(N_2H_4)_nCl]Cl_2$ when the $[Co(NH_3)_5Cl]Cl_2$ compounds are used as activators in the oxygen scavenging by hydrazine [10]. Considering these possibilities, we aimed at synthesizing several cobalt complexes and also their hydrazine complexes and used them along with the hydrazine to enhance the oxygen scavenging action of hydrazine in the boiler feed water after duly de-aerating mechanically the de-mineralized water to bring the dissolved oxygen to 4 to 5 ppm in a home built de-aerator.

The main objective, however, is to minimize the use of hazardous hydrazine in the continuous running of the boilers by the use of catalysts and towards this objective investigate different catalysts for their effectiveness.

To realize the objectives a proto type de-aerator for boiler feed water was needed to be fabricated. However, since catalytic hydrazine oxygen scavenger was expected to enhance the scavenging efficiency, it was also expected that such use of catalyst might also reduce the quantum of toxic hydrazine use in the continuous running of the boiler, thereby, making the whole process environmentally friendly.

Keeping in mind the above aim and objectives, exhaustive literature survey was carried out and several cobalt based metal complexes were synthesized, characterized and in a proto type boiler all the investigations of oxygen scavenging with hydrazine and hydrazine plus cobalt complexes were performed. The details of all these investigations are presented in the present thesis.

Methodology

Synthesis:

i) Re-prepare the various already reported cobalt complexes- cobalt chloride 3, 4-diamino toluene (CDAT), $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ [7], cobalt -L-Proline complex (CP), $[\text{Co}(\text{L-Proline})_2(\text{H}_2\text{O})_2]$ [39], cobalt chloride carbohydrazide complex(CZ), $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$ where $\text{L}=(\text{H}_2\text{N-NH})_2\text{CO}$ [40], by slight modification, to improve the yield of each.

ii.) Re-synthesize a hydrazine complex, cobalt chloride hydrazinate (CH) $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ by a solution method as per the reported procedure [9,38] from cobalt chloride and by hydrazine equilibration method [32,33,37,41-43].

iii.) Synthesize all the cobalt complexes starting from cobalt chloride and also from cobalt acetate and hydrazinate them by solution method and hydrazine equilibration method. Following are the cobalt complexes and their hydrazinate complexes that are being considered in the present thesis;

cobalt chloride hydrazinate(CH), cobalt chloride 3, 4-diamino toluene (CDAT), cobalt chloride 3, 4-diamino toluene hydrazinate(CDATH), cobalt L-Proline(CP), cobalt L-Proline hydrazinate(CPH), cobalt hydroquinone (CHQ), cobalt hydroquinone hydrazinate(CHQH), cobalt chloride carbohydrazide (CZ), cobalt acetate hydrazinate(CAH), cobalt acetate 3, 4-diamino toluene (CADAT), cobalt acetate 3, 4-diamino toluene hydrazinate (CADATH), cobalt L-Proline (CAP), cobalt L-Proline hydrazinate (CAPH), cobalt hydroquinone (CAHQ), cobalt hydroquinone hydrazinate(CAHQH), cobalt acetate carbohydrazide (CAZ), cobalt salen(CS), cobalt salen hydrazinate(CSH).

Characterization: Characterize the various complexes through

(a) Chemical analysis

(b) Infra red Spectroscopy (IR)

(c) Magnetic Susceptibility using Gouy's balance.

(d) Thermal- Isothermal weight loss, Thermogravimetric(TG) and

differential scanning calorimetric (DSC)/ Differential Thermal analysis (DTA)

- (e) Electron spin resonance spectroscopy (ESR).
- (f) X-ray photoelectron spectroscopy (XPS)
- (g) X-ray diffraction (XRD)
- (h) Ultra violet- Visible Spectroscopy (UV-Vis) and Ultra violet - Diffuse Reflectance Spectroscopy (UV-DRS)

Investigation:

i) Fabricate a home-built de-aerator, to study and investigate the oxygen scavenging action of the various complexes as well as other compounds. Also incorporate the various compounds/complexes in a polymer matrix and further investigate their oxygen scavenging action by introducing them in the de-aerator and use the following analytical tools.

- (a) Winkler's Method for estimating the dissolved oxygen.
- (b) Lovibond Comparator 2000+ to estimate dissolved oxygen below 0.1 ppm.
- (c) UV-Visible Spectroscopy for hydrazine estimation.

ii) Measure Oxygen uptake using a simple apparatus depicted in Figure 1.1

iii) Compiling Results: Obtain the results of the synthesis of the above complexes and suggest a plausible formula. From the oxygen scavenging action carried out by hydrazine and by the various complexes; mainly the cobalt complexes whose starting source is cobalt chloride, hydrazinated and unhydrazinated; along with or without hydrazine in the de-aerator, find out the effectiveness of the scavengers and suggest a line of attack for minimizing the use of perilous hydrazine in the continuous running of the boilers, thereby making the whole process

conservational. From the oxygen uptake measurement by the cobalt complexes, advocate a higher oxygen uptake by the cobalt complexes in hydrazine and designate a catalytic/activator effect of the cobalt complex in the autoxidation of hydrazine.

iv) Conclusion and Future Work: For the first time we have lucratively prepared the cobalt complexes and suggested a plausible formula. The structure may be indomitable by obtaining the crystals.

Organization of Thesis

The Thesis consists of five chapters

Chapter I: Introduction

Chapter I gives the general introduction to the boiler material corrosion and scope for minimizing the corrosion by controlling the dissolved oxygen (DO) concentration by employing chemical oxygen scavengers such as hydrazine, carbohydrazide, hydroquinone, sodium sulfite and catalyzed oxygen scavengers. Based on the exhaustive literature survey; aim, objective and methodology of investigations have been drawn.

Chapter II: Characterization techniques

In Chapter II details of characterization techniques have been described.

Chapter III: Cobalt complexes

Chapter III deals with a thorough preparation of the various cobalt complexes and their characterization to fix the plausible chemical formulae. Details of synthesis of cobalt complexes starting from cobalt chloride; and using cobalt acetate as a cobalt source are described.

Chapter IV: Catalyzed Oxygen scavenging activity

In chapter IV the oxygen scavenging investigations have been described and discussed.

Chapter V: Summary and scope for future work

In chapter V summary and conclusion of the results on the various systems and methods studied in the present investigation are drawn. Also future scope of the work is projected.

References

References quoted in the body of the text in all Chapters are compiled here.

Chapter II

Characterization Techniques

Experimental:

The synthesis of the various cobalt complexes are described in detail in Chapter III. However the characterization techniques of all the investigations are explained in this chapter.

2.1. Chemical analysis

To characterize a sample, chemical analysis is the fundamental contrivance available in the laboratory. The percentage of hydrazine and metal ions are determined by the standard chemical methods [44].

Estimation of Hydrazine: Hydrazine estimation was done under Andrew's conditions [44].



Thus $\text{KIO}_3 = \text{N}_2\text{H}_4$

To the known amount of sample taken in a glass stoppered bottle, 15 mL of concentrated hydrochloric acid, HCl and 10 mL of double distilled water was added followed by carbon tetra chloride, CCl_4 . Standard potassium iodate, KIO_3 (5.350 g/L) was then added drop-wise from the burette with constant stirring and shaking the bottle until the CCl_4 layer decolorizes indicating the end point.

Percentage of hydrazine in the sample was then calculated by using the relation.

$$1 \text{ mL of } 0.025 \text{ M } \text{KIO}_3 = 0.0008103 \text{ g of } \text{N}_2\text{H}_4$$

Estimation of Cobalt: The Cobalt content of the various complexes was estimated by ethylene diamine tetra acetic acid (EDTA) complexometric titrations [44]. A

standard solution of 0.02 M EDTA was prepared by directly weighing disodium salt of EDTA and dissolving it in double distilled water. This EDTA solution was standardized by titration with zinc sulfate, $ZnSO_4 \cdot 7 H_2O$. A known weight of the sample, 100 mg of cobalt complex was dissolved in 1:1 HCl and heated in boiling water bath till dissolution. This was then diluted with distilled water and the volume was made to 100 mL. 25 mL of the sample was taken. A pinch of buffer Hexamine and ammonium hydroxide, NH_4OH were added to adjust and maintain pH =6. A few drops of xylene orange were added as an indicator. This solution was then titrated against 0.02 M EDTA till color changes from orange red to yellow indicating end-point.

Amount of metal ions present was calculated by the following relation

1000 mL of 1M EDTA \equiv 58.933 g of Co

'x' mL of 0.02 M EDTA \equiv 'y' g of Co

25 mL of the sample contains 'y' g of Co

Therefore 100mL of the sample contains 'z' g of Co

$\frac{\text{Amount of Co ('z' g)}}{\text{Weight of sample}} \times 100 = \% \text{ Co}$

2.2. Infra red Spectroscopy (IR)

Infrared (IR) Spectroscopy is a precious tool for analyzing samples. It is based on the fact that a molecule will have a number of fundamental vibration frequencies and each fundamental frequency may be associated with the absorption of radiation of its own frequency. It has been widely used for identifying the organic ligands bound to the metal ion; metal oxygen bonds as well as the adsorbed species on the

catalyst surface. IR instrument can be divided into two classes namely dispersive and non dispersive. The dispersive type of instrument is similar to UV-visible spectrophotometer while the non dispersive type has an interferometer in the place of monochromator and the instrument is called as Fourier Transform Infra-red Spectroscopy (FTIR). The different components of FTIR are 1) Source, 2) Michelson Interferometer, 3) Sample compartment, 4) Detector. The spectrum of the sample can be interpreted for the functional groups present by matching the corresponding group frequencies.

Infrared spectra of the metal precursors and their decomposed product were recorded on SHIMADZU FTIR instrument, model IR Prestige –21 fitted with diffuse reflectance accessories. The samples were mixed with spectroscopic grade KBr and ground well. IR spectra were scanned in the frequency range of 4000-400 cm^{-1} and the samples were recorded in percent transmittance (%T) mode against wave number ($1/\lambda$) cm^{-1} .

2.3. Magnetic Susceptibility using Gouy's balance

The most common *modus operandi* employed for measuring magnetic susceptibility is the Guoy's method wherein the sample under examination is placed in a magnetic field and its weight is measured. The pole pieces of the magnet are usually cylindrical so that the magnetic field is symmetrical about the axis of the magnet. The magnetic field is strongest at the centre where the bottom of the sample column is placed. The magnetic field falls off in radial directions so that it is very small at the top of the column. The sample is taken as a uniformly packed solid in a glass

tube suspended from the balance. Under these conditions, there is an apparent change in the weight of the sample when the magnetic field is turned on. The change in weight of the sample is related to the magnetic susceptibility of the magnetic substance in the sample. Magnetic susceptibility is the ratio of the intensity of magnetization of the specimen of the material and the strength of the magnetic field applied. It measures how easily the specimen can be magnetized.

The magnetic susceptibilities of the various cobalt complexes were brought into being by the Gouy method at room temperature with a field of the order of 8500 gauss using mercury tetrathiocyanatocobaltate ($\text{Hg}[\text{CoSCN}_4]$) as the standard reference material.

2.4. Thermal Analysis

Thermal analysis is comprehensively used in the characterization of materials, chiefly for metal precursors. The techniques include Isothermal weight loss, Thermo gravimetric Analysis (TGA), Differential Thermal Analysis(DTA) and Differential Scanning Calorimetry (DSC).

(i) Isothermal weight loss:

Isothermal weight loss concedes examination of weight loss. The various cobalt complexes were weighed in silica crucibles. The initial weight of the crucible and samples were noted. The crucibles containing the samples were placed in a muffle furnace and the temperature was slowly raised to 700°C. The weight loss of the cobalt complexes were measured by finding the difference in the final and initial weight of the crucibles + sample. The isothermal weight loss % was then calculated.

(ii) Thermogravimetric(TG) and differential scanning calorimetric (DSC)/

Differential Thermal analysis (DTA)

Thermogravimetry (TG) provides quantitative scrutiny of mass loss with thermally induced transitions. It also provides information regarding the thermal stability of the material. The changes in physical and chemical properties of the material can be monitored as a function of temperature. Thus the reaction mechanisms can be predicted based on the thermal data. Essential components of a TG analyzer are 1) Furnace, 2) Sample crucible with thermocouple, 3) Automatic recording balance and 4) Printer/plotter. Differential Scanning Calorimetry (DSC) analysis /Differential Thermal analysis (DTA) provides the differential heat flux between the sample and reference material as a function of temperature. The different components of a DSC instrument are 1) Sample and reference container, 2) Average temperature amplifier, 3) Differential temperature amplifier, 4) Programmer. Differential Thermal analysis (DTA) is one of the oldest and simplest thermal techniques used for the study of physical and chemical transformations in materials associated with the energy changes. In DTA, the temperature difference T between the sample and the thermally inert reference is measured as a function of temperature/time when both are heated simultaneously at the predetermined constant heating rate in the controlled atmosphere. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were performed on NETZSCH DSC-TG; STA 409PC. The heating rate was maintained at $10^{\circ}\text{C min}^{-1}$. The analysis was carried out in air.

2.5. Electron spin resonance spectroscopy (ESR)

Electron Spin Resonance (ESR) is a branch of spectroscopy in which electromagnetic radiation, usually of microwave frequency is absorbed by molecules, ions, or atoms possessing electrons with unpaired spins, i.e. electronic spin $S > 0$, which is a common feature of transition metals. The reversal of spins of these unpaired electrons in an applied magnetic field is recorded. The spectra are obtained by varying magnetic field at constant microwave frequency. The condition for absorption of resonant energy is $E = g\beta_e H$

Where β_e is a constant, i.e. the Bohr Magneton (BM), H is the strength of the applied magnetic field, the factor 'g' is the gyro magnetic ratio and has a value of 2.0023 for a free electron. ESR spectra are usually represented as the first derivative of the absorption. From ESR spectra we can obtain information on the paramagnetic ion and its immediate environment in the host structure. The Electron spin resonance (ESR) spectra were recorded on Bruker BioSpin Gx, with Field sweep width 8000 G and Microwave frequency 9.425 GHz. Reference compound used was DPPH (2,2-Diphenyl-1-picrylhydrazyl) with g value of 2.0036. The samples were scanned as solid at room temperature; and 120K as well as dissolved in dimethyl formamide (DMF) and scanned at 120K.

2.6. X-Ray Photoelectron spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy known as XPS or ESCA (Electron Spectroscopy for Chemical Analysis) has the ability to measure binding energy variations resulting from their chemical environment.

It measures the kinetic energy of the electrons that are emitted from matter as a consequence of bombarding it with ionizing radiations or high energy particles. There is direct ionization of an electron from either a valence or an inner shell. The kinetic energy E of the ionized electron is equal to the difference in energy of the incident radiation E_i and the binding energy of the electron E_g . Measurement of E_i and E_g therefore provides a means of the identification of the atoms. The ionizing radiation used is X-Rays and hence this technique is also known as X-Ray photoelectron spectroscopy (XPS). XPS analysis was done at 298K using Mg K_{α} radiation on a VG Microtech Multilab ESCA 3000 spectrometer. Binding energy (BE) calibration was performed with Au (4f7/2) core level at 83.9 eV. Al K alpha was used for nitrogen 1s level. All other core levels were recorded with Mg K alpha. Sample surfaces were scraped before analysis. Measurement conditions and parameters were verified to get the right carbon peak position (C 1s = 248.8 eV), assuming an error lower than 0.2 eV. Spectra were fitted with Gaussian-Lorentzian (80-20% respectively) peaks, considering a Shirley baseline.

2.7. X-Ray diffraction (XRD)

The X-Ray diffraction technique is most extensively used for characterization of different crystalline solids. The position and intensities of X-Rays diffracted by a

crystalline solid provide a lot of information such as crystal structure, composition of the solid, particle size etc. X- Rays are a form of electromagnetic radiation of very short wavelength from 0.1 to 100 Å and are produced when high speed electrons are stopped by a solid object.

In a crystal different atoms and molecules are arranged in different planes in a systematic and repetitive manner. These inter-planar distances are of the same order of magnitude as the wavelength of the characteristic X-Rays emitted by the target. Hence the crystal planes act as a diffraction grating to the X-Rays and diffraction occurs. The necessary condition for X-Ray diffraction to occur is represented by Bragg's equation, $n\lambda = 2d \sin\theta$ where n is an integer (1, 2, 3 etc.) called the order of reflection, θ is the glancing angle of incident X-Ray beams on the crystal surface, d is the inter-planar spacing and λ is the wavelength of X-Rays. The phase identifications of the powdered samples, precursors and oxides of the cobalt chloride complexes were studied through powder diffraction technique. This method uses sample in powder form. Different components of powder diffractometer are evacuated X-Ray tube (source), sample compartment and detector. X-Ray diffraction studies of the decomposed products of the complexes were carried out on PHILIPS-X'Pert Industry using Co K α radiation and of the precursors by X'Pert Graphics using K alpha radiation.

2.8. Ultra violet- Visible Spectroscopy (UV-Vis) and Diffuse Reflectance

Spectroscopy (UV-DRS)

Transitions of electrons between outermost energy levels are associated with energy changes in the range $\sim 10^4$ to 10^5 cm^{-1} or 10^2 to 10^3 kJ mol^{-1} . These energies span the range from the near infrared through the visible to the ultraviolet and are therefore often associated with color. Various types of electronic transition occur and may be detected spectroscopically.

A reliable technique to find the unknown concentration of a moiety in the samples by finding the absorbance is Ultra violet -Visible Spectroscopy (UV-Vis). The concentration of hydrazine in the boiler feed water was pronounced by using a Shimadzu UV-2450 UV-Visible Spectrometer measured at a wavelength of 460 nm. Ultra violet -Diffuse Reflectance Spectroscopy (UV-DRS) is an authoritative technique to identify and characterize the metal ion coordination. It is a non destructive technique that uses the interaction of light, absorption and scattering, to produce a characteristic reflectance spectrum, providing information about the structure and composition of the medium. It also provides the information regarding the band gap of the materials, above all the semi conducting metal oxides. The diffuse reflectance spectra of dry samples, precursors were recorded using a Shimadzu UV-2450 UV-Visible Spectrometer equipped with a diffuse reflectance accessory in the wavelength range of 800–200 nm. BaSO_4 was used as a reference.

2.9 Home-built De-aerator: In order to study the oxygen scavenging action, we designed and fabricated a home-built de-aerator consisting of a large cylindrical stainless steel drum of length 50 cm, diameter 36 cm and 50L capacity, with electrical heating arrangement to maintain and raise the temperature of water to 90-100°C, continuous controlled stirring arrangement using a stirrer, a long stainless steel rod of length 29 cm with small stainless steel rods of length 6 cm and diameter 1 cm, welded to it horizontally and a rectangular acrylic plate of length, breadth and thickness 24.7 cm, 22.3 cm and 0.4 cm respectively. This plate has small holes and is fixed or joined to the long stainless steel rod. This arrangement was done to introduce and ensure good and proper agitation of the water containing dissolved oxygen; the major approach to reduce or bring down the dissolved oxygen level being, efficient mechanical de-aeration. Arrangement for inlet of water and two outlets; one for sampling of water and the other for washings or clean-up process were also made.

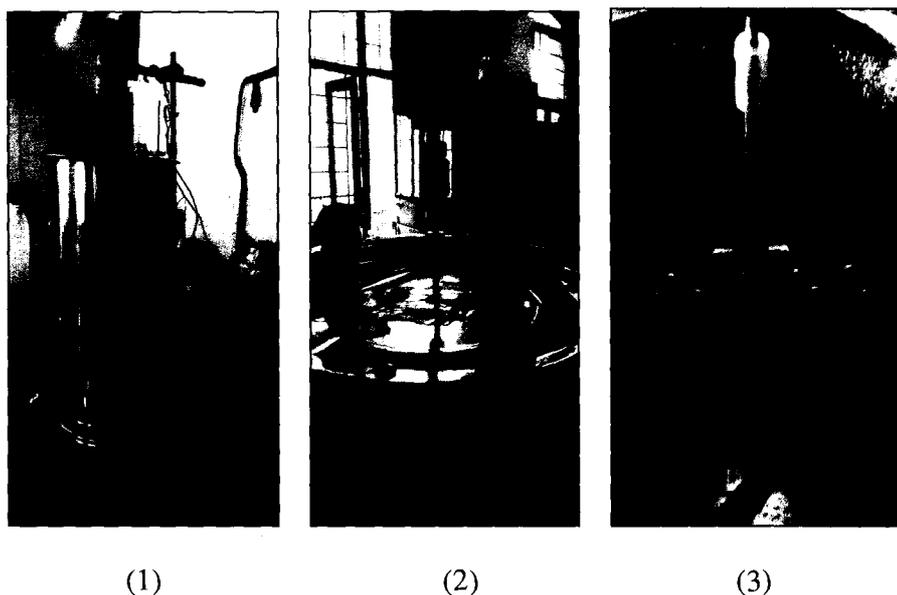


Figure 2.1: Home built de-aerator (1) front view (2) top view (3) internal view

2.10 Winkler's Method:

The Winkler's Method is a technique used to measure dissolved oxygen in freshwater systems. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution. This test is performed on-site, as delays between sample collections and testing may result in an alteration in oxygen content. This method uses titration to determine dissolved oxygen in the water sample. A sample bottle is filled completely with water; no air is left to skew the results. The dissolved oxygen in the sample is then "fixed" by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound that results in a color change. The point of color change is called the "endpoint," which coincides with the dissolved oxygen concentration in the sample. Dissolved oxygen analysis is best done on the field, as the sample will be less altered by atmospheric equilibration.

A 125 mL glass stoppered bottle was filled carefully with sample water. Immediately, 1mL of manganese sulfate, $MnSO_4$ was added to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. If the reagent was added above the sample surface, oxygen would be introduced into the sample. The pipette was slowly squeezed, so no bubbles were introduced via the pipette. 1mL of solution of sodium hydroxide, NaOH and potassium iodide, KI was added in the same manner. The bottle was stoppered with care to be sure no air was introduced. The sample was mixed by inverting several times. If oxygen was

present, a brownish-orange cloud of precipitate or floc would appear. Concentrated sulfuric acid, H_2SO_4 was added via a pipette held just above the surface of the sample. The volume of concentrated sulfuric acid added was noted. The bottle was carefully stoppered and inverted several times to dissolve the floc. From this, 50 mL of the sample was taken in a conical flask or stoppered bottle, and 1-2 drops of starch indicator was added and titrated against sodium thiosulfate by slowly dropping titrant solution from a calibrated burette into the flask and continually stirring or swirling the sample water. The color changed from blue to colorless.

The concentration in ppm of dissolved oxygen in the sample

$$\begin{aligned} & \text{'x' x } 0.025 \times 8 \times 1000 \\ = & \frac{\text{-----}}{a \times (b - c) / b} \end{aligned}$$

Where,

'x' = volume of titrant, sodium thiosulfate

a = volume of sample taken = 50 mL

b = volume of stoppered bottle = 125 mL

c = volume of $\text{H}_2\text{SO}_4 + \text{MnSO}_4 + \text{NaOH} + \text{KI}$ added

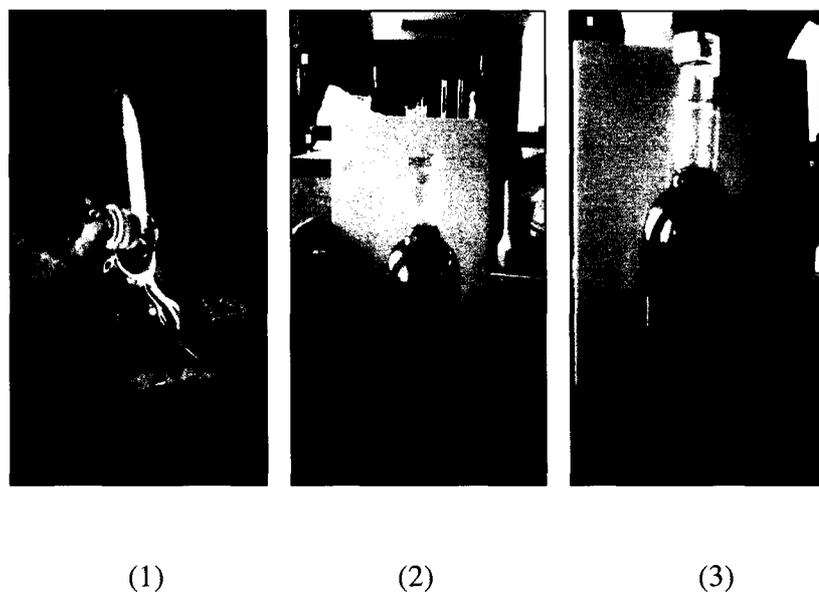


Figure 2.2: (1) sampling (2) appearance of floc (3) floc dissolved using H_2SO_4

2.11 Lovibond Comparator 2000⁺

The dissolved oxygen content in very minute quantity in the de-aerator and boiler feed water is measured by using indigo-carmine and the apparatus required is the Lovibond comparator. The one used by us was Lovibond Comparator 2000⁺. The appropriate test disc for dissolved oxygen was selected for its use and inserted into the comparator with values towards the front of the instrument. The disc covered the range 0 to 0.12 mL/L oxygen in steps 0.005, 0.01, 0.015, 0.03, 0.055, 0.08, 0.1, 0.12 mL/L. To convert mL/L to parts per million, the values in mL/L are multiplied by 1.43. The disc was used in conjunction with a special reaction glass vessel which has been developed for use with the Lovibond Comparator. The reagents used were indigo-carmine stock solution (prepared by dissolving 0.018 g indigo-carmine and 0.2 g glucose in 5 mL double distilled water further adding 75 mL glycerol. This

reagent is stable for 90 days if stored in a refrigerator and for 6 weeks at ambient temperature if stored in the dark), potassium hydroxide (KOH) (37.5 g dissolved in 62.5 mL of distilled water) and leuco reagent (freshly prepared in a small bottle by mixing 8 mL of indigo-carmin stock solution and 2 mL of KOH). After thoroughly mixing, the reagent was allowed to stand until the initial dark red color changed to lemon yellow in approximately 10 minutes. The water sample was taken and the reagents were added in the absence of atmospheric oxygen. Sampling was carried out by the "Submerged Bottle Method". With a dropping pipette the vial attached to the inner surface of the special reaction vessel was filled with leuco reagent. Any entrapped air bubbles were allowed to rise and disperse, so that the vial was completely full and free of air. It was then sealed by means of a glass ball which was placed in position by sliding the ball down a glass tube placed over the end of the vial. The sample was allowed to flow through the reaction vessel for 10 minutes, to remove any reagent on the outside of the vial. The reaction vessel was then removed from the sampling line and the stopper was inserted under water, to prevent the trapping of any air. The reaction vessel was then removed from the water, inverted to allow the ball to fall off the vial and the contents were thoroughly mixed. This reaction vessel was then placed in the right-hand compartment of the Lovibond comparator and a sample of water without reagents was placed in the left-hand compartment to serve as a blank. The color developed in the sample was then compared with the colors on the disc of the comparator.

2.12 Spectrophotometric Estimation of Hydrazine

In this method, the reddish coloration of a sample brought about by the reaction of p-dimethylamino-benzaldehyde (PDBA) on hydrazine in the boiler feed water was measured at a wavelength of 460 nm. The presence in the feed water of any oxidizing agent and a color resembling the red color or turbidity becomes an obstruction for estimation. As for its measuring range, this method is applicable for the hydrazine content 0.01-0.2 ppm.

Gravimetric Calibration curve: Diluting the standard hydrazine liquid (Dissolve 0.328 g of hydrazine dihydrochloric acid $N_2H_4 \cdot 2HCl$ together with 74 mL of hydrochloric acid in 100 mL of water, transfer this solution into one litre measuring flask, diluting it to one litre. 1 mL of this solution contains 0.1mg of hydrazine.) with hydrochloric acid (74 mL of hydrochloric acid in a one litre measuring flask and dilute it to one litre with water), a series of hydrazine solutions of 25 mL which contain various amounts of hydrazine in sequential order, in 50 mL stoppered measuring cylinders were prepared. 2 mL of HCl to each cylinder was added. 20 mL of PDBA solution (Dissolve 4 g of PDBA together with 15 mL of hydrochloric acid in 200 mL of ethanol, put the solution in a brown colored bottle and store it in a dark place) respectively was pipetted and added after shaking them well. After thoroughly mixing them, using as a blank sample a solution that has been separately prepared by adding 20 mL of PDBA solution to 27 mL of water (25 mL water + 2 mL HCl) that does not contain any hydrazine, the respective absorbance of the above mentioned solution with various hydrazine contents was measured spectrophotometrically, using a wave length of 460 nm. The spectrophotometer

used here was the one mentioned in section 2.8 of this chapter. Subsequently, a calibration curve that shows the relationship between the absorbance and hydrazine concentration in ppm was drawn.

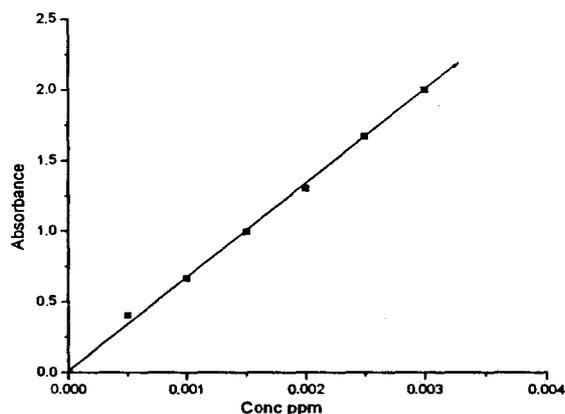


Figure 2.3: Calibration curve for concentration of hydrazine

The hydrazine content in the water collected or sampled out from the home- built de-aerator was measured by this method. As mentioned earlier, the measuring range by this method is applicable for the hydrazine content of 0.01- 0.2 parts per million (ppm). However, the hydrazine concentration in our measurements can be made even well below 0.003 ppm.

Chapter III

Cobalt Complexes

Our main aim is to use metal complexes in enhancing the oxygen scavenging of hydrazine, we have prepared several cobalt complexes and their hydrazine modifications and the results of such studies are presented in this chapter.

This chapter deals with a thorough re-preparation of the various already reported cobalt complexes- cobalt chloride 3, 4-diamino toluene (CDAT), $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ [7], cobalt L-Proline complex (CP), $[\text{Co}(\text{L-Proline})_2(\text{H}_2\text{O})_2]$ [39], cobalt chloride carbohydrazide complex(CZ), $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$ where $\text{L}=(\text{H}_2\text{N-NH})_2\text{CO}$ [40], by slight modifications, to improve the yield of each. In the present investigations, we further used cobalt acetate as a cobalt source to prepare the above complexes and cobalt salen, $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]$ [16].

A hydrazine complex, cobalt chloride hydrazinate (CH) $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ was re-synthesized by a solution method as per the reported procedure [9,38] from cobalt chloride. For the first time, the hydrazinate complexes of all the above complexes were synthesized by solution method from cobalt chloride and cobalt acetate; and that of cobalt salen from cobalt acetate. The hydrazine complexes were also synthesized by hydrazine equilibration method [32, 33,37, 41-43]. In equilibration method, the dried cobalt complexes were spread over the Petri dish and introduced in a desiccator containing hydrazine hydrate, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The hydrazine uptake was monitored titrimetrically by using KIO_3 as titrant [44]. To establish formula; chemical, thermal and spectroscopic studies were carried out. All the cobalt complexes were synthesized in a three-necked round bottom flask under continuous flow of inert nitrogen.

3.1 Synthesis:

The chemicals used for the synthesis were all of analytical grade (AR)

Section 1. Cobalt complexes: from cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

a) Cobalt chloride diaminotoluene complex, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ [7] (CDAT):

A stoichiometric amount of 3, 4-diaminotoluene (DAT) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, based on the formula of the complex, were weighed. An alcoholic/aqueous solution of the cobalt chloride was taken in the flask and alcoholic DAT was then run down slowly and then refluxed for 4 hours by continuously stirring with the magnetic stirrer. Temperature was maintained between 70 and 80°C. The precipitate (CDAT) was then filtered, washed and dried over CaCl_2 .

b) Cobalt L-Proline complex, $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$ [39] (CP):

A stoichiometric amount based on the formula, $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$ of an aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was run down into the flask containing L-Proline dissolved in 1M KOH and stirred continuously in an inert atmosphere. It was then cooled over ice bath and the precipitate (CP) was filtered, washed and dried over CaCl_2 .

c) Cobalt hydroquinone complex (CHQ): This complex was not reported in the literature, hence by trial and error method, and based on a possible formation of the complex, the synthesis was carried out. An aqueous solution of hydroquinone (HQ) was added to an aqueous solution of cobalt chloride to give cobalt -HQ complex

(CHQ) under inert atmosphere and refluxed for 4 hours. Needle-shaped crystals obtained were filtered, washed with ethanol and dried over CaCl_2 .

d) Cobalt chloride carbohydrazide complex, $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$ where $\text{L}=(\text{H}_2\text{N}-\text{NH})_2\text{CO}$ [40], (CZ):

A stoichiometric amount of an aqueous cobalt chloride and carbohydrazide were mixed thoroughly and refluxed for 4 hours under inert atmosphere. The precipitate obtained was filtered, washed and dried over CaCl_2 .

Section 2. Cobalt complexes: from Cobalt acetate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

All the above mentioned cobalt complexes were synthesized from cobalt acetate similar to the one from cobalt chloride described in Section 1 of this chapter. However, the cobalt salen, $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]$ was synthesized by slightly modifying the reported procedure [16].

a) SalenH₂: N, N'-bis(salicylaldehyde)ethylenediimine

To a solution of 4.9g (4.2mL) salicylaldehyde in 50mL boiling 95% ethanol was added 1.2g (1.3mL) ethylenediamine. The reaction mixture was stirred for 3-4 minutes and the solution was left to cool in an ice bath. The bright yellow flaky crystals were filtered under suction, washed with ethanol and air dried.

b) Cobalt(salen), $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]$

2.34g SalenH₂ + 120 mL ethanol (95%) taken in the three necked round bottom flask was stirred continuously under inert atmosphere at temperatures 70-80°C till the ligand dissolved. Then 2.17g cobalt acetate dissolved in 15mL hot water was

run down slowly and a brown gelatinous precipitate that formed immediately turned dark red on continued stirring and refluxing for one hour. The precipitate was filtered and washed with water and then with water and dried over CaCl_2 .

Section 3. Cobalt hydrazinate complexes:

i) **Solution Method:** from Cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

a) **Cobalt chloride hydrazinate complex (CH), $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$**

As per the reported procedure [9, 38], the hydrazine complex was synthesized by taking stoichiometric amount of cobalt chloride and slight excess of hydrazine hydrate in a three necked flask and refluxed under inert atmosphere at $40\text{-}50^\circ\text{C}$. The precipitate (CH) was filtered, washed with ethanol and dried over CaCl_2 .

NB: The hydrazine complexes of cobalt chloride 3, 4-diamino toluene (CDAT), $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$, cobalt -L-Proline complex (CP) $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$, were not in the literature and hence by trial and error method, the stoichiometries were fixed. Hence many a time the preparations were repeated.

b) **Cobalt chloride diaminotoluene hydrazinate complex (CDATH):**

To a mixture of alcoholic hydrazine hydrate and DAT, alcoholic cobalt chloride was added in an inert atmosphere and refluxed for 4 hrs to get cobalt chloride-DAT-hydrazine complex (CDATH).

c) Cobalt L-Proline hydrazinate complex (CPH):

To a mixture of hydrazine hydrate and L-Proline dissolved in 1M KOH, aqueous cobalt chloride was added in an inert atmosphere to obtain cobalt -L-Proline hydrazinated complex (CPH).

d) Cobalt hydroquinone hydrazinate complex (CHQH):

To a mixture of hydrazine hydrate and hydroquinone (HQ), aqueous cobalt chloride was added in an inert atmosphere and refluxed for 4 hours to get cobalt -HQ-hydrazine complex (CHQH).

The precipitates thus obtained from the above methods were filtered and washed thoroughly with alcohol and dried over CaCl_2 in a dessicator.

ii) Solution method: from Cobalt acetate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

All the above cobalt complexes were synthesized similar to the one described in section 3.1(a-d). by using cobalt acetate as the starting material.

iii) Hydrazine equilibration method:

All the dried complexes in Section 1 and 2 were spread over a Petri dish and introduced in a dessicator containing hydrazine hydrate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The hydrazine uptake was monitored titrimetrically by using potassium iodate, KIO_3 , as a titrant

[44] to establish the formulae and this was supported by chemical, spectroscopic and thermal studies that were carried out.

3.2 Results and discussion

Chemical formula fixation of cobalt complexes

Based on the chemical analysis of metal and hydrazine contents, as explained in Chapter II, section 2.1, isothermal weight loss supported by thermal analysis (DTA/TG), chemical formula of all the cobalt complexes were proposed. From infra red analysis, magnetic measurements, XPS and ESR studies the formation of the cobalt complexes were further confirmed.

a) Cobalt chloride, $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ and its hydrazinate complex, $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$

The AR grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ showed a total weight loss of 68.6% by isothermal heating and 68.1% by TG studies, and cobalt content of 24.35%, Table 1. The calculated weight loss of 66.37 % and Co content of 24.81 % based on the formula $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ suggest that the sample in hand was in pure form. Its magnetic susceptibility value was 5.2 BM.

Table 1: % Total weight loss values, % Cobalt, % Hydrazine and Magnetic Susceptibility in Bohr Magneton (BM)

(Code) /Formula	% wt loss Iso/ TG Observed (Calculated)	% Cobalt Observed (Calculated)	%Hydrazine Observed (Calculated)	Mag Sus BM
(CCl) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	68.6/ 68.1 (66.37)	24.35 (24.81)	-	5.2
(CH) $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$	63.8/63.81(64.47)	26.04(26.08)	40.8 (42.94)	4.88
(CDAT) $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$	84.16/83.7(83.81)	11.78/(11.88)	-	0.62
(CDATH) $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$	75.3/ 75.1 (74.59)	18.57(18.65)	20.16(20.25)	5.75
(CP) $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$	74.5/ 80(75.3)	18.38(18.13)	-	0.71
(CPH) $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$	66.8/70(66.82)	24.51(24.34)	9.4(13.2)	5.09
(CHQ) $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$	79.4/78(77)	14.6(15.1)	-	0.43
(CHQH) $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$	76.3/- (76.45)	16.5(17.28)	18.5(18.77)	5.29
(CZ) $[\text{Co}(\text{H}_2\text{N-NH})_2\text{COCl}_2(\text{H}_2\text{O})_2]$	67/64.76 (68.6)	22.4 (23)	-	5.28
(CA) $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	63.38/63.5 (67.8)	23.1(23.67)	-	4.89
(CAH) $[\text{Co}(\text{CH}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$	63.16/ 60.9(66.7)	26.8(24.46)	20.8 (26.56)	4.72
(CADAT) $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3](\text{CH}_3\text{COO})_2$	84.64/90.5(85.2)	11.3(10.85)	-	0.67
(CADATH) $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2](\text{CH}_3\text{COO})_2$	78.1/- (77.88)	16.02(16.23)	16.8(17.67)	5.4
(CAP) $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$	74.5/- (75.3)	17.9(18.13)	-	0.72
(CAPH) $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$	66.8/- (66.84)	24.51(24.34)	12.8(13.2)	4.96
(CAHQ) $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$	78.4/- (77)	16.6(16.88)	-	0.43
(CAHQH) $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$	76.1/- (76.45)	16.53(17.28)	18(18.77)	5.29
(CAZ) $[\text{Co}(\text{H}_2\text{N-NH})_2\text{CO}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$	72.6/- (73.5)	18.7(19.45)	-	5.2
(CS) $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]$	-	-	-	2.44
(CSH) $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)] \cdot \text{N}_2\text{H}_4$	-	-	3.84	4.81

The cobalt hydrazinate complex synthesized from cobalt chloride source indicated a total isothermal weight loss of 63.8%, TG loss of 63.81%, Co content of 26.04% and N_2H_4 content of 40.8% Table 1, and based on the already reported complex, $[Co(N_2H_4)_3]Cl_2$, [9,38] the calculated total loss of 64.47%, Co content of 26.08% and hydrazine content of 42.94% match well with the observed values suggesting that the complex achieved the composition of the reported one. The hydrazinate complex showed magnetic susceptibility value of ~ 4.88 BM. The value of 4.8 – 5.2 BM are usually assigned for high spin octahedral Co^{2+} species in complexes such as $CoCl_2$ (5.04 BM), $CoSO_4 \cdot 7H_2O$ (5.06 BM), $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$ (5.00 BM), $Co(N_2H_4)_2SO_4 \cdot H_2O$ (4.31 BM), [40,45,46]

The Infrared peaks of Cobalt chloride (CCl) and its Hydrazinate (CH) are as shown in Figure 3.1 and Table 2,

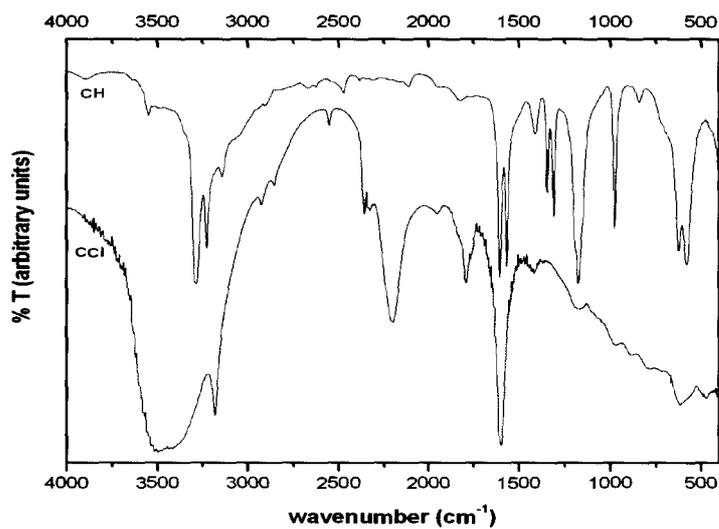


Figure 3.1: IR spectra of cobalt chloride (CCl) and its hydrazinate(CH)

Table 2: Infra red peaks in cm^{-1} of cobalt compounds

(Code)/ Formula	$\nu_{\text{OH}}/\nu_{\text{NH}}$ $\nu_{\text{CH(aromatic)}}$ $\nu_{\text{OH}}/\nu_{\text{CH(sup)}}$	ν_{CH} $\nu_{\text{C=C}}$	δ_{NH_2} / NH δ_{NH} /CH(sup) / δ_{CH}	O-C-O ν_{asym} / ν_{sym}	ν_{CO} ν_{CC}	ν_{NN}	δ_{OH} / δ_{OCO}
(CCl)/ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	3300-3100						
(CH)/ $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$	3300-3100		1600			974	
(CA)/ $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	3562-3066	2356		1566/ 1410	1348/ 1026		879/ 800
(CAH)/ $[\text{Co}(\text{CH}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$	3562	2356	1600	1566/ 1410	1348/ 1026	974	879/ 800
(CDAT)/ $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$	3200/3100 /3000	1630	1600/ 1562				
(CDATH)/ $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$	3300-3100		1600/ 1566			974	
(CADAT)/ $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3](\text{CH}_3\text{COO})_2$	3300-3100	2356	1600/ 1562	1566/ 1410	1311/ 1026		810
(CADATH)/ $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2](\text{CH}_3\text{COO})_2$	3300-3100	2356	1600/ 1562	1566/ 1410	1311/ 1026	970	810

The broad O-H stretching, $\nu_{\text{OH}} \sim 3300\text{-}3100 \text{ cm}^{-1}$ [47], in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ gets sharpened in hydrazine complex, $\text{CoCl}_2 \cdot 3\text{N}_2\text{H}_4$ due to N-H. The N-H and N-N stretching $\nu_{\text{NH}} \sim 3300\text{-}3100 \text{ cm}^{-1}$, $\nu_{\text{NN}} \sim 974 \text{ cm}^{-1}$ and NH_2/NH bend, $\delta_{\text{NH}_2/\text{NH}} \sim 1600 \text{ cm}^{-1}$ in the hydrazine complex further suggest that hydrazine is linked to the metal and a bidentate nature of the N_2H_4 , $\nu_{\text{NN}} \sim 974 \text{ cm}^{-1}$ is invoked here [20,37,41-43,47]. The cobalt complex with 3 bidentate hydrazine molecules is octahedral in nature and its observed magnetic susceptibility value is $\sim 4.88 \text{ BM}$ further confirms the octahedral nature of the complex.

Thermal traces TG/DTA:

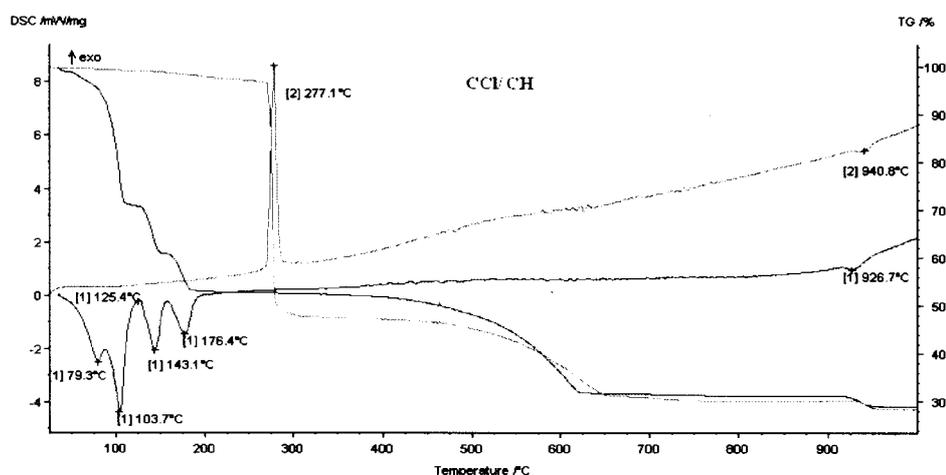
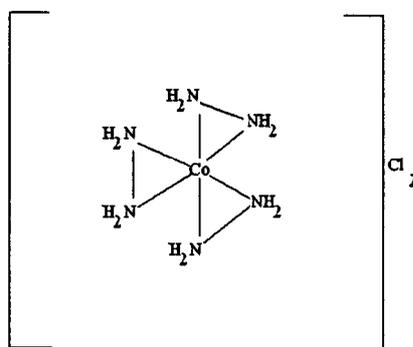


Figure 3.2: TG/DSC (DTA) of cobalt chloride (CCl) and its hydrazinate(CH)

$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ loses $\sim 45\%$ weight in three steps $<180^\circ\text{C}$ accompanied by 4 endothermic peaks, $\sim 80, 103, 143$ and 176°C . The next major weight loss was observed in $400\text{-}600^\circ\text{C}$ and a minor weight loss of $<2\%$ above 900°C which is

accompanied by an endothermic kink. On the other hand, the hydrazine complex, $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ showed a sharp weight loss in the temperature of 270-280°C accompanied by intense exothermic peak ~276°C. The next major weight loss was observed between 460 and 650°C without observable endothermic/exothermic process as in the unhydrazinated complex, but there occurred, however, an endothermic kink and weight loss >900°C. These results clearly show that the hydrazine modification of the cobalt chloride decompose exothermically like many metal hydrazine complexes [30-37]



Structure of cobalt chloride hydrazinate(CH)

b) Cobalt acetate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4(\text{H}_2\text{O})$ and its hydrazinate Complex:

The observed total loss, isothermal weight loss of 63.38% (TG loss of 63.49%) and the Co content of 23.1% are, respectively, very close to the calculated one of 67.86% and 23.67% based on the formula $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, suggesting the compound is pure. The hydrazinated complex, on the other hand, indicated total isothermal loss of 63.16% (TG 60.94%), cobalt content of 26.8% and hydrazine 20.8%. Based on these values a plausible chemical formula of $[\text{Co}(\text{CH}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$ was suggested, since the calculated total loss of 66.68%,

Co content of 24.46% and hydrazine content of 26.56% are very close to the observed values.

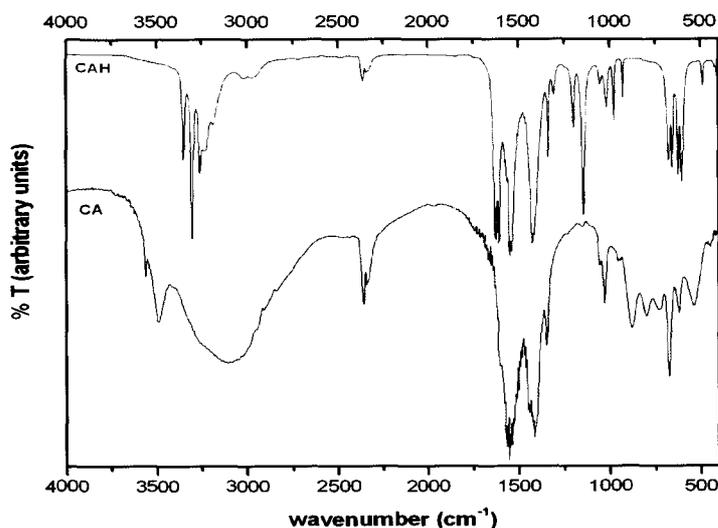
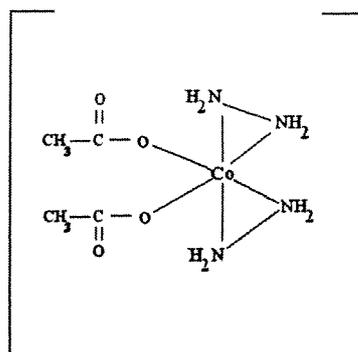


Figure 3.3: IR spectra of cobalt acetate (CA) and its hydrazinate(CAH)

The broad O-H stretching $\nu_{OH} \sim 3562/3066\text{cm}^{-1}$ (superimposed ν_{CH}); [47] O-C-O $\nu_{asym}/\nu_{sym} \sim 1566/1410\text{cm}^{-1}$; $\nu_{CH} \sim 2356\text{cm}^{-1}$; $\nu_{CO} \sim 1348\text{cm}^{-1}$; $\nu_{CC} \sim 1026\text{cm}^{-1}$; $\delta_{OH} \sim 879\text{cm}^{-1}$; $\delta_{OCO} \sim 800\text{cm}^{-1}$, are observed for the $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Table 2, figure 3.3, while for hydrazine complex, $[\text{Co}(\text{CH}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$, the broad O-H stretching band sharpened due to N-H. In addition to this the N-N stretch, $\nu_{NN} \sim 974\text{cm}^{-1}$ and NH_2/NH bend, $\delta_{\text{NH}_2/\text{NH}} \sim 1600\text{cm}^{-1}$ suggests hydrazine linkage to the cobalt acetate complex. A bidentate hydrazine link is observed, $\nu_{NN} \sim 974\text{cm}^{-1}$ [20,37,41-43,47]. And the other peaks due to $\nu_{OH} \sim 3562\text{cm}^{-1}$; $\nu_{CH} 2356\text{cm}^{-1}$; O-C-O $\nu_{asym}/\nu_{sym} \sim 1566/1410\text{cm}^{-1}$; $\nu_{CO} \sim 1348\text{cm}^{-1}$; $\nu_{CC} \sim 1026\text{cm}^{-1}$, $\delta_{OH} \sim 879\text{cm}^{-1}$; $\delta_{OCO} \sim 800\text{cm}^{-1}$ further confirm the formation of the complex. The magnetic susceptibility

value of 4.89 BM of cobalt acetate and 4.72 BM of that of the hydrazinate complex indicate high spin octahedral nature of the complex. The reported 4.56 BM [40, 45, 46] value for $\text{Co}(\text{N}_2\text{H}_4)_2(\text{CH}_3\text{COO})_2$ further confirms the formation of the complex.



Structure of cobalt acetate hydrazinate(CAH)

c) Cobalt 3, 4-diamino toluene and their hydrazinate complexes:

Both cobalt chloride and cobalt acetate were used as a starting material for the preparation of the cobalt diaminotoluene complexes;

Cobalt chloride diaminotoluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ and its hydrazine complex

The cobalt chloride 3,4 diaminotoluene complex that synthesized from the cobalt chloride source showed a total weight loss of 84.16% (TG 83.74%) and cobalt content of 11.78% which are close to the calculated ones, respectively, based on the reported formula $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$, of 83.81% and 11.88% indicate the complex is formed. The observed total weight loss of the cobalt diaminotoluene hydrazinate complex is 75.3% (TG 75.08%). The Co and hydrazine contents observed 18.57% and 20.16% respectively. Based on these observed values a plausible formula of $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ was proposed as the calculated value

this formula of total loss, 74.59%, Co 18.65% and N_2H_4 20.25% are very close to the observed ones.

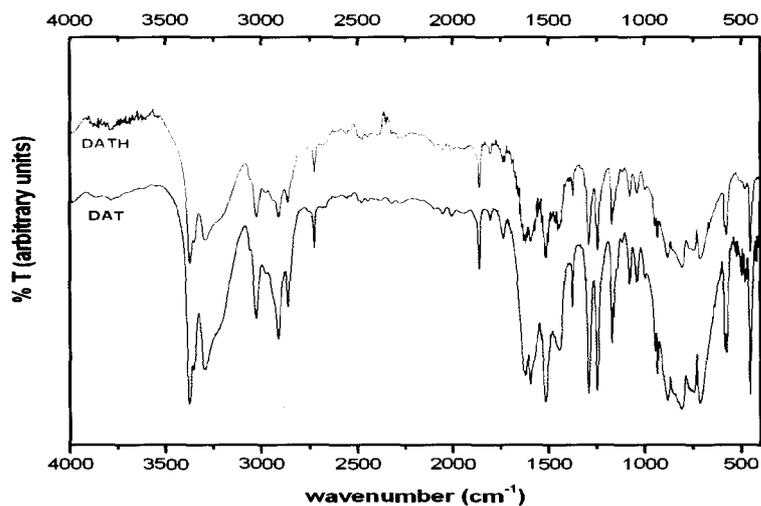


Figure 3.4: IR spectra of 3, 4-diaminotoluene (DAT) and its hydrazinate (DATH)

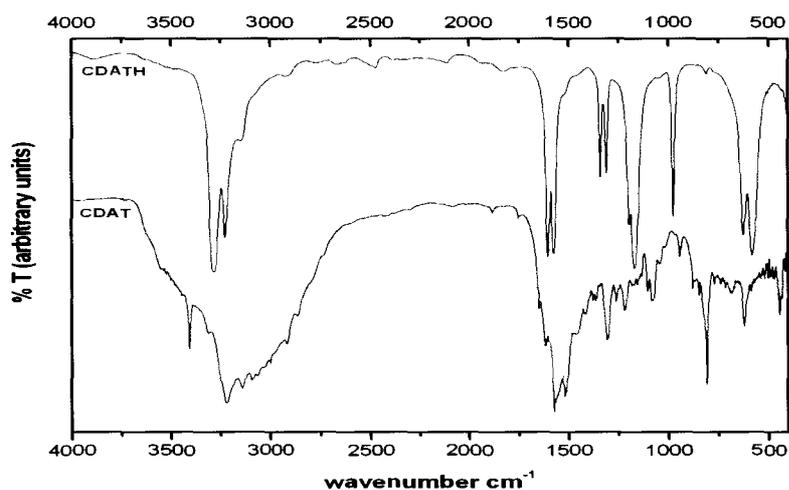
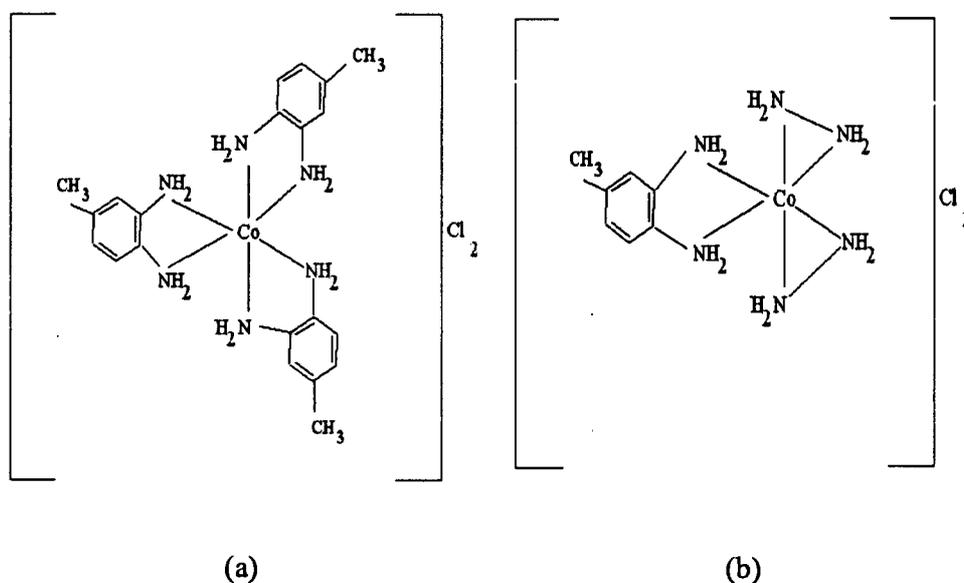


Figure 3.5: IR spectra of cobalt chloride diaminotoluene (CDAT) and its hydrazinate (CDATH)

Infrared red peaks of the cobalt chloride diaminotoluene, $[Co(C_7H_{10}N_2)_3]Cl_2$ table 2, figure 3.5 shows N-H stretch at $\sim 3200cm^{-1}$, $\delta_{NH/CH}(\text{superimposed}) \sim 1600cm^{-1}$, $\nu_{C=C} \sim$

1630cm^{-1} , $\nu_{\text{CH}(\text{aromatic})} \sim 3100\text{cm}^{-1}$, $\nu_{\text{CH}} \sim 3000\text{cm}^{-1}$, $\delta_{\text{NH}_2/\text{NH}} \sim 1600, 1562\text{cm}^{-1}$, whereas in the case of its hydrazinated complex, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, sharp N-H and N-N stretching between $\sim 3300\text{-}3100\text{ cm}^{-1}$ due to ν_{NH} , and at $\sim 974\text{cm}^{-1}$ due to ν_{NN} and NH_2/NH bend, $\delta_{\text{NH}_2/\text{NH}} \sim 1600\text{cm}^{-1}$ and $\delta_{\text{CH}} \sim 1566\text{cm}^{-1}$ was observed. A bidentate hydrazine link to the metal was suggested due to the presence of N-N stretch band $\sim 974\text{cm}^{-1}$ [20, 37, 41-43, 47].



Structure of (a) Cobalt chloride diaminotoluene (CDAT) and (b) its hydrazinate (CDATH)

Cobalt acetate diamino toluene and its hydrazinate complex

The cobalt acetate diamino toluene complex that was prepared from cobalt acetate source shows total weight loss of 84.64% (TG 90.5%) and Co content of 11.3%.

Based on this a plausible formula of $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3](\text{CH}_3\text{COO})_2$ was proposed, as

the calculated value for the total loss amounts to 85.2% and Co content of 10.85% which are close to the observed ones. Similarly, a reasonable formula for the hydrazine complex was proposed as $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2](\text{CH}_3\text{COO})_2$ based on the observed values of total loss 78.1% , Co of 16.02% and N_2H_4 of 16.8% and the calculated values of total loss of 77.88%, Co of 16.23% and N_2H_4 of 17.67%.

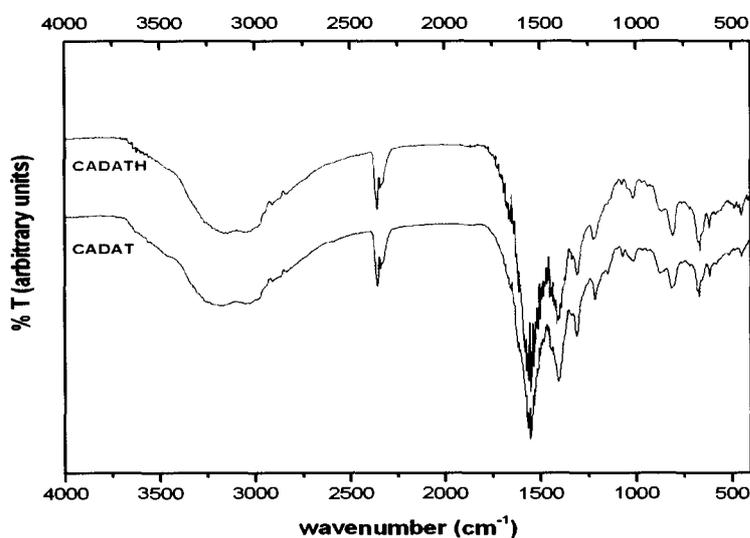
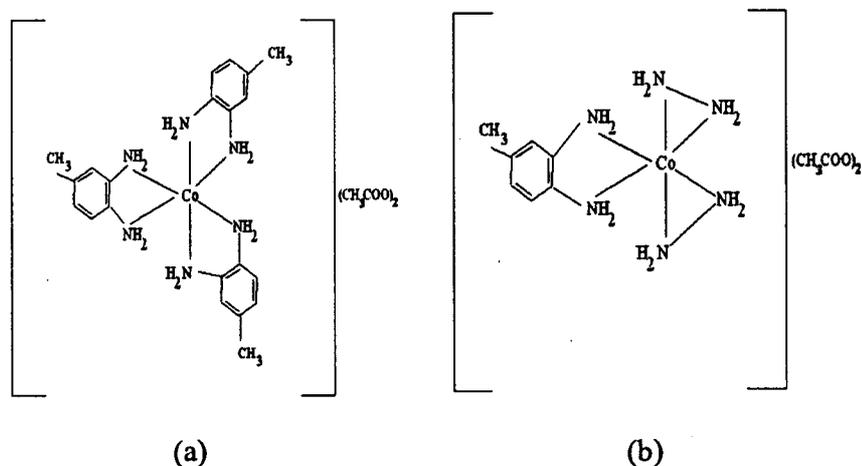


Figure 3.6: IR spectra of cobalt acetate diaminotoluene (CADAT) and its hydrazinate (CADATH)

Both cobalt acetate diaminotoluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3](\text{CH}_3\text{COO})_2$ and cobalt acetate diaminotoluene hydrazine complex, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2](\text{CH}_3\text{COO})_2$ show the bands ν_{OH} (superimposed ν_{CH}) $\sim 3300\text{-}3100\text{cm}^{-1}$; $\nu_{\text{CH}} \sim 2356\text{cm}^{-1}$; $\delta_{\text{NH/CH}}$ (superimposed) $\sim 1600\text{cm}^{-1}$, $\delta_{\text{NH}_2/\text{NH}} \sim 1562\text{cm}^{-1}$; O-C-O $\nu_{\text{asym}}/\nu_{\text{sym}} \sim 1566/1410\text{cm}^{-1}$; $\nu_{\text{CO}} \sim 1311\text{cm}^{-1}$; $\nu_{\text{CC}} \sim 1026$; $\delta_{\text{OCO}} \sim 810\text{cm}^{-1}$, and in addition to these, the hydrazine complex shows

many peaks in the region $\sim 1600\text{-}1500\text{cm}^{-1}$ and $\sim 970\text{cm}^{-1}$ due to $\delta_{\text{NH/CH}}$ (superimposed), $\delta_{\text{NH}_2/\text{NH}}$ and ν_{NN} .

The magnetic susceptibility high spin value of 5.75 BM and 5.4 BM was observed, respectively for $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ and $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2](\text{CH}_3\text{COO})_2$, however, the unhydrazinated complexes $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ and $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3](\text{CH}_3\text{COO})_2$ indicated a value of just ~ 0.67 BM, suggesting likely presence of Co^{3+} in the complex. In the preparation of hydrazine complex, may be the hydrazine being a reducing agent does not allow the cobalt to go to higher oxidation state.



Structure of (a) Cobalt acetate diaminotoluene (CADAT) and (b) its hydrazinate (CADATH)

d) Cobalt L-Proline and its hydrazinate complex:

Both cobalt chloride and cobalt acetate were used as a starting material for preparing the cobalt L-Proline complexes

The complex that was prepared from cobalt chloride source indicated an observed total weight loss of 74.5% (TG 80.00%) and Co content of 18.38% These values are

close to the calculated ones based on the reported [39] formula $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$ of, respectively, 75.3% and 18.13% indicate the complex is formed. Its hydrazinate complex showed a total loss of 66.8% (TG 70.0%), Co content of 24.51% and N_2H_4 of 9.4%. Based on these values a probable formula of $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$ was proposed, as the calculated values were very close to the observed ones: total loss 66.8%, Co 24.34% and N_2H_4 13.2%.

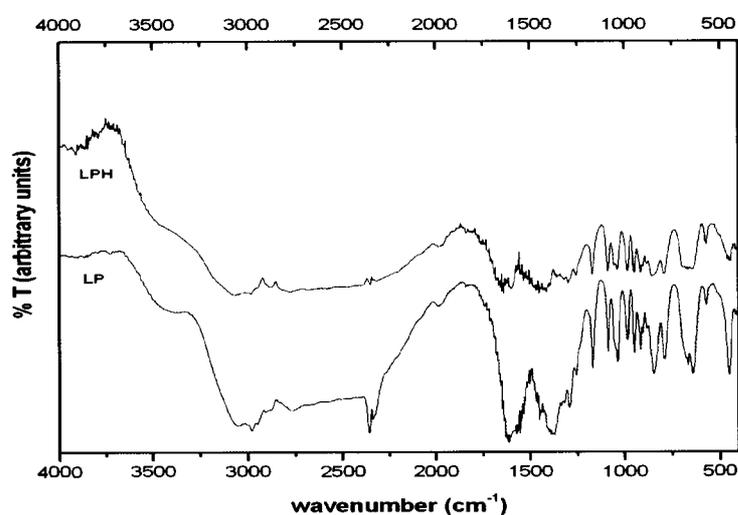


Figure 3.7: IR spectra of L-Proline (LP) and its hydrazinate (LPH)

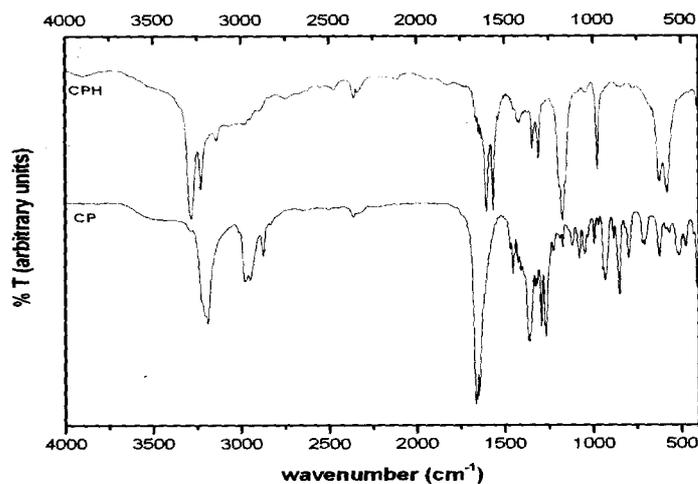


Figure 3.8: IR spectra of Cobalt L-Proline (CP) and its hydrazinate (CPH)

The Infrared peaks of $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$ figure 3.8 showed $\nu_{\text{NH/OH}} \sim 3200\text{cm}^{-1}$; $\nu_{\text{CH}} \sim 2900\text{cm}^{-1}$; $\nu_{\text{asym}}/\nu_{\text{sym}} \text{COO} \sim 1650/1400\text{cm}^{-1}$; $\delta_{\text{NH}} \sim 1643\text{cm}^{-1}$, whereas in the case of its hydrazinated complex, $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$ indicated sharpening of the N-H and an additional $\nu_{\text{NN}} \sim 974\text{cm}^{-1}$ peak suggesting hydrazine link to the metal [20, 37, 41-43,47].

The magnetic susceptibility value of 0.71 BM was observed for $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$, while the hydrazine complex, $\text{Co}(\text{C}_5\text{H}_9\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$ indicated a value of 5.0 BM. The cobalt L-proline complex $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2]$ prepared by us, however, indicates diamagnetic character as compared to the reported high spin one, $\text{Co}^{\text{II}}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2$ [39] suggesting cobalt in the trivalent state, $\text{Co}^{\text{III}}(\text{C}_5\text{H}_8\text{NO}_2)_2(\text{H}_2\text{O})_2$ in our preparation. The hydrazine complex that showed high spin behavior suggests that in the preparation of it, the reducing atmosphere created by the hydrazine does not allow the cobalt to get oxidized.

The cobalt L-Proline complex prepared from cobalt acetate showed a total weight loss of 74.5% and Co content of 17.9 %. Based on the formula reported, $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2 (\text{H}_2\text{O})_2$, the calculated values of total loss of 75.3% and cobalt content 18.13% confirm the formation of the complex. Cobalt L-proline hydrazine complex indicated total loss 66.8%, Co content of 24.5% and N_2H_4 of 12.8% and based on these values a formula, $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2) (\text{N}_2\text{H}_4) (\text{H}_2\text{O})_2$, was proposed as the calculated values of total loss of 66.84%, Co of 24.34% and N_2H_4 of 13.2% which are very close to the observed values.

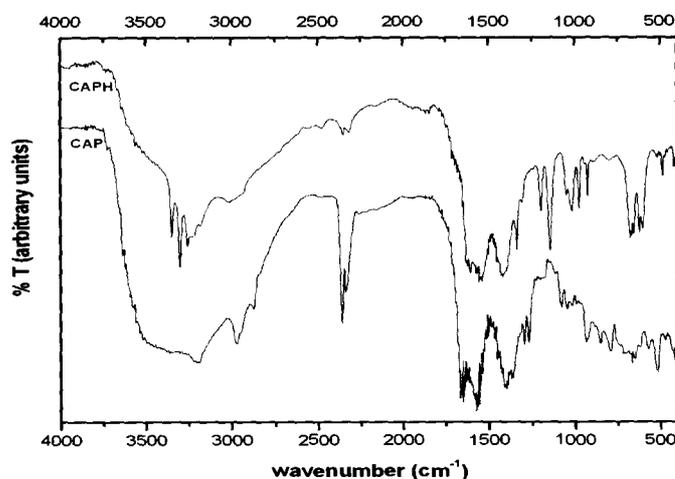
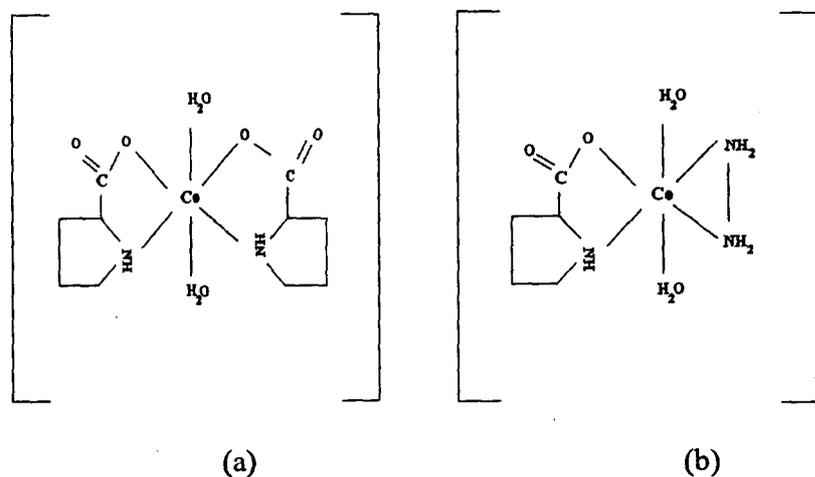


Figure 3.9: IR spectra of Cobalt L-Proline (CAP) and its hydrazinate (CAPH)

The infra red peaks for $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2 (\text{H}_2\text{O})_2]$ showed a broad band in the region $3350\text{-}3100\text{cm}^{-1}$ $\nu_{\text{OH}}/\nu_{\text{NH}}$; $\nu_{\text{CH}} \sim 2972\text{cm}^{-1}$; $\nu_{\text{asymCOO}} \sim 1650\text{cm}^{-1}$; $\delta_{\text{NH}} \sim 1643\text{cm}^{-1}$, $\nu_{\text{symCOO}} \sim 1400\text{cm}^{-1}$ whereas in the case of its hydrazinated complex [47], $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2) (\text{N}_2\text{H}_4) (\text{H}_2\text{O})_2$, showed peaks in the region $3350\text{-}3100$: $\sim 3348\text{cm}^{-1}$, 3300cm^{-1} and 3257cm^{-1} due to ν_{NH_2} and ν_{NH} ; $\nu_{\text{CH}} \sim 3000\text{cm}^{-1}$; $\delta_{\text{NH}_2/\text{NH}} \sim$

$1600/1566\text{cm}^{-1}$ and $\nu_{\text{NN}} \sim 974\text{cm}^{-1}$, suggesting the hydrazine linkage to the cobalt [20, 37, 41-43,47]. The magnetic susceptibility values of ~ 5.09 BM for cobalt L-proline hydrazine complex from cobalt chloride and ~ 4.96 BM for the complex from cobalt acetate source indicated octahedral high spin complex, while the unhydrazinated cobalt L-proline obtained from both cobalt chloride and acetate showed ~ 0.7 BM. The lower susceptibility values suggest likely presence of cobalt in +3 state.



Structure of (a) Cobalt L-Proline (CP/CAP) and (b) its hydrazinate (CPH/CAPH)

e) Cobalt hydroquinone and its hydrazine complex:

Both cobalt chloride and cobalt acetate were used as a starting material for preparing the cobalt hydroquinone complexes;

Cobalt hydroquinone and its hydrazine complex from cobalt chloride

The complex that was prepared from cobalt chloride source indicated an observed total weight loss of 79.4% (TG 78%) and Co content of 14.6 % and by considering a plausible formula $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$, as the calculated values of total loss of 77% and Co 15.1% were very close to the observed ones.

Its hydrazinate complex showed a total loss of 76.3%, Co content of 16.5% and N_2H_4 of 18.5%. Based on these values a probable formula of $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$ was proposed, as the calculated values were very close to the observed ones: calculated total loss, 76.45%, Co 17.28% and N_2H_4 18.77%.

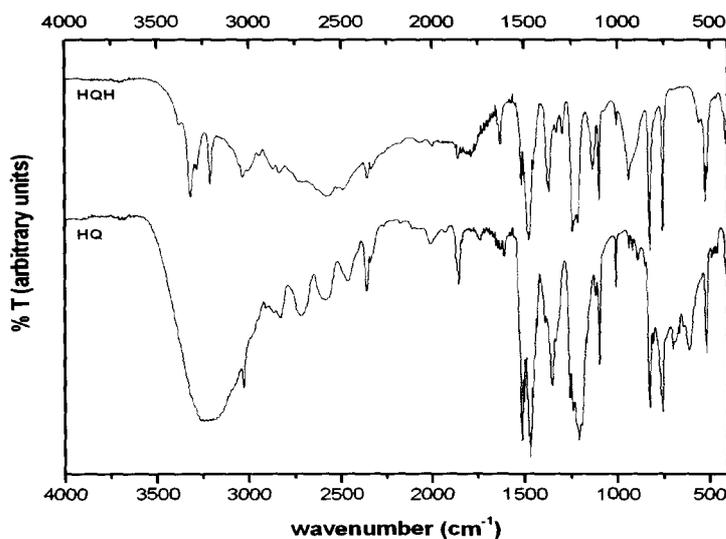


Figure 3.10: IR spectra of hydroquinone (HQ) and its hydrazinate(HQH)

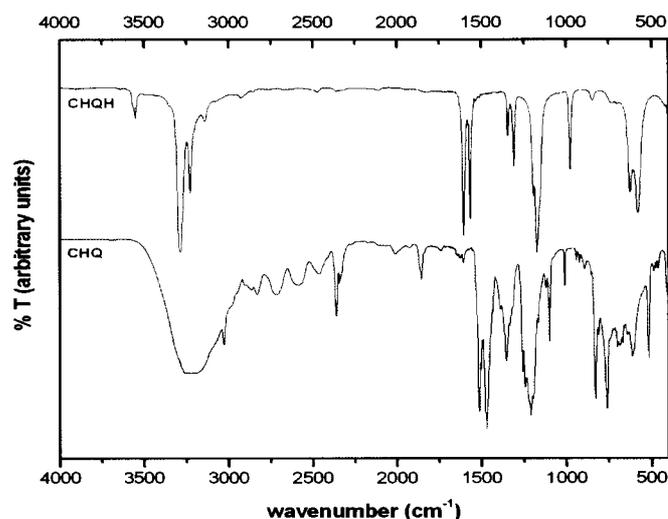


Figure 3.11: IR spectra of cobalt hydroquinone (CHQ) and its hydrazinate (CHQH)

Infrared spectrum of hydroquinone, $C_6H_4(OH)_2$, indicates a broad band $\nu_{OH} \sim 3250-3100\text{cm}^{-1}$ and small band $\sim 3030\text{cm}^{-1}$; $\nu_{CH} \sim 2820, 2720, 2560, 2480, 2358\text{cm}^{-1}$; whereas in the case of hydrazinated hydroquinone the broad band $3300-3100\text{cm}^{-1}$ of hydroquinone is split into two bands : $3319, 3209\text{cm}^{-1}$ leaving the band $\sim 3030\text{cm}^{-1}$ intact. The five peaks that observed in hydroquinone in the range $2800-2350\text{cm}^{-1}$ are broadened on hydrazination. Along with the usual N-H stretching bands, a band $\sim 938\text{cm}^{-1}$ is observed due to the monodentate [20] nature of hydrazine link to the hydroquinone. The chemical analysis of the compound formed by reacting hydroquinone with hydrazine in an inert atmosphere indicated 25.12% of N_2H_4 and from the plausible formula of $C_6H_4(OH)_2 \cdot N_2H_4$ the calculated value of hydrazine amounts to 22.6%, suggesting likely formation an adduct of hydrazine-hydroquinone.

IR spectra of cobalt hydroquinone $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ shows a broad O-H stretch, $\nu_{\text{OH}} \sim 3250\text{-}3100 \text{ cm}^{-1}$ and a small band $\sim 3030 \text{ cm}^{-1}$; $\nu_{\text{CH}} \sim 2820, 2720, 2560, 2480, 2358 \text{ cm}^{-1}$. In the hydrazine complex, $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$ the broad O-H band splits to 3284 and 3228 cm^{-1} indicating N-H stretch. The $\nu_{\text{CH}} \sim 2820, 2720, 2560, 2480, 2358 \text{ cm}^{-1}$ bands of the cobalt hydroquinone complex are reduced in their intensities. The band $\nu_{\text{NN}} \sim 974 \text{ cm}^{-1}$ suggested hydrazine link and bidentate nature [20, 37, 41-43, 47].

Cobalt hydroquinone and its hydrazine complex from cobalt acetate

The cobalt hydroquinone complex prepared from cobalt acetate showed a total weight loss of 78.4 % and Co content of 16.6 % .Based on this a probable formula, $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ was suggested as the calculated values of total loss of 77.0% and Co content of 16.88% matched well with the observed ones. The hydrazine complex showed total loss of 76.1%, Co of 16.53% and N_2H_4 18.0% and the calculated values based on the formula $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$, respectively, 76.45%, 17.28% and 18.77%, matched well with the observed ones.

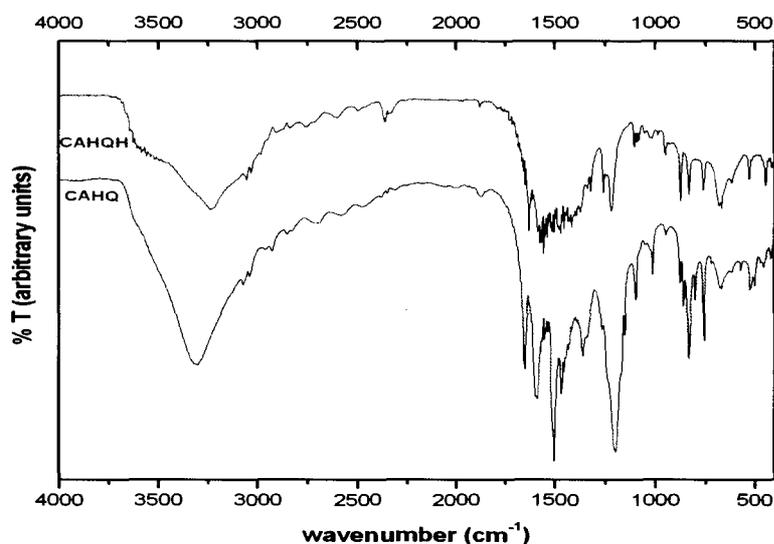


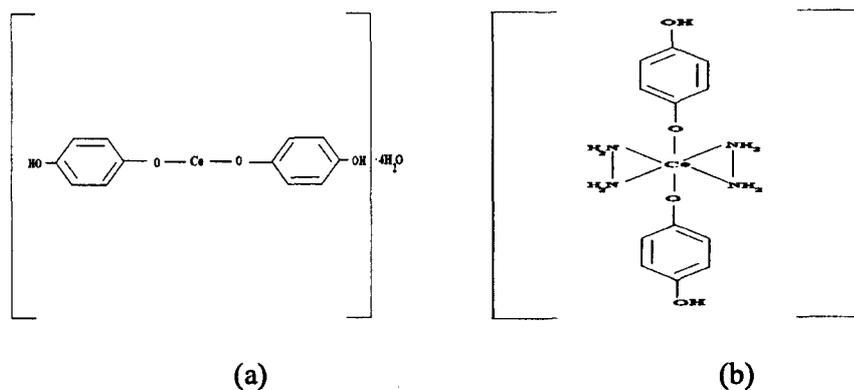
Figure 3.12: IR spectra of cobalt hydroquinone (CAHQ) and its hydrazinate (CAHQH)

$\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ shows bands $\sim 3315 \text{ cm}^{-1}$ due to O-H stretch which shifts to 3240 cm^{-1} in the $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 (\text{N}_2\text{H}_4)_2]$ may be due to the involvement of N-H stretch. Further, number of smaller bands in the region 3000 to 2350 cm^{-1} that found in the hydroquinone which were submerged in the hydroquinone hydrazine adduct, however, do remain in insignificant intensities in both the complexes, but the significant bands in the region 1600 - 1100 cm^{-1} of $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ are now submerged in the hydrazine complex showing extra peaks due to N-N $\sim 948 \text{ cm}^{-1}$ possibly due to the monodentate nature of the N_2H_4 [20].

The magnetic susceptibility values of $\sim 5.29 \text{ BM}$ for cobalt hydroquinone hydrazine complex from cobalt chloride and $\sim 5.29 \text{ BM}$ for the complex from cobalt acetate source indicated octahedral high spin complex, while the unhydrazinated cobalt

hydroquinone obtained from both cobalt chloride and acetate showed ~ 0.43 BM.

The lower susceptibility values suggest likely presence of cobalt in +3 state.



Structure of (a) cobalt hydroquinone (CHQ) and (b) its Hydrazinate (CAHQH)

The cobalt hydroquinone and their hydrazinate complexes explained here were not reported in the literature. However the complex $\text{Fe}^{\text{II}}(\text{salpren})$ [48] reacts over a 36-h period in THF with 9,10-PhenQ and 3,5-DtBQ to give o-semiquinone complexes with the composition $\text{Fe}^{\text{III}}(\text{salpren})$ (o-semiquinone). The reaction of $\text{Fe}^{\text{II}}(\text{salpren})$ with p-BQ gives a binuclear ferric complex bridged by the dianion of the hydroquinone (oxidatively):



Oxidative addition of an o-quinone to $\text{Fe}^{\text{II}}(\text{salen})$ leads to a folding of the salen ligand to accommodate the chelating o-semiquinone ligand in the $\text{Fe}^{\text{III}}(\text{salen})$ (osemiquinone) product. In this regard it was of interest to see the influence of the

added inflexibility associated with the o-phenylene moiety in Fe^{II} (saloph). The complexes Fe^{II} -(salprenOH) and Fe^{II} (saldien) each have an additional basic site which might serve as a ligand atom and therefore affect the ability of an o-quinone to oxidatively add to the iron(II) complex.

f) Carbohydrazide complexes with cobalt chloride and cobalt acetate:

The complex that was prepared from cobalt chloride source indicated an observed total weight loss of 67 % (TG 64.76%) and Co content of 22.4% and match well with the calculated values, respectively of 68.6% and 23.0%, by considering the reported formula $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$ where $\text{L}=(\text{H}_2\text{N}-\text{NH})_2\text{CO}$ [40]. The cobalt acetate source, however, indicated the compound of the type $[\text{CoL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$, based on the observed and calculated values of total loss 72.6% (73.5%), Co of 18.7% (19.45%), where the bracketed values are calculated ones.

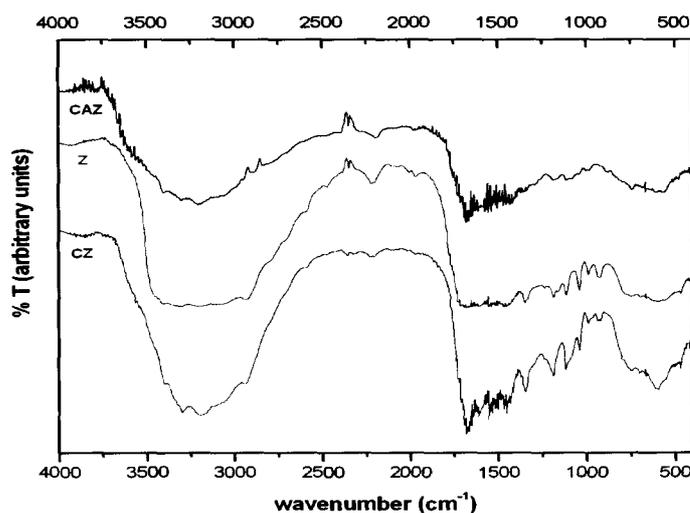
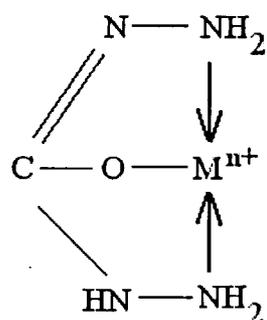


Figure 3.13: IR spectra of carbohydrazide(Z) cobalt chloride carbohydrazide (CZ) and cobalt acetate carbohydrazide (CAZ)

The IR peaks of carbohydrazide(Z), indicate broad bands $\sim 3400-2950\text{cm}^{-1}$; $\sim 1700-1400\text{cm}^{-1}$ and peaks $\sim 1300, 1186, 1100, 1040, 980$ and 920cm^{-1} . In the cobalt complex, $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$, the broad band $3400-2933\text{cm}^{-1}$ of carbohydrazide shifted showing peaks $\sim 3304, 3200\text{cm}^{-1}$. Also the broad band $\sim 1700-1400\text{cm}^{-1}$ that was observed for carbohydrazide is now sharpened showing several ill-defined peaks $\sim 1620, 1600, 1450\text{cm}^{-1}$. The peaks that were in carbohydrazide such as at $1300, 1186, 1100, 1039, 980, 921\text{cm}^{-1}$ now found $\sim 1346, 1150, 1114, 1050, 987, 931\text{cm}^{-1}$ showing consistently shifting towards high frequency indicating carbohydrazide coordinating the cobalt.

IR peaks in the $[\text{CoL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$, show a broad band $\nu_{\text{NH/OH}} \sim 3400-3100$ and obscured bands in the region $1700-1400\text{cm}^{-1} \sim 1656, 1566, 1400\text{cm}^{-1}$ may be due to $\nu_{\text{O-C-C/O}}$.

Both $[\text{CoLCl}_2(\text{H}_2\text{O})_2]$ and $[\text{CoL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ show magnetic susceptibility values of 5.28 BM and 5.2 BM, respectively suggesting high spin octahedral nature of the complexes.



Structure of metal carbohydrazide

g) Cobalt salen and its hydrazine complex:

Cobalt salen synthesized from cobalt acetate and its hydrazinate modification showed magnetic susceptibility values of 2.44 BM and 4.81BM respectively.

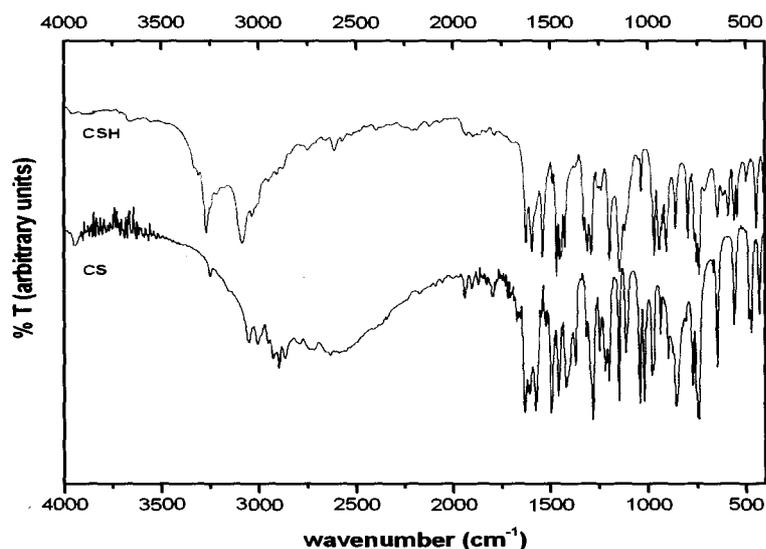


Figure 3.14: IR spectra of cobalt salen (CS) and its hydrazinate (CSH)

The IR peaks in the region 3200-2500 and 1700-400 cm^{-1} of the cobalt salen[Co ($\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2$)] and its hydrazinate [Co ($\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2$)] \cdot N_2H_4 are as below.

Co(salen) [Co ($\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2$)] : 3051(medium), 2899(medium), 2560(broad small), 1633, 1577, 1496, 1419, 1282, 1199, 1149, 1041, 1000, 979, 855, 742, 648, 563, 472, 432 cm^{-1}

Co(salen)hydrazinate [Co ($\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2$)] \cdot N_2H_4 : 3271(sharp), 3088(sharp), 1625-1600(doublet), 1541, 1469, 1427, 1290, 1197, 1147, 1036, 968, 950, 860, 798, 744, 646, 559, 447, 406

Hydrazine content observed for the hydrazinate complex is 3.84%.

described in section 2.8 of Chapter II. The spectral scans are displayed in Appendix III and IV of this thesis.

The TG/DSC (DTA) Analysis of all the cobalt complexes and their hydrazinates, hydrazinated diamino toluene and hydrazinated hydroquinone complexes have been carried out. The traces are presented in Appendix V of the present thesis.

The X-Ray diffraction (XRD) studies of the precursors as well as the decomposed products of the cobalt compounds were carried out as described in section 2.7 of Chapter II. The phase identifications of the cobalt complexes decomposed at 700°C, 900°C, 1000°C, 1200°C, were studied through powder diffraction technique and indicated the formation of cobalt oxide(s). At 700°C and 900°C, the phase was identified as spinel Co_3O_4 (*JCPDS file 01-1152*); while at 1000°C it indicates CoO type phase (*JCPDS file 43-1004*). The XRD scans are presented in Appendix VI and VII of the present thesis.

Chapter IV

Catalyzed Oxygen Scavenging Activity

The chapter describes in detail the systematic investigations done on a home built de-aerator, (Chapter II Section 2.9). The de-aerator was always loaded with demineralized water from one source having dissolved oxygen (DO) concentration of 4.5 to 5.0 ppm. The dissolved oxygen concentration was monitored by Winkler's method, as well as, through Lovibond comparator, described in Chapter II Section 2.10 and 2.11. Hydrazine was used here as the main oxygen scavenger after mechanical de-aeration the water. Mechanical scavenging of water of DO, 4.5 to 5.0 ppm, normally brought down the DO level to ~ 2ppm at the highest temperature of de-aeration of 90°C, but most of the oxygen scavenging studies carried out here were after the mechanical de-aeration done at 45°C, which had brought down the DO level to ~3.1ppm. Though hydrazine was the main oxygen scavenger, studies were also carried out using the other oxygen scavengers such as solid sodium sulfite, carbohydrazide, to get to know about their oxygen scavenging capacities. As our objective was to understand the effect of metal compounds in enhancing the oxygen scavenging of hydrazine, we orderly performed the oxygen scavenging action of hydrazine, hydrazine + cobalt compounds in the de-aerated water. For our better understanding, we also performed studies to see whether only the cobalt compounds have any oxygen removing capacities in the absence of hydrazine from the water. Further, we also inspected gaseous oxygen absorption/reaction capacity of hydrazine, cobalt compounds, hydrazine + cobalt compounds by fabricating oxygen uptake set up [16]. Since the solid cobalt compounds are difficult to bodily remove from the boiler assembly, it was considered to ease this problem by embedding them in a polymer base. The polymer based cobalt compounds were

then studied for their oxygen scavenging action individually and along with the hydrazine in the boiler feed water. Along with the dissolved oxygen concentration in the water body, the concentration of hydrazine was monitored spectrophotometrically as a function of time, temperature, amount of cobalt compound, hydrazine etc. From the results obtained by these exhaustive investigations, a probable mechanism of the oxygen scavenging action or the catalyzing effect of the metal compounds has been put forward.

4.1 Experimental

a) Mechanical de-aeration

Mechanical de-aeration of the boiler feed water of 4.5 to 5.0 ppm. DO at 30/45/60/75/90°C was performed for 1, 8, 16 and 24 hours. The de-aerator assembly was filled with 30L of the de-mineralized water.

b) Chemical oxygen scavenging

After the mechanical scavenging the chemical oxygen scavenging studies were carried out on the water in the home built de-aerator using hydrazine, cobalt compounds + hydrazine, cobalt compounds, polymer based cobalt compounds, and hydrazine + polymer based cobalt compounds. The cobalt compounds that which were synthesized as described in the Chapter III were all tested for their oxygen scavenging action. In order to see whether the ligands which were used in the

preparation of the metal compounds have any reasonable oxygen reactivity, experiments were also carried either alone or with hydrazine in the water body.

c) Oxygen uptake

Oxygen uptake setup [16] was used to study the oxygen absorption of liquid hydrazine, metal compounds dry and in dimethyl sulphoxide (DMSO), metal compounds + hydrazine + DMSO.

4.2 Results and discussion

a) Mechanical de-aeration

Mechanical de-aeration of the 30L capacity boiler feed water of 4.5 to 5.0 ppm DO at 30/45/60/75/90°C were performed for 1, 8, 16 and 24 hours, Table 3 . The results of the de-aeration carried out for one hour duration at 30, 45, 60, 75 and 90°C do not show any further measurable decrease in the DO level on increasing the duration of the de-aeration. The percentage scavenging was calculated by considering the initial DO of 5.0 ppm of the de-mineralized water. The percentage (%) scavenging of DO of 30, 38, 43, 49 and 60 was observed, respectively, at 30, 45, 60, 75 and 90°C for one hour duration which amounted to the DO of 3.5, 3.1, 2.9, 2.6 and 2.0 ppm.

Table 3: % Scavenging as a function of time at temperatures 30/75°C of boiler feed water of 4.5 to 5.0 ppm of DO by mechanical de-aeration and chemical scavengers

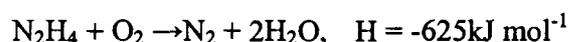
Scavenger used	Time (Hours)			
	1	8	16	24
30°C				
Mechanical de-aeration	30%	30%	30%	30%
<u>Chemical Scavenger</u>				
Hydrazine Hydrate , $N_2H_4 \cdot H_2O$ (0.1mL/L)	98	98	98	98
Cobalt chloride , $CoCl_2 \cdot 6H_2O$ (1mg/L)	38	38	38	38
Cobalt chloride hydrazinate , $[Co(N_2H_4)_3]Cl_2$ (1mg/L)	70	70	70	70
Cobalt chloride diaminotoluene, $[Co(C_7H_{10}N_2)_3]Cl_2$ (1mg/L)	85	85	85	85
Cobalt chloride diaminotoluene hydrazinate, $[Co(C_7H_{10}N_2)(N_2H_4)_2]Cl_2$ (1mg/L)	86	86	86	86
75°C				
Mechanical de-aeration	49	49	49	49
<u>Chemical Scavenger</u>				
Hydrazine Hydrate , $N_2H_4 \cdot H_2O$ (0.1mL/L)	100	100	100	100
Cobalt chloride , $CoCl_2 \cdot 6H_2O$ (1mg/L)	66	66	66	66
Cobalt chloride hydrazinate , $[Co(N_2H_4)_3]Cl_2$ (1mg/L)	80	80	80	80
Cobalt chloride diaminotoluene, $[Co(C_7H_{10}N_2)_3]Cl_2$ (1mg/L)	98	98	98	98
Cobalt chloride diaminotoluene hydrazinate, $[Co(C_7H_{10}N_2)(N_2H_4)_2]Cl_2$ (1mg/L)	98	98	98	98

b) Chemical scavengers**i) Hydrazine, $N_2H_4 \cdot H_2O$**

The de-aerator of 30L water capacity that had been mechanically de-aerated was used for investigating the chemical oxygen scavenging at different temperatures and concentration of hydrazine. The results are compiled in Table 4.

i) 0.01% hydrazine (0.1ppm)

3mL of hydrazine hydrate (Qualigens, India; 99-100% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was added to the mechanically de-aerated 30L water (of 3.5ppm DO). The DO level of 3.5 ppm came down to 0.1ppm, indicating ~98% oxygen scavenging at the end of one hour. Thus, just 0.1 ppm hydrazine (0.01% hydrazine) brings down the DO level tremendously low, as hydrazine reacts with molecular oxygen [9];



At 45°C the mechanically de-aerated water of 3.1ppm DO showed ~99% oxygen scavenging. Similarly at 60, 75 and 90°C the mechanically de-aerated water of DO level, respectively, 2.9, 2.6, 2.0 ppm reduced to almost zero ppm as measured by Winkler's method and Lovibond Comparator described in Chapter II, section 2.10 and 2.11.

ii) 0.001% hydrazine (0.01ppm)

On decreasing the hydrazine addition, say 0.3mL, to the 30L de-aerated water, at 30°C, there occurred 54% oxygen scavenging and this, as compared to 98% scavenging with 3mL hydrazine suggests that lower the hydrazine content, lower is the oxygen scavenging.

iii) 0.0001% hydrazine (0.001ppm)

On decreasing the hydrazine addition, say 0.03mL, to the 30L de-aerated water, at 30°C, there occurred 31% oxygen scavenging and this as compared to 98% scavenging with 3mL hydrazine and 54% with 0.3mL hydrazine suggests that the oxygen scavenging is concentration dependent. Similar concentration dependence of scavenging action was observed at 45, 60, 75°C too.

ii) Cobalt compound: Winkler's method

Cobalt chloride and its hydrazinate

30 mg cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (CCl) was added to the de-aerated 30L water. 38, 45, 51, 66, 86% scavenging occurred at 30, 45, 60, 75 and 90°C, Table 4. As compared to mere mechanical de-aeration experiments, the % scavenging of 30, 38, 43, 49 and 60 at 30, 45, 60, 75 and 90°C, the addition of cobalt compound indicates ~7 to 8% improvement. If these results are compared with the scavenging action of 31, 38, 41 and 72% by the 0.0001% hydrazine at 30, 45, 60 and 75°C, respectively, it may be boldly said that one can avoid adding venomous hydrazine to the water to remove oxygen and use cobalt chloride solid instead.

Table 4: % Oxygen scavenging by various scavengers at different temperatures

Temperature °C →	30	45	60	75	90
Scavenger used ↓with code/formula					
Mechanical de-aeration /without scavenger	30	38	43	49	60
Cobalt chloride, (CCI) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	38	45	51	66	86
CCI-PVA	39(30)	47(39)	53(43)	68(49)	88(62)
Cobalt chloride hydrazinate (CH)	70	72	74	80	98
CH-PVA	72(32)	74(40)	80(45)	90(51)	100(64)
Cobalt acetate hydrazinate (CAH)	72	74	85	98	100
CAH-PVA	74(34)	80(42)	86(47)	98(53)	100(66)
Hydrazine hydrate (HH) (0.01%)	98	99	100	100	100
HH (0.001%)	54	58	65	95	98
HH (0.0001%)	31	38	41	72	-
Sodium sulphite, Na_2SO_3 (0.01 g/L)	38	-	-	66	-
Hydrazine sulphate in PVA, $\text{N}_2\text{H}_4\text{SO}_4$ -PVA	97(32)	99(40)	100(44)	100(50)	100(64)
Cobalt chloride diaminotoluene (CDAT)	85	87	90	98	100
CDAT-PVA	86(32)	88(42)	92(44)	98(50)	100(62)
Cobalt acetate diaminotoluene (CADAT)	86	87	92	97	100
CADAT-PVA	86(32)	88(42)	84(46)	97(50)	100(62)
Hydrazinate of CDAT (CDATH)	86	88	92	98	100
CDATH-PVA	87(33)	88(42)	92(46)	98(50)	100(62)
Hydrazinate of CADAT (CADATH)	88	90	94	96	100
CADATH-PVA	90(33)	91(44)	94(48)	98(50)	100(62)
3,4- diaminotoluene (DAT)	61	71	73	75	77
DAT -PVA	61(30)	72(38)	73(44)	76(50)	78(60)
Hydrazinate of DAT (DATH)	85	88	92	98	100
DATH-PVA	86(32)	89(42)	92(44)	98(51)	100(62)
Cobalt L-Proline from cobalt chloride (CP)	39	45	50	62	86
CP-PVA	50(32)	52(40)	64(44)	78(50)	90(62)
Cobalt L-Proline from cobalt acetate (CAP)	50	55	62	72	86
CAP-PVA	52(33)	59(41)	64(45)	74(51)	90(63)
Hydrazinate of CP (CPH)	39	47	51	68	90
CPH-PVA	70(33)	72(42)	80(46)	84(52)	100(64)
Hydrazinate of CAP (CAPH)	74	77	82	88	94
CAPH-PVA	75(34)	80(43)	82(47)	89(53)	100(65)
Cobalt hydroquinone from CCI (CHQ)	41	43	52	62	74
CHQ-PVA	42(32)	44(42)	54(44)	64(50)	76(62)
Cobalt hydroquinone from acetate (CAHQ)	42	44	54	63	76
CAHQ-PVA	44(33)	46(43)	56(45)	65(52)	78(64)
Hydrazinate of CHQ (CHQH)	44	46	77	86	100
CHQH-PVA	45(33)	47(42)	78(46)	88(52)	100(62)
Hydrazinate of CAHQ (CAHQH)	45	47	78	87	100
CAHQH-PVA	46(34)	49(44)	79(48)	89(54)	100(64)
Cobalt chloride carbohydrazide (CZ)	70	72	73	81	96
CZ-PVA	71(30)	73(39)	74(45)	82(51)	97(60)
Cobalt acetate carbohydrazide (CAZ)	71	73	74	83	97
CAZ-PVA	72(32)	74(39)	76(46)	84(52)	98(60)

* Bracketed values are of re-used polyvinyl alcohol, PVA

On the other hand, 30 mg hydrazine complex, $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ in 30 L water showed 70, 72, 74, 80 and 98%, Table 4, respectively at 30, 45, 60, 75 and 90°C. Comparing this scavenging value with mere mechanical de-aeration of 30, 38, 43, 49 and 60% and with cobalt chloride addition of 38, 45, 51, 66 and 86%, respectively at 30, 45, 60, 75 and 90°C, the hydrazine complex seems to improve the action consistently. The oxygen scavenging action at 45°C is 38, 45 and 72%, respectively for non-scavenger (mechanical de-aeration), cobalt chloride and cobalt hydrazine complex case, suggesting the hydrazine modified complex is superior in oxygen removal. Sodium sulfite is a well known industrial oxygen scavenger applied in low pressure boilers, as it readily reacts with dioxygen, $2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4$

Sodium sulfite, Na_2SO_3

0.3g of sodium sulfite in 30L de-aerated water showed 38 and 66% oxygen scavenging at 30 and 75°C, respectively. The scavenging remained almost same even on increasing the duration of the action for 8, 16 and 24 hours. As compared to the oxygen removal by mechanical de-aerator of 30 and 49% at 30 and 75°C, respectively, and cobalt chloride of 38 and 66%, the sodium sulfite is similar in its action to the cobalt chloride. Cobalt chloride too will react with dioxygen and oxidize the Co^{2+} to Co^{3+} , and probably a reaction of the type may occur, $\text{CoCl}_2 \rightarrow (\text{CoO}) \rightarrow \text{Co}_3\text{O}_4 + \text{Cl}_2$.

Cobalt diaminotoluene and its hydrazinate complex

30mg in 30L water, the cobalt chloride diaminotoluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$, showed 85, 87, 90, 98 and 100% scavenging, respectively, at 30, 45, 60, 75 and 90°C, as compared to mechanical de-aeration of 30, 38, 43, 49 and 60% at 30, 45, 60, 75 and 90°C. As compared to cobalt hydrazine complex $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$, which showed % scavenging of 70, 72, 74, 80 and 98 respectively at 30, 45, 60, 75 and 90°C, the cobalt chloride diaminotoluene seems to be much better in its action. While the hydrazine complex of the cobalt chloride diaminotoluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, showed 86, 88, 92, 98 and 100% scavenging at 30, 45, 60, 75 and 90°C, respectively, indicated, however, hydrazine modification has no much effect of scavenging action.

Cobalt L-proline and its hydrazinate

30mg of cobalt L-proline, $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2](\text{H}_2\text{O})_2$, (CP) in 30L de-aerated water indicated 39, 45, 50, 62 and 86% oxygen scavenging and its hydrazine complex, $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$, (CPH) 39, 47, 51, 68 and 90% respectively, at 30, 45, 60, 75 and 90°C, suggested that both the complexes have almost similar action. The reactivity for oxygen, however, is almost similar to that of cobalt chloride, and certainly better than mere mechanical de-aeration. Cobalt L-proline is a good oxygen scavenger that may be used in preserving food, drugs and cosmetic from deteriorating from environmental attack of oxygen [39] as it effortlessly reacts with dioxygen in aqueous medium, $\text{Co}^{\text{II}}(\text{L-proline})_2 + \text{O}_2 \rightarrow \text{Co}^{\text{III}}(\text{L-proline})_2$. The diamagnetic nature of the oxidized product indicated the presence of Co^{III} species suggesting oxidation taking place.

Cobalt hydroquinone and its hydrazinate

30mg of cobalt hydroquinone, $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (CHQ) in 30L de-aerated water showed 41, 43, 52, 62 and 74% and its hydrazine complex $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$ (CHQH) of 44, 46, 77, 86 and 100% oxygen scavenging, at 30, 45, 60, 75 and 90°C, respectively. The values are better than without scavenger (mere mechanical de-aeration), but are nearly similar to cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, cobalt L-proline, $[\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)_2](\text{H}_2\text{O})_2$ and lower than that of cobalt chloride diamino toluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$.

Cobalt carbohydrazide

30mg of cobalt chloride carbohydrazide, $[\text{Co}(\text{H}_2\text{N}-\text{NH})_2\text{COCl}_2(\text{H}_2\text{O})_2]$ (CZ) in 30L de-aerated water scavenged 70, 72, 73, 81 and 96% oxygen and the action is better than the cobalt complexes mentioned above and is almost similar to cobalt chloride hydrazinate, $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$.

Cobalt salen and its hydrazinate

5, 10, 15, 20, 25 and 30mg of cobalt salen, $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]$ (CS) and its hydrazine complex $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)] \cdot \text{N}_2\text{H}_4$ (CSH) were separately studied at 30, 45, 60, 75°C by introducing in to 30L de-aerated water and the oxygen scavenging was monitored Table 5 . The 25 mg cobalt salen and its hydrazinate at 45°C scavenge oxygen, 42 and 52%, respectively.

Table-5: % O₂ scavenging by hydrazine hydrate (HH), cobalt salen(CS) , cobalt salen hydrazinate(CSH), CS+HH and CSH+HH at different temperatures

Figures amount to % scavenging

Temperature	CS/CSH/CS-PVA/CSH-PVA 5/10/15/20/25/30 mg	HH	CS+HH/CSH+HH/CS-PVA+HH/CSH- PVA+HH 5/10/15/20/25/30 mg
30°C	CS -/-/20/30/41/-	31	CS+HH -/-/52/61/71/-
45°C	CS 29/30/40/41/42/- CSH 33/36/40/42/52/- CS-PVA 12.5mg- 36 CS-PVA reused - 16 CSH-PVA 12.5mg- 38 CSH-PVA reused - 17	38	CS+HH 52/70/80/80/86/- CSH+HH 62/71/81/86/90/- CS-PVA (12.5 mg)+HH-74 CS-PVA reused +HH -51 CSH-PVA (12.5 mg)+HH-76 CSH-PVA reused +HH -52
60°C	CS 29/37/-/-/-/- CSH 40/41/-/-/-/- CS-PVA 12.5mg-40 CS-PVA reused - 17 CSH-PVA 12.5mg- 41 CSH-PVA reused - 17	41	CS+HH 54/71/-/-/-/- CSH+HH 65/76/-/-/-/- CS-PVA (12.5 mg)+HH-76 CS-PVA reused +HH -50 CSH-PVA (12.5 mg)+HH-77 CSH-PVA reused +HH -52
75°C	CS 36/43/-/-/-/- CSH 44/52/-/-/-/- CS-PVA (5mg)-45	72	CS+HH 86/100/-/-/-/- CSH +HH 86/100/-/-/-/- CS-PVA (5mg)+HH-87

Catalytic effect of cobalt complexes

The 5, 10, 15, 20 and 25mg of cobalt salen at 45°C scavenges, respectively, 29, 30, 40, 41 and 42% oxygen when added to 30L de-aerated water, while the hydrazinate complexes scavenge, respectively, 33, 36, 40, 42 and 52%, Table 5. These results clearly suggest that the oxygen scavenging increases as a function of weight, the dependencies are more with the hydrazine complexes.

On the other hand, when 5, 10, 15, 20 and 25mg of cobalt complexes were introduced in the 30L de-aerated water containing 0.001ppm of hydrazine, the scavenging percentages observed at 45°C were, respectively, 52, 70, 80, 80 and 86 % for cobalt salen and that for cobalt salen hydrazine complex were 62, 71, 81, 86 and 90%. These studies suggest that the increased amount of cobalt complexes keeping hydrazine concentration constant at constant temperature show increased scavenging. The increased scavenging with the increased cobalt in hydrazine, hence, is due to the catalytic effect of the cobalt complex. The catalytic effect is, however, found to be more with the hydrazine complexes.

Polymer based Cobalt complexes

In general the cobalt compounds/complexes were found to have their own oxygen scavenging action which compare well and even better with the widely used solid industrial oxygen scavenger sodium sulfite, Na_2SO_3 , oxygen scavenger. Since solid Na_2SO_3 gives solid reaction products, it is problematic in industrial boiler as the solid waste powder needs to be removed by blow-down operation or the boiler requires to be shut down which is not palatable for the continuous industrial production dependent on boiler operation. The cobalt compound/complexes studied here too leave behind solid reaction products. In order to alleviate this problem related with the solid waste, we considered embedding the cobalt compound in a polymer base and then investigate the oxygen scavenging action.

Preparation of cobalt compound dispersed in Poly vinyl alcohol (PVA) film:

In the recovery of hydrocarbons from petroliferous formations [49] wherein water is injected into the formation through a borehole, oxygen is scavenged from water employed in recovery applications requiring low oxygen levels by mixing with a source of sulfite ion, said mixture then being passed over a cation exchange resin on which a cobalt ion or other metallic catalyst is adsorbed. The catalyst increases the reaction rate of the sulfite ion and the oxygen to form sulfate ion, while the resin maintains the cobalt in place. The formation of nanostructured materials with interesting electrical, magnetic and thermal properties were obtained when nanoscale metal oxides were incorporated in a polymer matrix [50-53]. The authors [50] also report the solvent casting method for the synthesis of MoO₃- PVA composite film. First attempts to disperse the cobalt complex [Co(L-Proline)₂](H₂O)₂ into a polymer film (PVA) were done [39] and led to a film where the cobalt complex was homogeneously dispersed. This film presented exactly the same absorption capacity, towards molecular dioxygen than the isolated complex which was found very promising for its use in multilayer packaging- modified atmosphere packaging (MAP) of foods. In view of this and in order to tone down this problem related with the solid waste, we embedded each of the cobalt compounds in a polymer base and then investigated the oxygen scavenging action.

*
In the method we employed for the synthesis of the cobalt compound-PVA, say cobalt chloride hydrazinate, [Co(N₂H₄)₃]Cl₂ -PVA (CH-PVA), 1 g of PVA was dissolved in double distilled water and stirred well on a magnetic stirrer with hot plate to obtain a viscous liquid of PVA. 25 mg of the cobalt compound

$[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ was then added and the stirring was continued to disperse the cobalt compound homogeneously into the PVA. The entire mass was poured uniformly to a clean Petri dish and allowed to dry at room temperature and pressure to form a polymer film free from air bubbles and with uniformly dispersed cobalt compound.

Cobalt diaminotoluene and its hydrazinate

25mg of cobalt chloride diaminotoluene in PVA, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ -PVA (CDAT-PVA) in 30L de-aerated water showed 86, 88, 92, 98 and 100% oxygen scavenging and that of the hydrazine complex, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ -PVA (CDATH-PVA) indicated 87, 88, 92, 98 and 100%, respectively, at 30, 45, 60, 75 and 90°C. The 30mg in 30 L de-aerated water of $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ (CDAT) and $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ (CDATH) without embedding in PVA, (4.2 b) ii), however, indicated 85, 87, 90, 98 and 100% and 86, 88, 92, 98 and 100 % oxygen scavenging, respectively at 30, 45, 60, 75 and 90°C. The results indicate that the cobalt complexes embedded in polymer show higher oxygen scavenging action as compared to the complexes without polymer base.

Reuse of the polymer based complex

The investigations were performed on the polymer based complexes once and had been tested once again for oxygen scavenging and indicated 32, 42, 44, 50 and 62%, by CDAT-PVA and that by CDATH-PVA of 33, 42, 46, 50, 62%, respectively at 30, 45, 60, 75 and 90°C, suggesting possibility of the reuse of the

complexes. But more importantly, it indicates that the solid catalyst can be easily removed from the boiler body, thereby, avoiding the boiler shutdown.

Cobalt L-proline and its hydrazinate

25mg of cobalt L-Proline in PVA, $\text{Co(II)(L-proline)}_2(\text{H}_2\text{O})_2$ -PVA (CP-PVA) in 30 L de-aerated water found scavenging oxygen of 50, 52, 64, 78 and 90% and that of its hydrazinate $\text{Co(C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$ -PVA (CPH-PVA) 70, 72, 80, 84 and 100%, respectively at 30, 45, 60, 75 and 90°C. The reuse indicated 32, 40, 44, 50 and 62% oxygen scavenging in both the cases. In their preliminary studies of cobalt L-proline, $\text{Co(II)(L-proline)}_2(\text{H}_2\text{O})_2$ the authors [39] by investigating the polymer base complex in oxygen absorption studies found its use as oxygen scavenger in packaging films.

Cobalt hydroquinone and its hydrazinate

25mg of cobalt hydroquinone in PVA, $\text{Co(OC}_6\text{H}_4\text{OH)}_2 \cdot 4\text{H}_2\text{O}$ (CHQ-PVA) in 30L de-aerated water scavenges 42, 44, 54, 64 and 76% and that of $[\text{Co(OC}_6\text{H}_4\text{OH)}_2(\text{N}_2\text{H}_4)_2]$ (CHQH-PVA) of 45, 47, 78, 88 and 100%, respectively, at 30, 45, 60, 75 and 90°C The reuse of the polymer based complexes show almost similar % oxygen scavenging of 32, 42, 44, 50 and 62%, respectively, at 30, 45, 60, 75 and 90°C

Cobalt carbohydrazide

25mg of cobalt carbohydrazide in PVA, $[\text{Co(H}_2\text{N-NH)}_2\text{COCl}_2(\text{H}_2\text{O})_2]$ (CZ-PVA) in 30L de-aerated water showed % oxygen scavenging of 71, 73, 74, 82 and 97%, respectively, at 30, 45, 60, 75 and 90°C. The reuse of the polymer base complex

indicated 32, 39, 45, 51 and 60% of oxygen scavenging, respectively at 30, 45, 60, 75 and 90°C.

Cobalt hydrazine complex

25mg of cobalt chloride hydrazine in PVA, $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{Cl}_2$ (CH-PVA) in 30L de-aerated water scavenged 72, 74, 80, 90 and 100%, and the reused one of 32, 40, 45, 51 and 64%, respectively, at 30, 45, 60, 75 and 90°C.

Limitations of polymers: use of additives

Poly Vinyl Alcohol (PVA) has its own limitation, Figure 4.1-4.2 A-D. It is water soluble and thus crumbles fast when the catalyst embedded polymer is used for scavenging purpose. To avoid this some additives such as dioctyl phthalate (OP) and triphenyl phosphate (PP) were added to the polymer base. 1g PVA was dissolved in distilled water, 5 % OP or PP was added by dissolving it in methanol and was kept in a beaker overnight. The polymer film was made by raising the temperature to around 80°C and following the same procedure as that done earlier without the additives.

The cobalt complexes embedded in PVA along with the additives OP and PP were tested for their oxygen scavenging capacity in the home built de-aerator and their % scavenging observations were found to be similar to the ones without the additives as indicated in table 3, 4 and 5. Both the additives dioctyl phthalate (OP) and triphenyl phosphate (PP) in PVA gave better strength to the polymer and helped in prolonging the crumbling. They did not crumble down up to 45°C when taken for

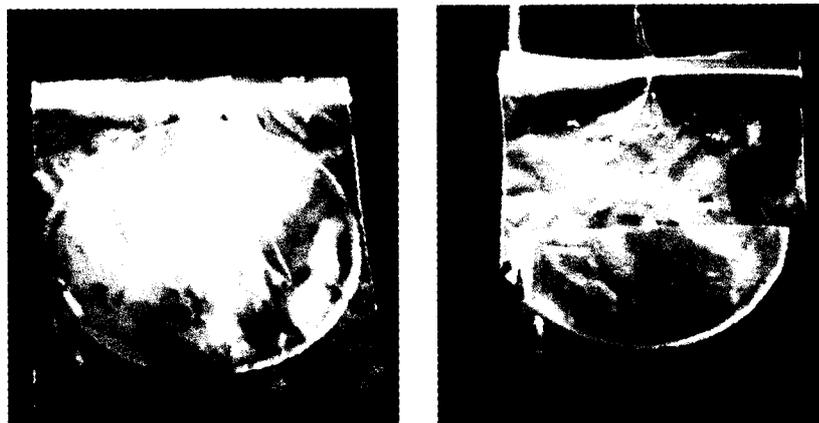
their oxygen scavenging action. The additive OP was found to give fairly better stability to the polymer PVA even at higher temperatures and did not crumble or deteriorate even upto 75°C. It showed superior property; but however crumbled above 75°C.

Poly Vinyl Chloride (PVC) based catalysts

We also used another polymer, Poly Vinyl Chloride (PVC) in our studies. 1g PVC along with 25 mg cobalt compound was ground well using mortar and pestle. Polymer film was made by raising the temperature to around 150°C.

Investigations on the catalysts embedded in Poly vinyl Chloride (PVC) were done. The oxygen scavenging action carried out in the de-aerator for the various temperatures were found to be similar to those with poly vinyl alcohol indicated in Table 3, 4 and 5.

Studies indicate that no crumbling of the polymer takes place even when the water was heated to 75°C, further to 90°C and above , approximately 100°C, Figure 4.3; and hence is superior.



(a)

(b)

CSH-PVA (a) whole (b) part in self-sealing bag
Before immersing in water at room temperature (RT)



(a)

(b)

(c)

After immersing in water heated to (a) 30°C (b) 45°C and (c) 60°C

Figure 4.1: Stages of crumbling of PVA



Blank PVA

Blank PPPVA

Blank OPPVA

Before immersing in water at RT



Blank PVA

Blank PPPVA

Blank OPPVA

After immersing in water heated to 30°C and then 45°C

* No change was observed at 45°C; same after 30°C

Figure 4.2 A: Improved strength of PVA with additives from RT to 45°C

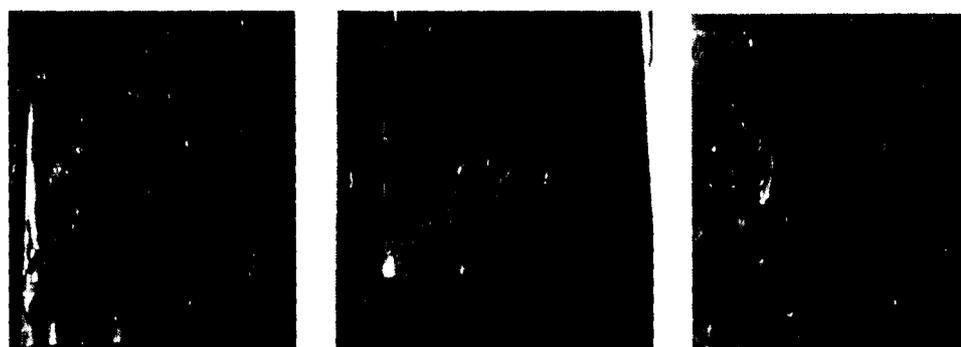


Blank PVA

Blank PPPVA

Blank OPPVA

Water heated to 60°C



Blank PVA

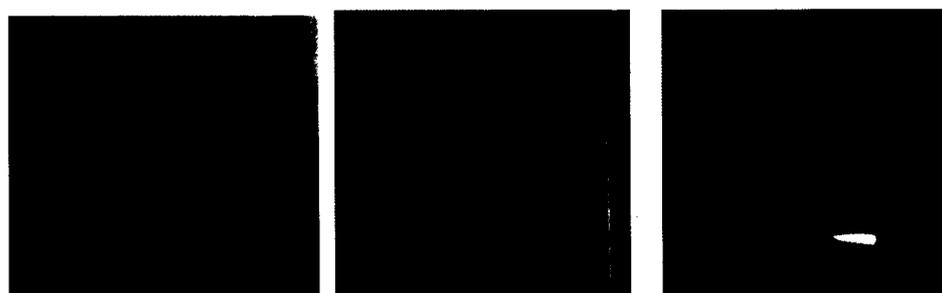
Blank PPPVA

Blank OPPVA

Water heated to 75°C and then to 90°C

* Blank OPPVA remained same

Figure 4.2 B: Improved strength of PVA with additives from 60°C to 90°C

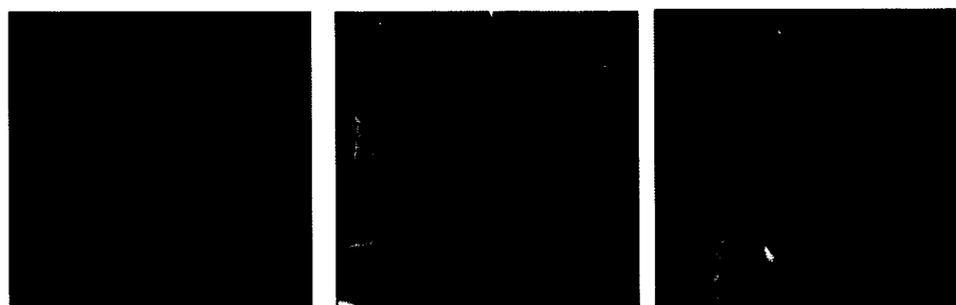


CH-PVA

CH-PPPVA

CH-OPPVA

Before immersing in water at RT



CH-PVA

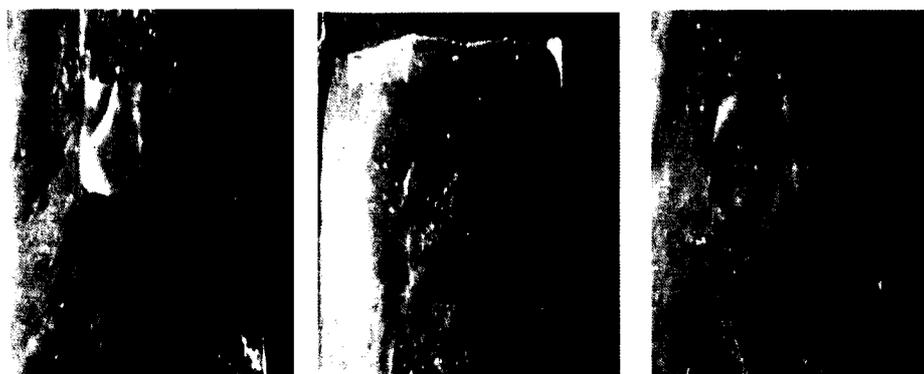
CH-PPPVA

CH-OPPVA

After immersing in water heated to 30°C and then 45°C

* No change observed at 45°C; same after 30°C

Figure 4.2 C: Improved strength of CH-PVA with additives from RT to 45°C

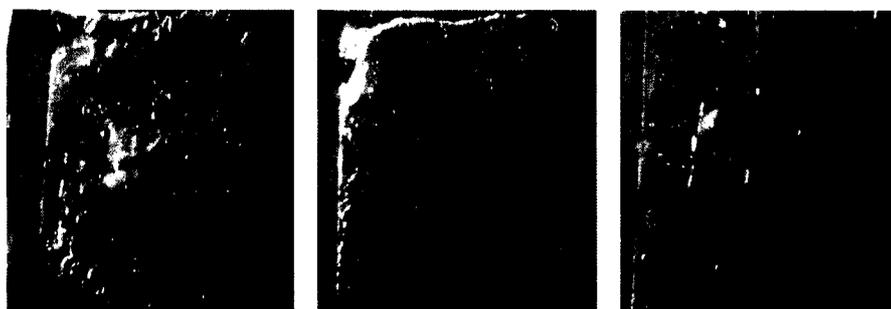


CH-PVA

CH-PPPVA

CH-OPPVA

Water heated to 60°C



CH-PVA

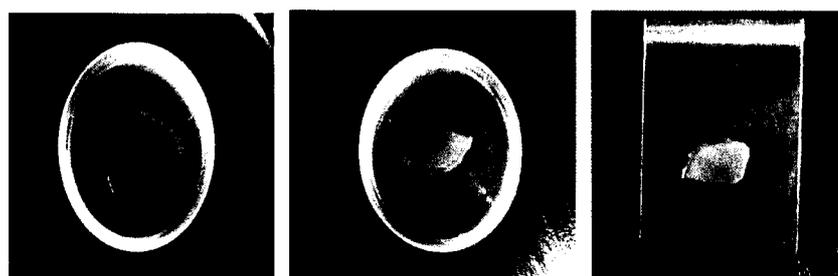
CH-PPPVA

CH-OPPVA

Water heated to 75°C and then to 90°C

* CH-OPPVA remained same

Figure 4.2 D: Improved strength of CH-PVA with additives from 60°C to 90°C



(a) (b) (c)
CH-PVC (a) whole (b) part (c) part in self-sealing bag
Before immersing in water at RT



(a) (b) (c)
After immersing in water heated to (a) 30°C (b) 45°C (c) 60°C



(d) (e) (f)

Water heated to (d) 75°C (e) 90°C and (f) above 90°C

Figure 4.3: Better strength of PVC

Polymer based Cobalt compound: Spectrophotometric method

In section 4.2 b) i), ii), the oxygen scavenging studies were performed by monitoring dissolved oxygen concentration through Winkler's method of various metal complexes and hydrazine at different temperatures. In section 4.2 b) i), we observed 3mL (0.01% or 0.1ppm) addition of hydrazine to 30L at 30°C scavenged 98% and it remained ~99% at 45°C. Whereas, 0.3mL (0.01ppm) addition of hydrazine at 30°C showed 54% oxygen scavenging which marginally increased to 58% at 45°C. On the other hand, 0.03mL (0.001ppm) addition of hydrazine showed at 30°C mere 31% oxygen scavenging which tremendously increased to 53% at 45°C. Thus there was 31 to 98% oxygen scavenging occurrence in the present investigations. As Winkler's method was time consuming as well it had some limitations, we considered an alternate method to investigate the scavenging. Since hydrazine was the main ingredient in all our investigations and metal compounds were in minor quantity, we considered monitoring hydrazine left behind in all investigations to get to know the oxygen scavenging. Since in research organizations the decomposition of hydrazine in preserved boilers are normally carried out at 45°C [54], we considered it apt to restrict to one temperature for further investigations, and thus we performed the following investigations at 45°C; and also instead of investigating different concentration of hydrazine addition, we restricted to one concentration of 0.001ppm (0.0001%).

At 45°C the 0.03mL (0.0001% or 0.001ppm) addition of hydrazine to 30L de-aerated water showed 53% oxygen scavenging. If temperature had been increased to 90°C or if hydrazine concentration had been increased to 0.01 ppm, the oxygen

scavenging would have increased > 90%. Hence 45°C would be an ideal temperature and 0.001ppm the ideal concentration of hydrazine to effectively study the scavenging by the use of spectrophotometer to estimate the hydrazine as a function of time. In the following studies, to the 30L de-aerated water, 0.03mL of hydrazine was added and polymer based cobalt compounds were dipped in the water. All cobalt compounds in the polymer were ~ 12.5mg; p-dimethylamino-benzaldehyde(PDBA) reagent was used for the color development of the water samples removed intermittently from the de-aerator assembly to monitor hydrazine by UV-Vis Spectrophotometer described in Chapter II, section 2.8, 2.9 and 2.12.

Hydrazine

0.03mL hydrazine was added to the 30L de-aerated water and hydrazine concentration was monitored at different duration of time at 45°C. Hydrazine present in the water after 10, 60, 120 and 180 minutes of duration was monitored. Hydrazine present observed in every measurement after the particular time duration was then deducted from the original value and thereby, the actual hydrazine consumed was calculated at different duration of time due to the oxygen scavenging by hydrazine. Hydrazine consumed at 45°C by the de-aerated water after 10 minutes was 51.3% which marginally increased to 53.2% after 60 minutes and then finally remained at 60.2% at the end of 180 minutes. The results suggest that at 30 °C the dissolved oxygen present in the de-aerated water of 4.5 to 5.0 ppm, changed to 3.1ppm at 45°C by mechanical de-aeration and further reduced to 1.9 ppm of dissolved oxygen. The hydrazine left behind after 180 minutes of ~ 40% remained unreacted, though there was dissolved oxygen present in the water. The oxygen

scavenging at 45°C, however, found to be 51.3 and 63.0%, respectively after 10 and 180 minutes.

Cobalt diaminotoluene and its hydrazinate

12.5 mg of cobalt chloride diaminotoluene in PVA, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ -PVA (CDAT-PVA) immersed in 30L de-aerated water containing 0.03mL hydrazine showed at 45°C the hydrazine consumed of 13.0% after 10 minutes and 40% after 180 minutes. The oxygen scavenging of 73 and 74.3%, respectively, was observed after 10 and 180 minutes. Comparing the oxygen scavenging of 51.3 and 63.0%, respectively after 10 and 180 minutes by hydrazine in section 4.4.2.4.i), the cobalt complex addition showed an enhancement of oxygen scavenging to 73 and 74.3%, indicating an activating effect of cobalt in the oxygen scavenging action of hydrazine. The hydrazine left behind unreacted was found to be 60% after 180 minutes, while 40% was found for only hydrazine addition. Thus only hydrazine scavenges 63% oxygen and leaves behind 40% of hydrazine unconsumed after 180 minutes, while the cobalt compound in hydrazine enhances the scavenging to 74.3 and leaves behind 60% of hydrazine. These results of an increased scavenging by decreased hydrazine consumption clearly indicate some catalyzing effect of the added cobalt compound.

12.5 mg of the hydrazine complex of cobalt chloride diaminotoluene, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ -PVA (CDATH-PVA) when introduced to the de-aerator water containing 0.03mL hydrazine, though showed 73.8% oxygen scavenging which was close to the one found for $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$ -PVA (CDAT-PVA) after 10 minutes, the hydrazine consumed found to be 5.67% which was very low compared to the

one with CDAT-PVA of 13.0%, suggesting clearly very less hydrazine is required for scavenging oxygen. It is still a clear indication of some catalytic effect of the hydrazinated cobalt complex than the unhydrazinated one. The hydrazine in the complex seems to be playing an important role.

Cobalt L-proline and its hydrazinate

~73% oxygen scavenging was observed when 12.5 mg cobalt L-Proline, $\text{Co(II)(L-proline)}_2(\text{H}_2\text{O})_2$ -PVA (CP-PVA) was added to de-aerator water containing 0.03mL hydrazine at 45°C after 10 minutes by consuming 8.5% hydrazine, while the oxygen scavenging remained to ~73% with the hydrazinate of cobalt L-Proline $\text{Co}(\text{C}_5\text{H}_8\text{NO}_2)(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_2$ -PVA (CPH-PVA), but the hydrazine consumption was found to be just 3.8%, suggesting again the catalyzing effect of the cobalt compounds, more so with the hydrazinate complex.

Cobalt hydroquinone and its hydrazinate

~72% oxygen scavenging by consuming 34% hydrazine was observed by 12.5 mg of cobalt hydroquinone in PVA, $\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2 \cdot 4\text{H}_2\text{O}$ -PVA (CHQ-PVA) on introducing to the de-aerated water containing 0.03mL hydrazine at 45°C, after 10 minutes. The introduction of the 12.5mg hydrazinate complex, $[\text{Co}(\text{OC}_6\text{H}_4\text{OH})_2(\text{N}_2\text{H}_4)_2]$ (CHQH-PVA), on the other hand, indicated ~73% oxygen scavenging by consuming 23.8% hydrazine, again suggesting a catalytic effect of the cobalt complexes.

Cobalt carbohydrazide

12.5mg of cobalt chloride carbohydrazide in PVA $[\text{Co}(\text{H}_2\text{N-NH})_2\text{COCl}_2(\text{H}_2\text{O})_2]$ - PVA (CZ-PVA) showed 72.4% oxygen scavenging on addition to the de-aerated

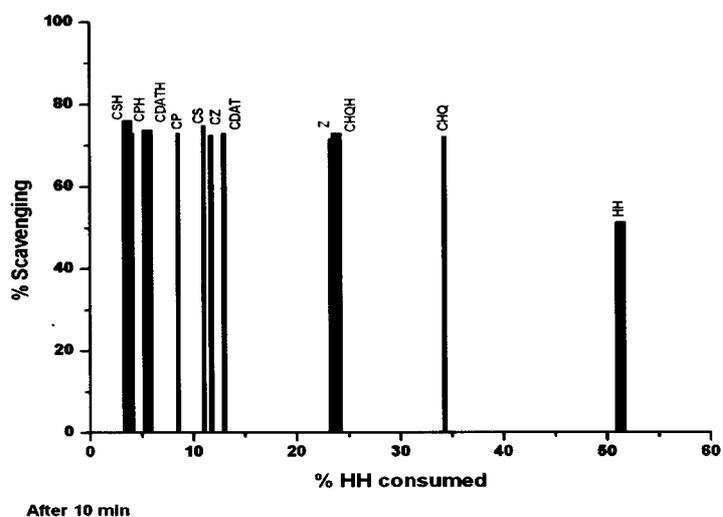
water containing hydrazine 0.03mL at 45°C, after 10 minutes and it remained almost in that range of oxygen scavenging of ~73.5% after 180 minutes by consuming ~35.7% hydrazine.

Only carbonylhydrazide in PVA of 12.5 mg when added to the de-aerated water containing hydrazine 0.03mL also showed ~71.6% oxygen scavenging after 10 minutes by consuming 23.6% hydrazine, while CZ-PVA consumed just 11.7% hydrazine, indicating clearly the catalytic action of the cobalt compound.

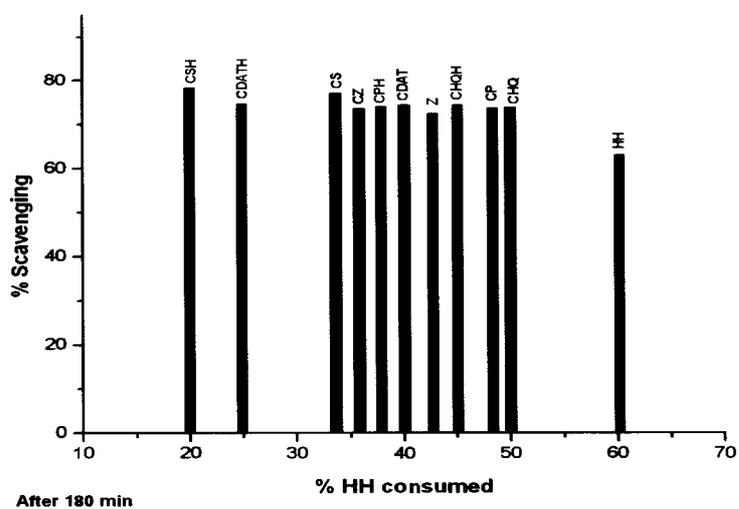
Cobalt salen and its hydrazinate

12.5 mg of cobalt salen in PVA, $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)]\text{-PVA}$ (CS-PVA) showed oxygen scavenging at 45°C of 74.9% after 10 min in de-aerated water (30L) containing 0.03mL hydrazine and hydrazine consumption 11.0%, while the hydrazinate complex, $[\text{Co}(\text{C}_{16}\text{O}_2\text{H}_{12}\text{N}_2)] \cdot \text{N}_2\text{H}_4\text{-PVA}$ (CSH-PVA) scavenged 76% of oxygen by consuming 3.6% of hydrazine.

In general, an enhancing of oxygen scavenging of hydrazine by the addition of cobalt complex with better performance by the hydrazine complexes was observed. But the hydrazine consumption to scavenge oxygen has been found to be low for the hydrazine complex and the lowest ever found in the present investigation was by the cobalt salen hydrazinate. A plot of % oxygen scavenging versus hydrazine consumed of all the investigated systems have been compiled in Figure 4.4 by taking both the values obtained after 10 and 180 minutes of experimentation.



(a)



(b)

Figure 4.4: Relation between hydrazine hydrate consumption and oxygen scavenging action by polymer based cobalt complexes, after a) 10 minutes b) 180 minutes

From the results, the order of activity of cobalt complexes based on the % oxygen scavenging and hydrazine % consumed is agreed. Based on the hydrazine consumed, the order follows as below

CSH>CPH>CDATH>CP>CS>CZ>CDAT>Z~CHQH>CHQ>HH

As compared to hydrazine hydrate (HH) the cobalt salen hydrazinate complex addition to the de-aerated water along with the hydrazine shows the maximum activity, hydrazine shows the lowest. And all other complexes find their activity in between these two CSH and HH. Besides, the hydrazinate complexes of the cobalt seem to show superior effect compared to the one without hydrazine in the complex.

4.3 Role of the cobalt complex: significance of hydrazine

Though the cobalt complexes show enhancing the effect of oxygen scavenging efficiency of hydrazine, it is not clear how this happens. Whether it is cobalt ion or the ligand or the complex that plays a role, systematic studies need to be undertaken. In a patent (US Patent No 4540494) claimants suggest a method for removal of oxygen dissolved in water, especially from reservoir drinking water and for the preservation purposes based on hydrazine, having no organic activator. Cationic and anionic complexes of trivalent cobalt with inorganic ligand or mixtures thereof are used as activators. Preferred activators are $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$. Hydrazine solutions with these activators were found to be suitable

for the removal of oxygen. In yet another patent (US Patent No 4012195) titled “catalyzed hydrazine compound corrosion inhibiting composition and use”, the claimants describe the corrosion inhibiting composition consisting of hydrazine compound and an organo-metallic complex such as $[\text{Co}(\text{3,4-toluene diamine})_2]\text{Cl}_2$ which scavenge oxygen from the corrosive environment. However, these claimants have not shown the mechanism by which the oxygen scavenging is catalyzed or enhanced by the incorporation of the cobalt compounds. In our studies we have observed the efficiency of cobalt complexes in enhancing the oxygen scavenging and also the lesser consumption of hydrazine due to the presence of these metal compounds. Since we observed that the cobalt complexes once used can be reused, though with lesser efficiency, the reusability clearly indicates that the complex has not changed drastically. It means that once the oxygen is scavenged, the removed oxygen has no effect on the catalyst electronic structure and hence cobalt complex acts as catalyst, because, it can be reused. To ensure these possibilities, we carried out oxygen absorption studies on all these cobalt complexes and hydrazine

Oxygen uptake

In Chapter I, figure 1.2, we have described some of the salient features of the cobalt complexes which take up oxygen, may be reversibly.

Hydrazine

The studies carried out for the oxygen uptake on the set up, Chapter I, Figure 1.1, indicates that in general the oxygen uptake takes place linearly with time, Chapter I, Figure 1.2. A maximum of 0.233 moles is taken up by 0.1mL hydrazine/L water in 900 minutes, while 0.01mL hydrazine/L water absorbed 0.225 moles in 700

minutes and 0.001mL hydrazine/L water absorbed 0.151 moles in 400 minutes. The 0.0001mL hydrazine/L water took up 0.123 moles oxygen in 430 minutes. Graphically it can be seen that 0.001mL hydrazine/L water is taking more oxygen in lesser time and in our spectrophotometric studies of the oxygen scavenging we used 0.03mL in 30L water which amounts to 0.001mL per litre of water.

The oxygen absorption clearly suggests that the hydrazine reacts with the oxygen linearly.

Cobalt diaminotoluene (CDAT) and its hydrazinate (CDATH)

10mg of CDAT/CDATH in dimethyl sulphoxide, DMSO (3mL) take up oxygen and plots, Figure 4.5, almost overlapping on each other up to 400 minutes showing 0.07 moles oxygen in 6 ½ hours, suggesting that the cobalt complexes have affinity for oxygen.

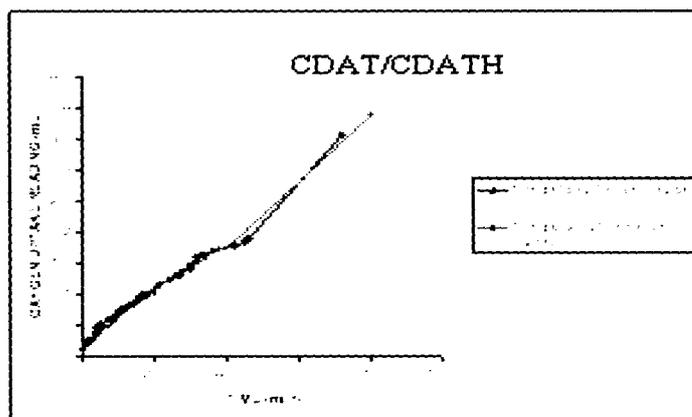


Figure 4.5: O₂ uptake versus time of cobalt diaminotoluene (CDAT) and its hydrazinate complex (CDATH) in DMSO

Cobalt L-proline (CP) and its hydrazinate (CPH)

1mg CP in DMSO showed 0.262 moles oxygen taken up in 500 minutes and CPH 0.147 moles in 400 minutes. The oxygen absorption by CPH is lower than that of

CP. On the other hand, the complexes without DMSO showed almost similar linear absorption of oxygen which is reversible too, Figure 4.6 and 4.7;

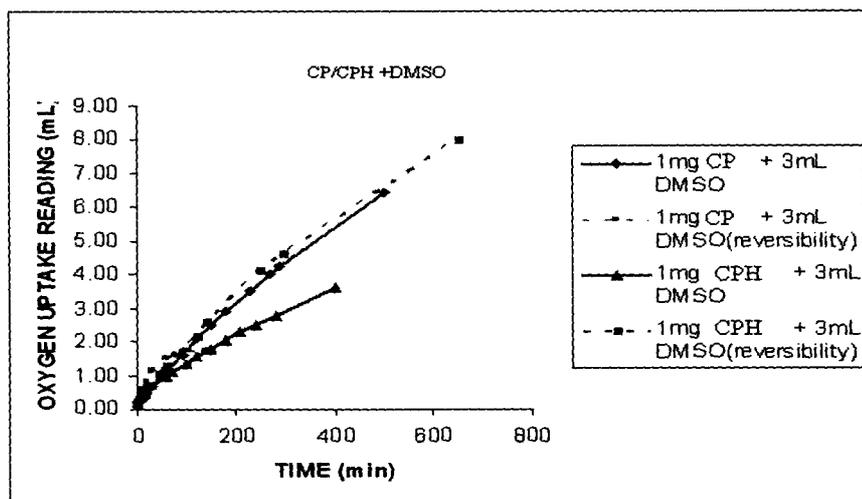


Figure 4.6: O₂ uptake versus time of cobalt L-Proline (CP) and its hydrazinate (CPH) in dimethyl sulphoxide (DMSO)

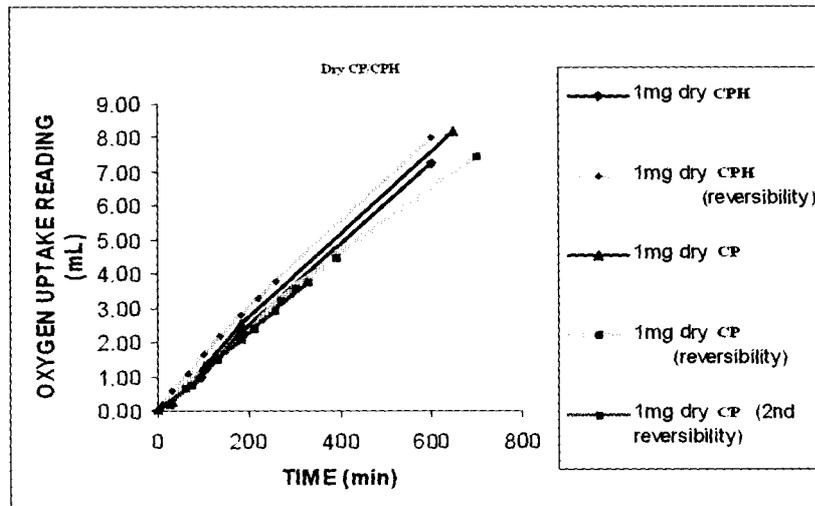


Figure 4.7: O₂ uptake versus time of cobalt L-Proline and its hydrazinate (CP/CPH)

Cobalt salen (CS) and its hydrazinate (CSH)

1mg CS and CSH in 3mL DMSO as a function of time show an increase in oxygen uptake and are reversible too.

The experiment carried for the uptake of oxygen by hydrazine and cobalt complex together are compiled in the Figure 1.4 of Chapter I.

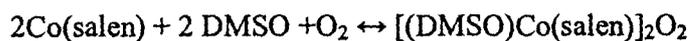
0.001mL hydrazine in 1 L water took up oxygen 0.151 moles in 380 minutes, while 0.001mL hydrazine + 1 mg CS indicated 0.20 moles oxygen in 380 minutes, and maximum uptake of 0.268 and 0.368 moles, respectively, at the end of 12 hours, suggesting clearly the oxygen uptake of hydrazine is enhanced by the addition of the small amount of cobalt complex.

The studies done on 1 mL of 0.1mL hydrazine in 1L water at temperatures 30, 45 and 60°C showed, respectively, 0.041 moles, 0.081 moles and 0.123 moles oxygen uptake, indicating temperature dependence of hydrazine reaction with oxygen. Higher the temperature higher is the reactivity of hydrazine with oxygen.

1 mL of 0.1mL hydrazine in 1L water + 1mg CS and CSH at 60°C indicated in 180 minutes an oxygen uptake of 0.106 moles and 0.078 moles, respectively, and a maximum of 0.167 moles in 300 minutes.

The studies of oxygen uptake, however, require to be quantified, but, in general, it seems the cobalt complexes do take up oxygen. In the case of cobalt L-proline the electrochemical properties of the $\text{Co(II)(L-proline)}_2(\text{H}_2\text{O})_2$ complex under argon atmosphere in outgassed water studied by cyclic voltametry revealed an

electrochemically irreversible oxidation of the Co(II) complex which was assigned to the $\text{Co}^{\text{II}}(\text{Pro})_2/\text{Co}^{\text{III}}(\text{Pro})_2$ couple. The reversible oxygen uptake by cobalt salen in DMSO was considered through the formation of an oxygen adduct,

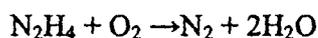


While studying the autoxidation of hydrazine, hydroxylamine and cystein by the Cobalt (II) chelate complex of 3,10,17,24-tetrasulphophthalocyanine (H_2tspc) [11], the authors found the complex to be an efficient catalyst for the oxidation of the target compounds in an aqueous solution by molecular oxygen. The oxidation of hydrazine and hydroxylamine involves the initial formation of a 1:1 adduct between $[\text{Co}^{\text{II}}(\text{tspc})]$ and the substrate which then reacts with molecular oxygen yielding oxidation products of hydrazine and hydroxylamine leaving the complex $[\text{Co}^{\text{II}}(\text{tspc})]$ intact. In the case of cystein, the oxidation process involves an electron-transfer reaction resulting in the formation of $[\text{Co}^{\text{I}}(\text{tspc})]^-$ and cystein. Simple oxygenation of $[\text{Co}^{\text{II}}(\text{tspc})]$, however, leads [11] to an irreversible oxygen adduct of the type $[\text{Co}^{\text{III}}(\text{tspc})(\text{O}_2)]$. On the other hand, a binary adduct of the type $[\text{Co}^{\text{II}}(\text{tspc})(\text{N}_2\text{H}_4)]$ that identified in an aqueous solution when bubbled with oxygen a Co(I) chelate of the type $[\text{Co}^{\text{I}}(\text{tspc})]^-$ formation occurred indicating no molecular oxygen adduct formation unlike in the simple oxygenation of $[\text{Co}^{\text{II}}(\text{tspc})]$. It further suggested that the molecular oxygen reaction with the adduct involves electron transfer and no evidence for the formation of a ternary adduct involving $[\text{Co}^{\text{II}}(\text{tspc})]$, hydrazine and oxygen was found. The oxidation of hydrazine has been shown to involve the initial formation of a binary adduct with $[\text{Co}^{\text{II}}(\text{tspc})]$. The adduct formation is pH dependent involving deprotonation of the species NH_2NH_3^+

~ pH 11.5. At pH > 11.5 the reduction to a Co^{I} species indicates the hydrazine is oxidized by simple electron transfer. Since activator effect of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [US Patent No. 4540494] and catalytic effect of $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2$ [US Patent 4012195] are not clearly indicated in the patents, it is difficult to comprehend how the effect takes place in the autoxidation of hydrazine. Though a hydrazine compound formation was mentioned in the case of $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2$, a clear composition or formula was not revealed. However, our attempt to prepare hydrazine complex of $[\text{Co}(3,4\text{-TDA})_2]\text{Cl}_2 \approx [\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)_3]\text{Cl}_2$, clearly showed the formation of a complex of the type, $[\text{Co}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{N}_2\text{H}_4)_2]\text{Cl}_2 \approx [\text{Co}^{\text{II}}(\text{DAT})(\text{N}_2\text{H}_4)_2]$. Probably such hydrazine complex, $[\text{Co}^{\text{II}}(\text{DMT})(\text{N}_2\text{H}_4)_2]$, which is similar to the adduct $[\text{Co}^{\text{II}}(\text{tspc})(\text{N}_2\text{H}_4)]$ and hence the mechanism of autoxidation may also be same, without forming a ternary adduct.

In their studies of the reaction between hydrazine and oxygen at 25°C and 70°C in alkaline solution the authors [12] have shown that the observed rate is due to catalysis by traces of impurities. It was found that copper (II) and manganese (II) were the most active catalysts; and under certain conditions, the copper (II)-catalyzed reaction appeared to be homogeneous. Evidence was presented that catalysis occurs by redox reactions. The reaction was followed by measurement of the hydrazine concentration. The authors [12] did not make any attempt to measure the oxygen concentration during the reaction, owing to the great difficulty involved in the determination of oxygen in the presence of hydrazine when both are disappearing at an appreciable rate. Therefore, in the kinetic experiments they arranged that dissolved oxygen should be in sufficient excess over the hydrazine so

that changes in the concentration of oxygen during the reaction could be ignored. The practice of bubbling air through the solution to maintain a constant oxygen concentration during a reaction was open to objection. Not only would it involve assumptions on the rate of oxygen absorption but it might have led to the loss of hydrazine and /or ammonia from the solutions. In order that the stoichiometry of the reaction i.e. the number of molecules of hydrazine reacting with one molecule of oxygen might be determined, they found it necessary to verify that the reaction was complete [12]. At 25 ° C and pH 9, in the presence of ammoniacal copper (II) catalyst, 8 ppm of dissolved oxygen completely oxidized 1 ppm of hydrazine or were completely reduced by 20 ppm of hydrazine. When hydrazine was in excess over oxygen, it was found that after all oxygen had disappeared, the excess hydrazine concentration remained constant, showing that there was no appreciable breakdown of hydrazine and also no interference by traces of oxygen in the blanketing nitrogen. When oxygen was readmitted, the hydrazine concentration began to fall again [12]. Within experimental error, the stoichiometry was 1 at 25 ° C and 70 ° C. This was consistent with the overall reaction;



Hence, little or no ammonia was formed at pH 9 in this temperature range. When hydrazine was in excess over oxygen, the catalyst would be in the form of Cu (I) at the end of the reaction. Therefore, the observed hydrazine consumption would include that used in reducing Cu (II) to Cu (I). With the amount of catalyst used by them [12] the error involved in the determined stoichiometry is not greater than 0.25%.

As explained earlier, in section 4.2 of this chapter, we have in our studies observed the efficiency of cobalt complexes in enhancing the oxygen scavenging and also the lesser consumption of hydrazine due to the presence of these metal compounds.

The % oxygen scavenging versus % hydrazine consumption as a function of time of the boiler feed water of 4-5 ppm dissolved oxygen have been carried out for the cobalt complexes and have been plotted and shown in Appendix VIII of this thesis.

The % oxygen scavenging versus temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for the various cobalt complexes, their hydrazinates, all complexes embedded in PVA, Hydrazine hydrate and Hydrazine sulphate ($N_2H_5SO_4$) have been displayed in 3-Dimensional (3D) and 2-Dimensional (2D) view in Appendix VIII of the present thesis.

Chapter V

Summary and Scope for Future Work

The conclusion of the results on the various systems and methods studied in the present investigation are drawn. Also future scope of the work is projected.

Conclusion:

For the first time several cobalt complexes and their hydrazine complexes have been lucratively prepared and their plausible formulae suggested. The structure may be indomitable by obtaining the crystals. Cobalt complexes can be easily synthesized. These cobalt complexes were also used alone as well as along with hydrazine to enhance the oxygen scavenging action of hydrazine in the boiler feed water, after duly de-aerating mechanically the de-mineralized water to bring the dissolved oxygen to 4-5 parts per million in a home built de-aerator. The de-aerator for boiler feed water was fabricated and used successfully in the studies of oxygen scavenging action using the various scavengers. An exhaustive literature survey was also carried out. Each of the cobalt compounds have been effectively incorporated in a polymer matrix and then the oxygen scavenging action was investigated. The significant observation of the present studies was that, the catalyst could be easily removed from the boiler water assembly, when the cobalt complexes were embedded in the polymer matrix. The main objective, however, was to minimize the use of perilous hydrazine in the continuous running of the boilers by the use of catalysts and towards this objective investigate different catalysts for their effectiveness. It was seen that the reactivity of hydrazine with oxygen was enhanced by the cobalt complexes. The consumption of hydrazine was reduced when the cobalt complexes were modified with hydrazine. Lower consumption of hydrazine by the use of cobalt complex as catalysts indicate the potentiality of the catalysts in

minimizing the use of venomous hydrazine in the boiler feed water, making the whole process environmentally friendly.

Scope for Future work:

The Electron spin resonance (ESR) spectra, the X-Ray Photoelectron Spectroscopy (XPS) of the cobalt complexes have been carried out. The thermal analysis (TG/DSC (DTA) of the cobalt complexes have also been carried out. The phase identifications of the powdered samples, precursors and oxides of the cobalt complexes were studied through the X-Ray (XRD) powder diffraction technique. The phase identifications of the cobalt complexes decomposed at 700°C, 900°C, 1000°C, 1200°C, indicated the formation of cobalt oxide(s). The Ultra violet-Visible Spectroscopy (UV-Vis) and Diffuse Reflectance Spectroscopy (UV-DRS) of the various cobalt complexes have been recorded. However, since the structure needs to be determined by obtaining the crystals of the various cobalt complexes and a further detailed study may be accomplished in future, the spectral scans may be useful and are therefore displayed in Appendix I-VII of this thesis.

The % oxygen scavenging versus % hydrazine consumption as a function of time of the boiler feed water of 4-5 ppm dissolved oxygen have been carried out for the cobalt complexes synthesized from cobalt chloride source and plotted as presented in Appendix VIII of this thesis. As the cobalt complexes synthesized from cobalt chloride may leave behind some dissolved solids, the cobalt complexes from cobalt acetate were also synthesized and used in the de-aerator for oxygen scavenging studies, Table 4 of Chapter IV. However, the spectrophotometric studies for hydrazine consumption of these complexes may be carried out in future.

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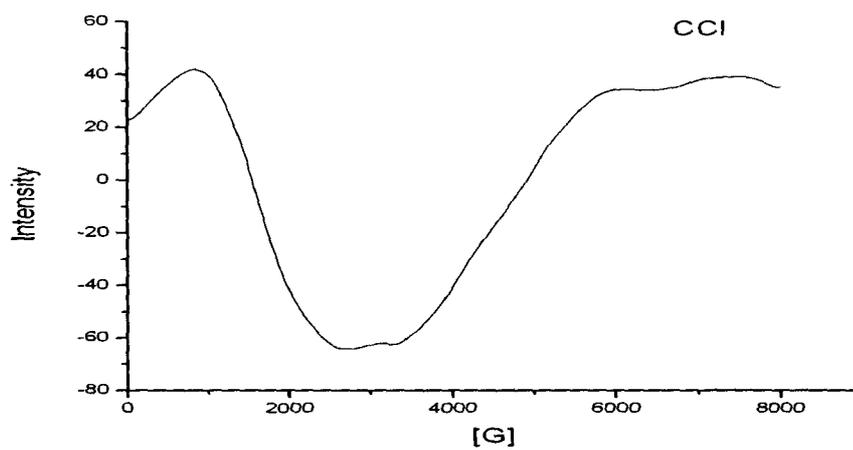
APPENDIX-I**Electron Spin Resonance (ESR) SPECTRA**

Figure 1: ESR of cobalt chloride (CCl)

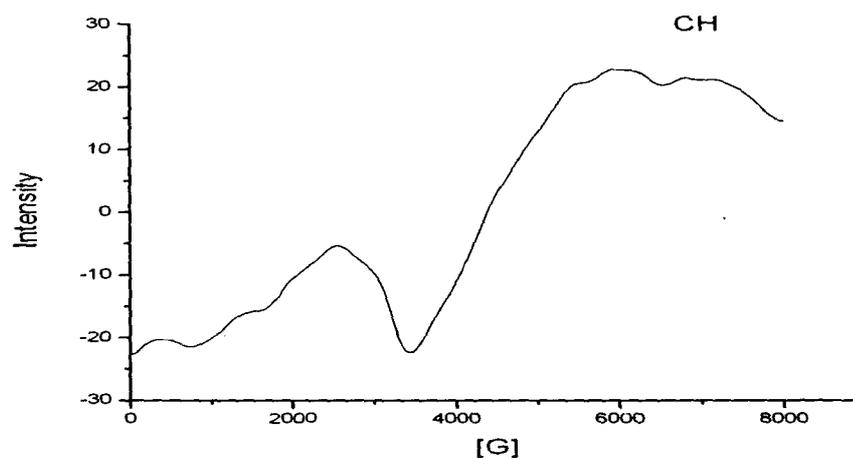


Figure 2: ESR of cobalt chloride hydrazinate (CH)

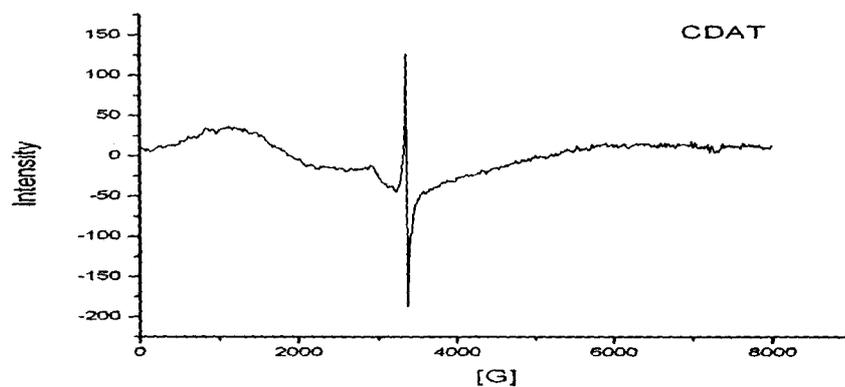


Figure 3: ESR of cobalt chloride diaminotoluene (CDAT)

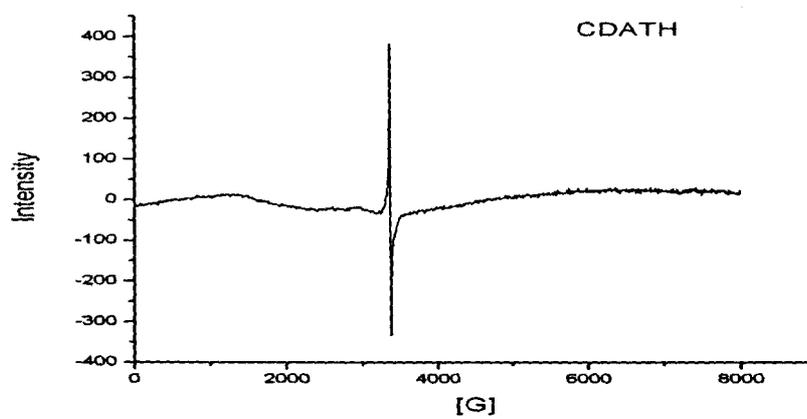


Figure 4: ESR of cobalt chloride diaminotoluene hydrazinate (CDATH)

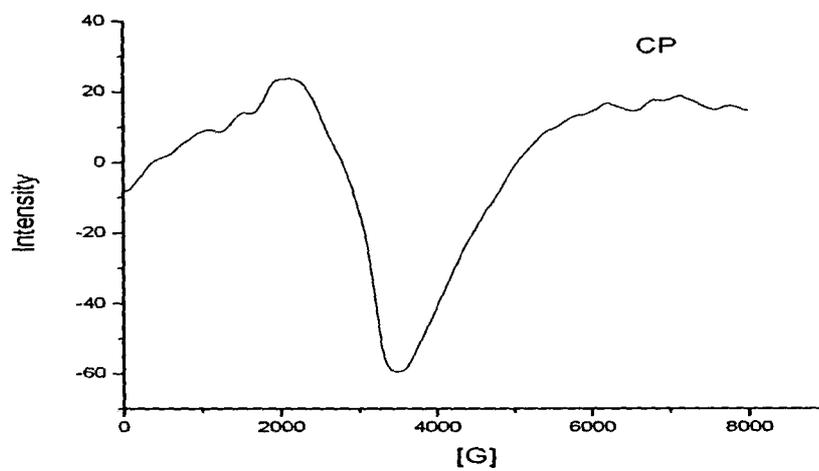


Figure 5: ESR of cobalt L-Proline (CP)

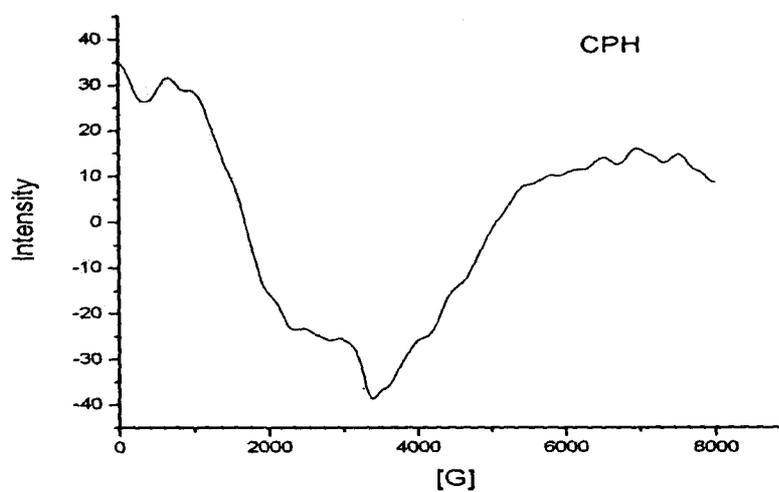


Figure 6: ESR of cobalt L-Proline hydrazinate (CPH)

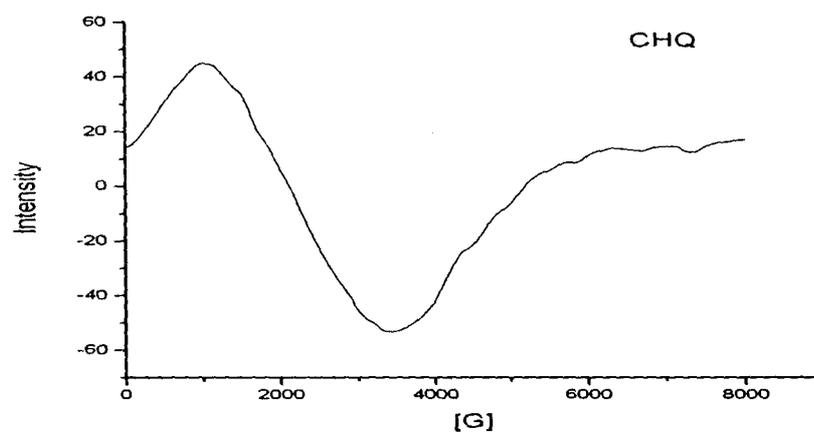


Figure 7: ESR of cobalt hydroquinone (CHQ)

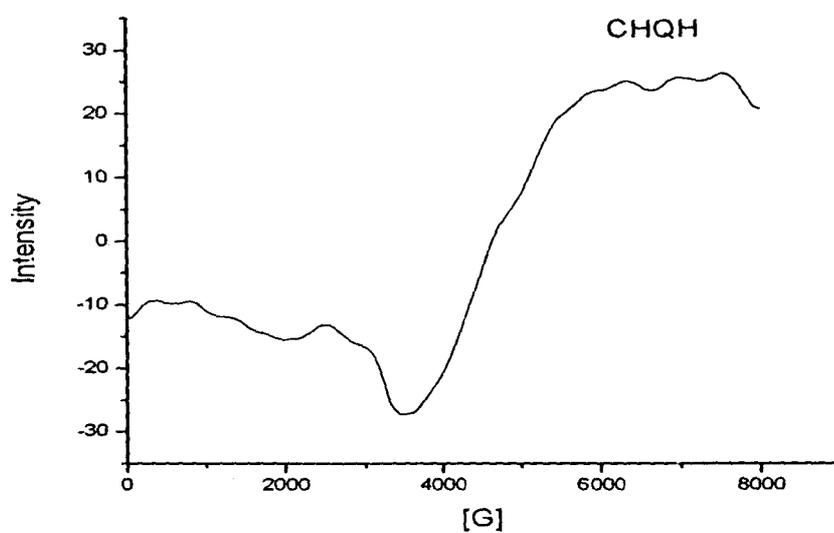


Figure 8: ESR of cobalt hydroquinone hydrazinate (CHQH)

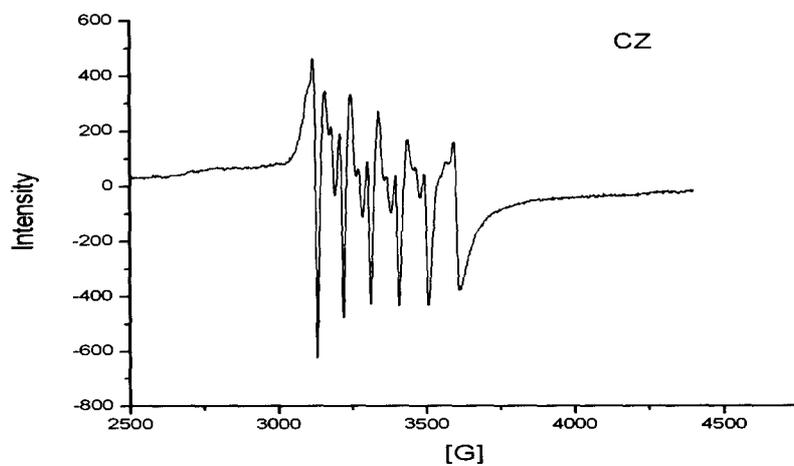


Figure 9: ESR of cobalt chloride carbohydrazide (CZ)

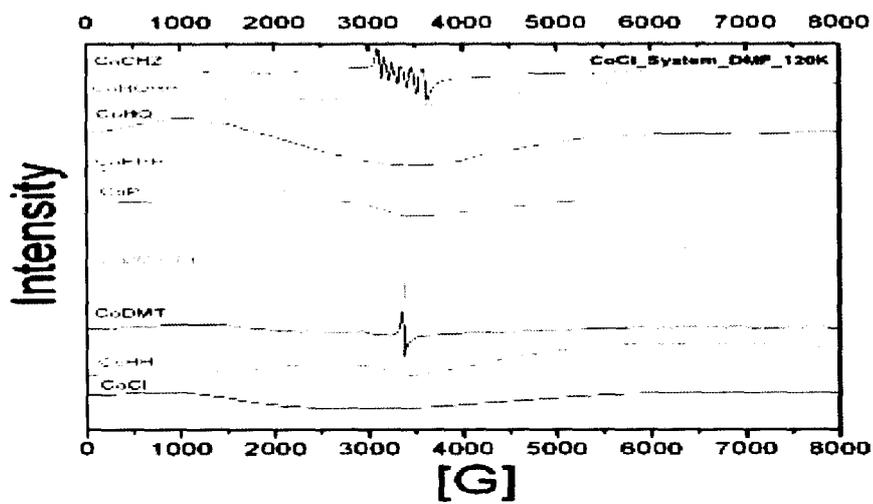


Figure 10: ESR of cobalt compounds: cobalt chloride source

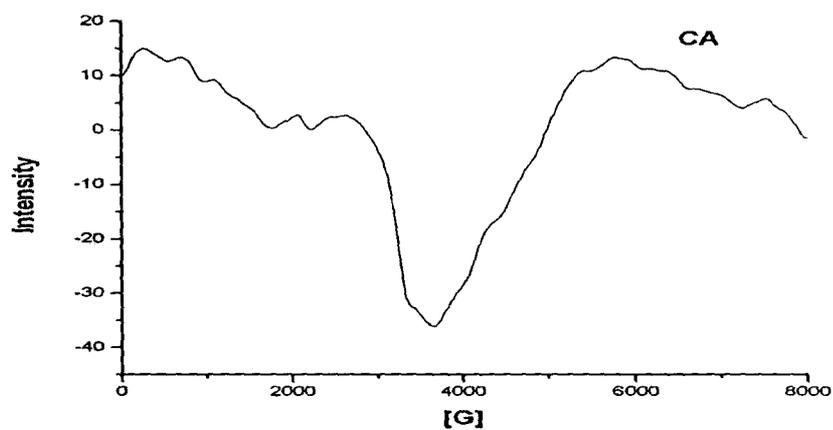


Figure 11: ESR of cobalt acetate (CA)

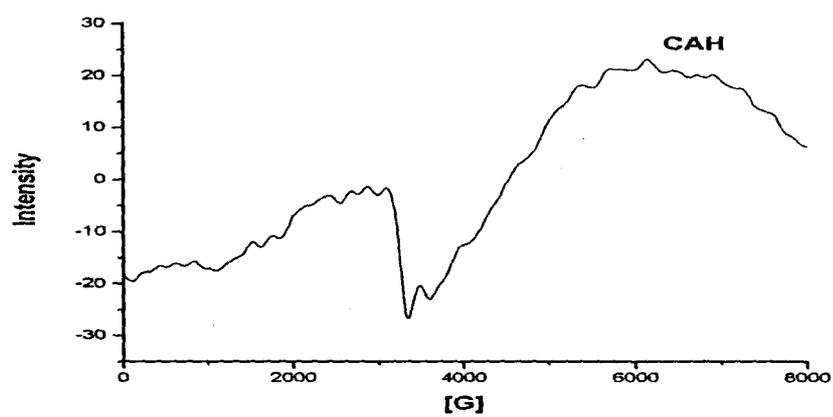


Figure 12: ESR of cobalt acetate hydrazinate (CAH)

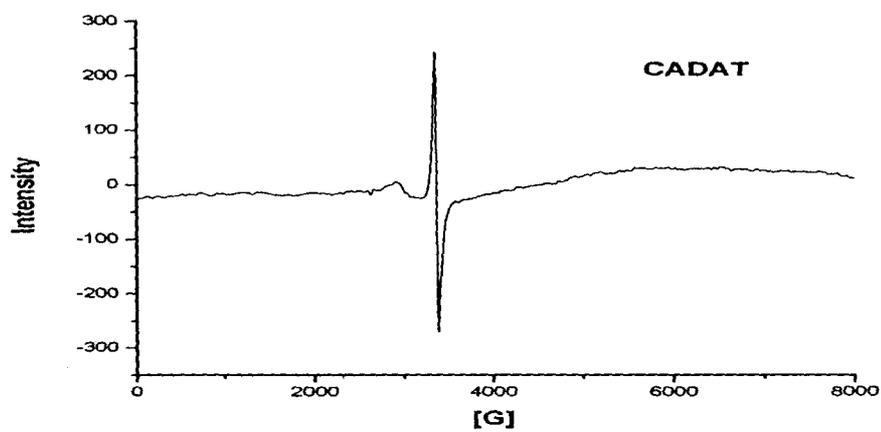


Figure 13: ESR of cobalt acetate diaminotoluene (CADAT)

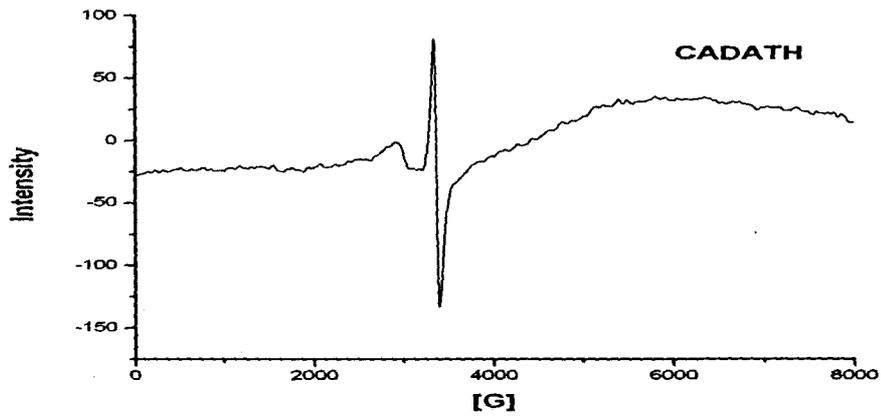


Figure 14: ESR of cobalt acetate diaminotoluene hydrazinate (CADATH)

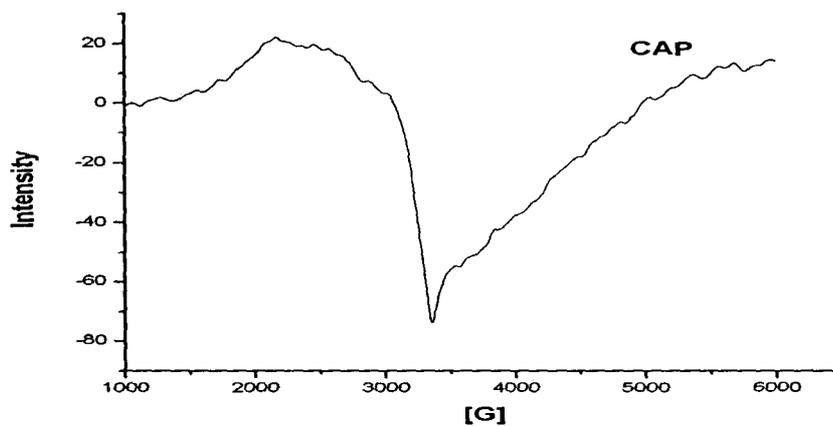


Figure 15: ESR of cobalt L-Proline (CAP)

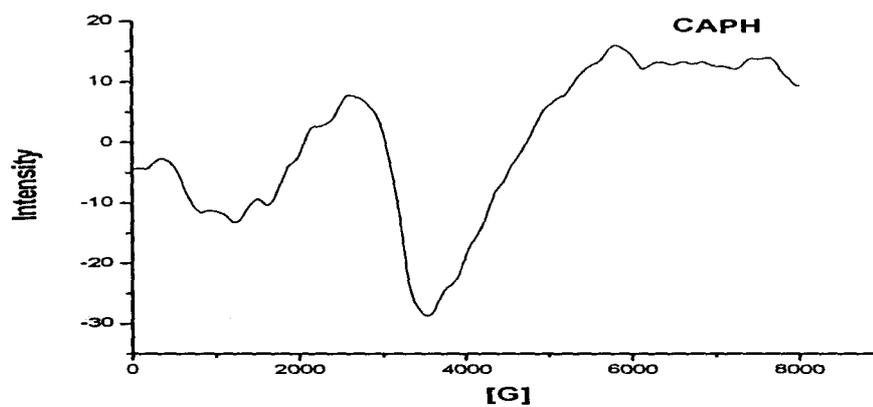


Figure 16: ESR of cobalt L-Proline hydrazinate (CAPH)

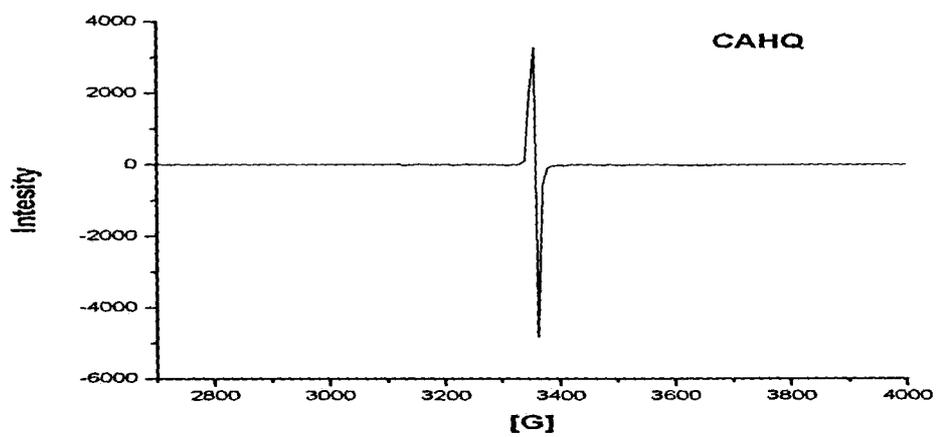


Figure 17: ESR of cobalt hydroquinone (CAHQ)

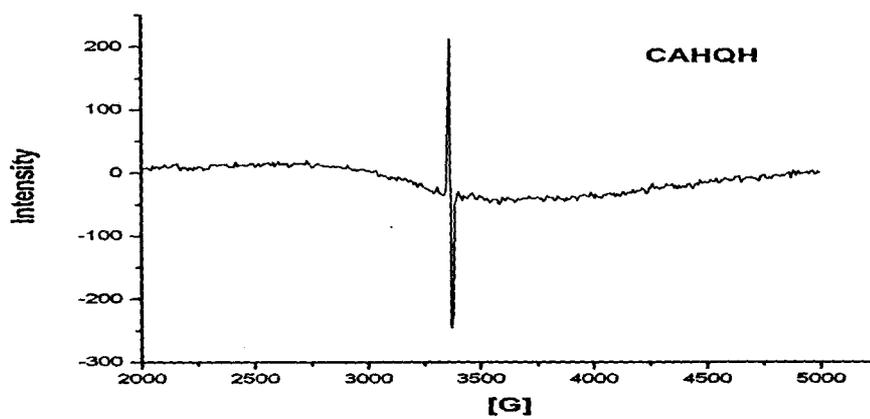


Figure 18: ESR of cobalt hydroquinone hydrazinate (CAHQH)

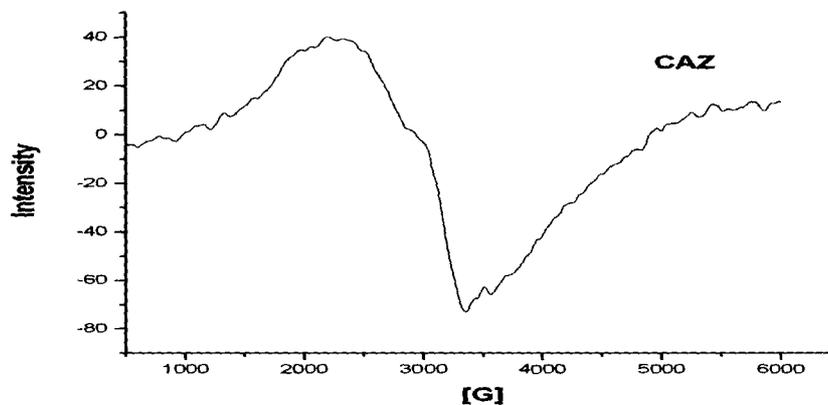


Figure 19: ESR of cobalt acetate carbohydrazide (CAZ)

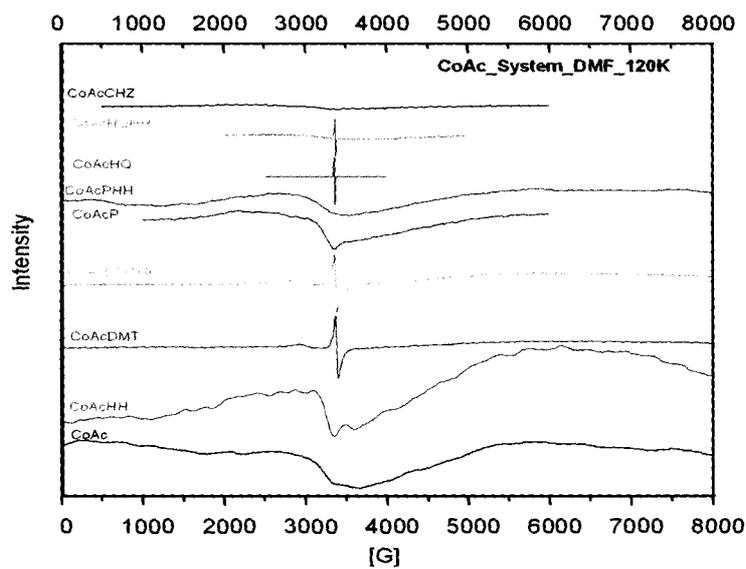


Figure 20: ESR of cobalt compounds: cobalt acetate source

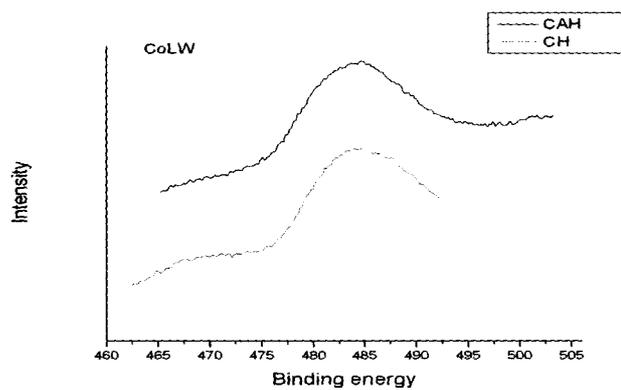
APPENDIX-II**X-Ray Photoelectron spectroscopy (XPS SPECTRA)**

Figure 21: XPS of hydrazinate of cobalt chloride (CH) and cobalt acetate (CAH)

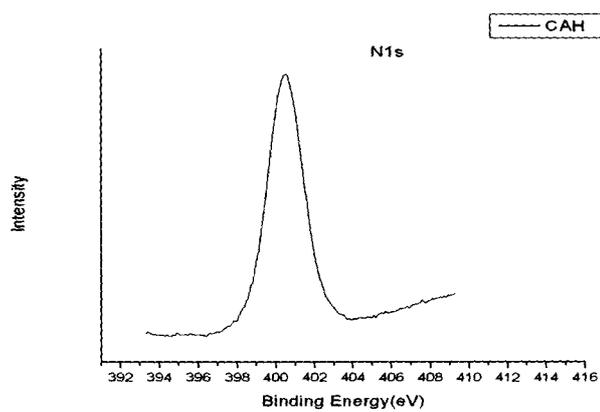


Figure 22: XPS of hydrazinate of cobalt acetate (CAH)

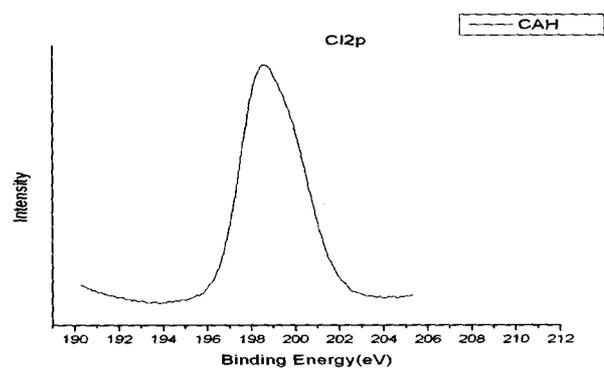


Figure 23: XPS of hydrazinate of cobalt acetate (CAH)

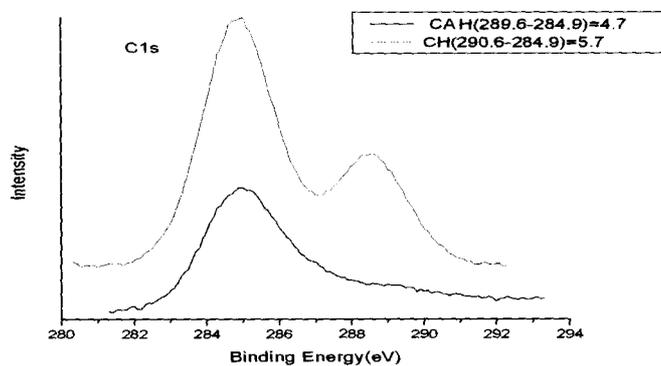


Figure 24: XPS of hydrazinate of cobalt chloride (CH) and cobalt acetate (CAH)

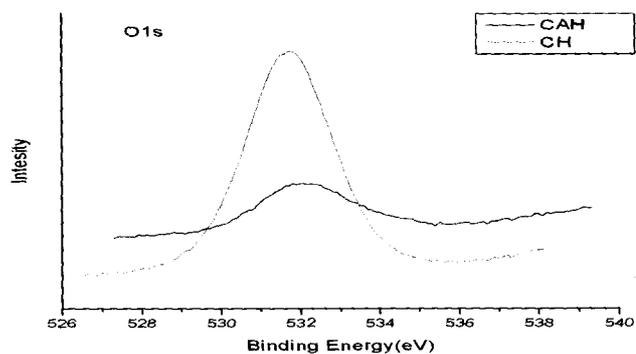


Figure 25: XPS of hydrazinate of cobalt chloride (CH) and cobalt acetate (CAH)

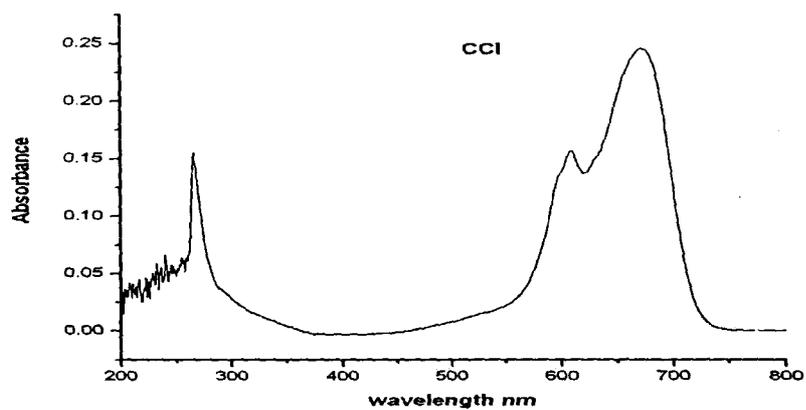
APPENDIX-III**Ultra violet- Visible Spectroscopy (UV-VIS) SPECTRA**

Figure 26: UV-Vis of cobalt chloride (CCl)

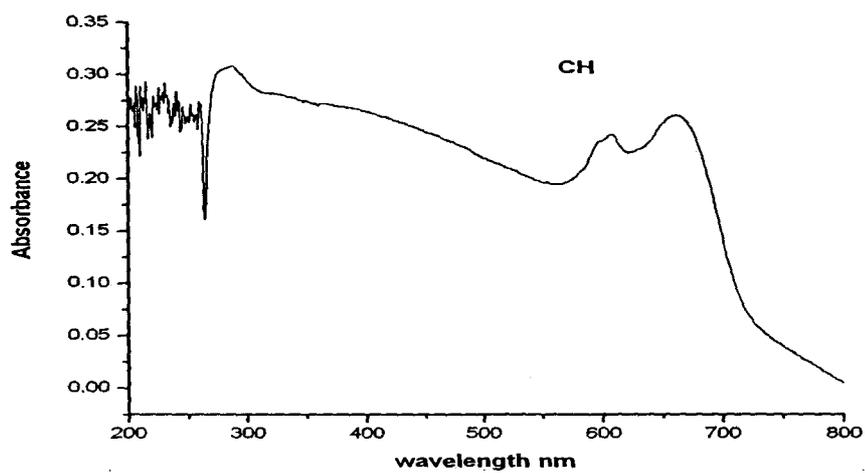


Figure 27: UV-Vis of cobalt chloride Hydrizinate (CH)

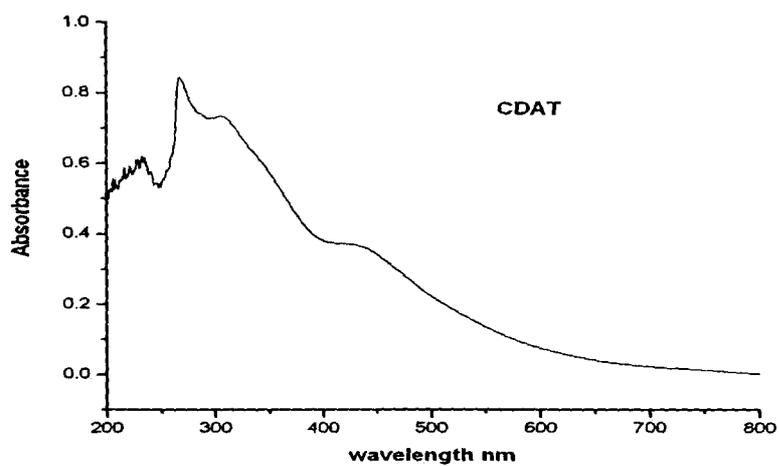


Figure 28: UV-Vis of cobalt chloride diaminotoluene (CDAT)

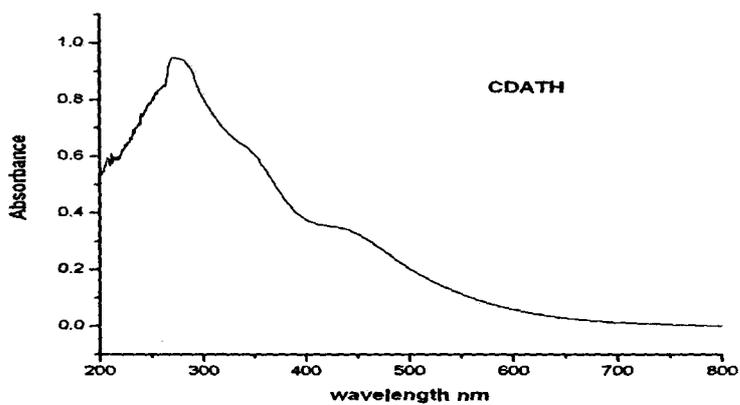


Figure 29: UV-Vis of cobalt chloride diaminotoluene hydrazinate (CDATH)

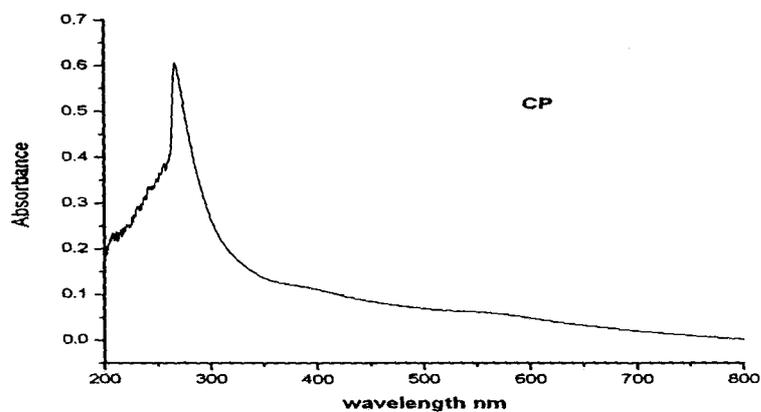


Figure 30: UV-Vis of cobalt L-Proline (CP)

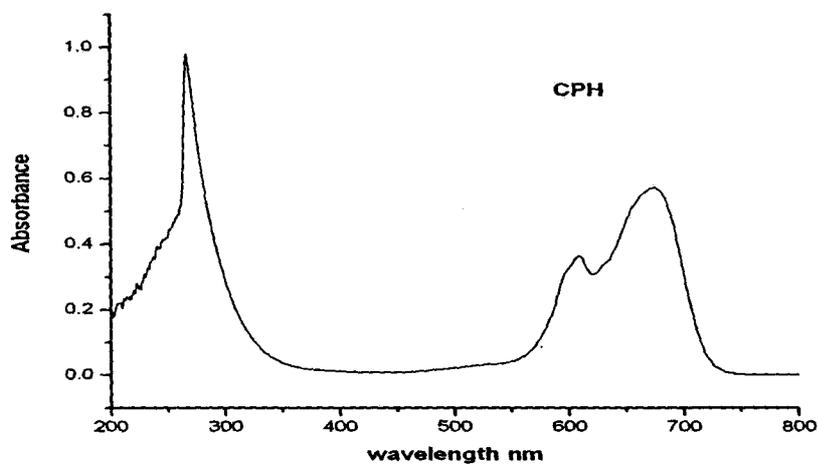


Figure 31: UV-Vis of cobalt L-Proline Hydrazinate (CPH)

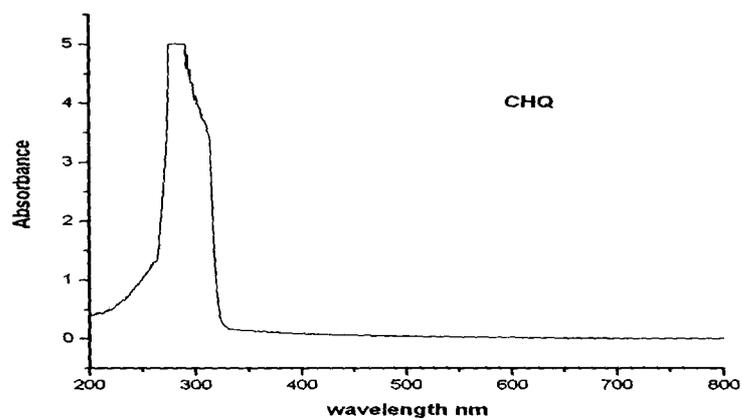


Figure 32: UV-Vis of cobalt Hydroquinone (CHQ)

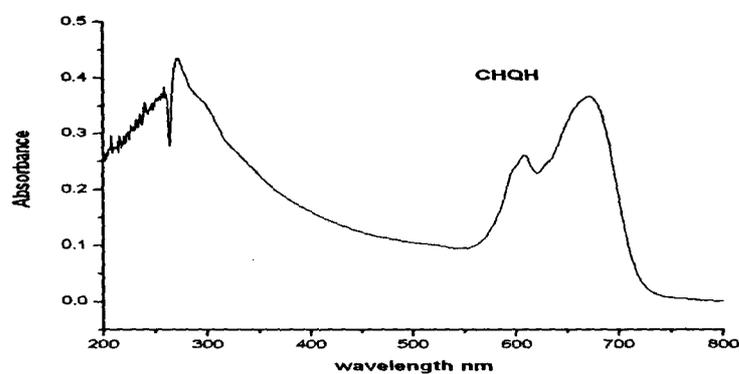


Figure 33: UV-Vis of cobalt hydroquinone hydrazinate (CHQH)

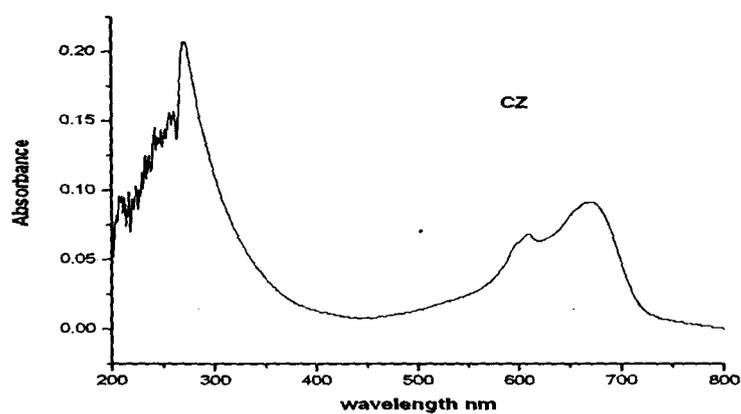


Figure 34 : UV-Vis of cobalt chloride carbohydrazide (CZ)

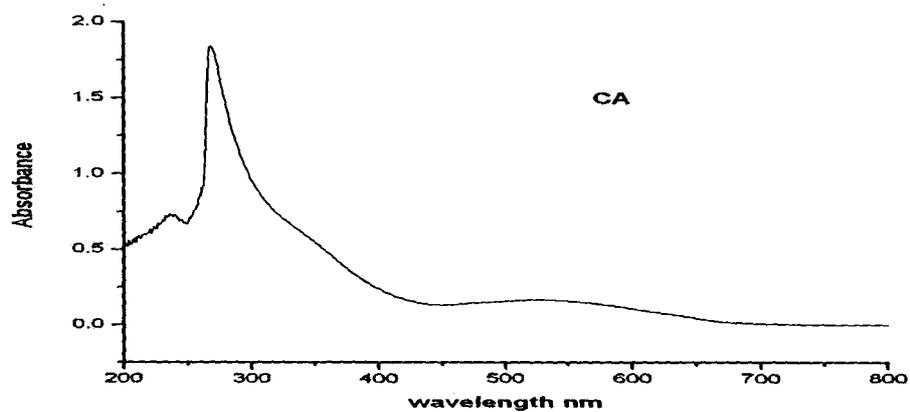


Figure 35: UV-Vis of cobalt acetate (CA)

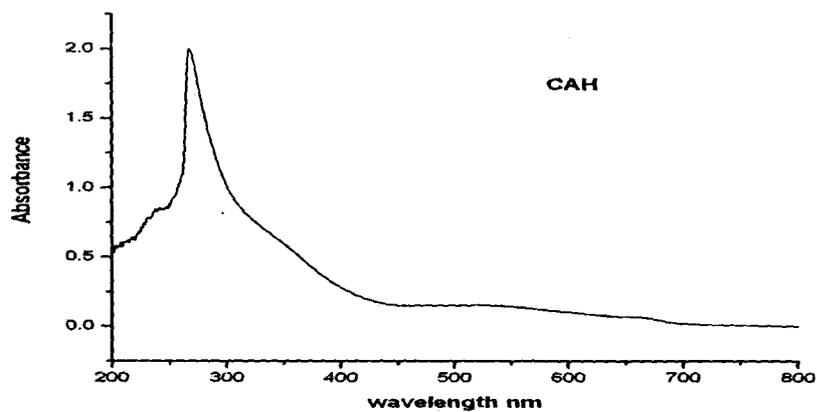


Figure 36: UV-Vis of cobalt acetate Hydrazinate (CAH)

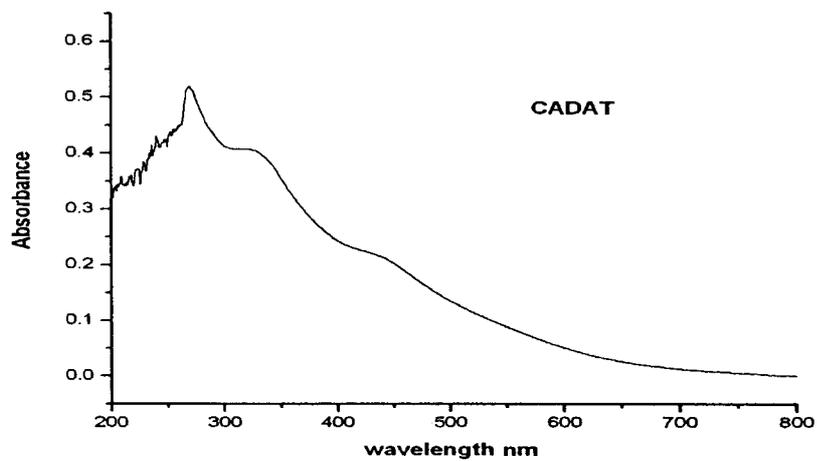


Figure 37: UV-Vis of cobalt acetate diaminotoluene (CADAT)

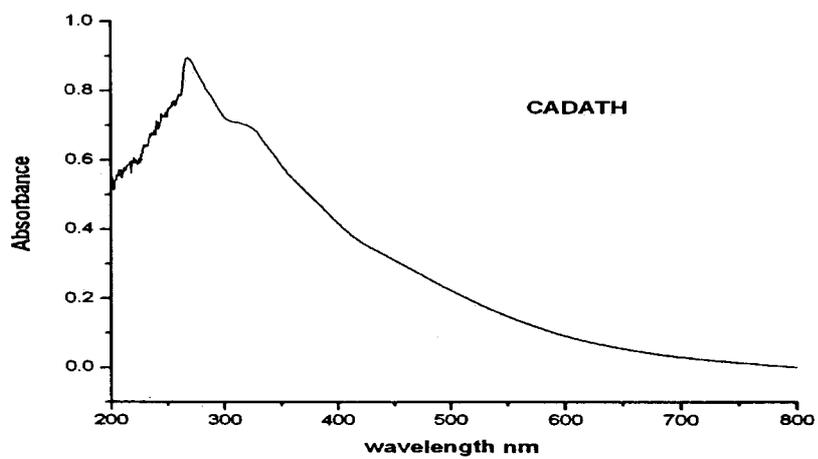


Figure 38: UV-Vis of cobalt acetate diaminotoluene hydrazinate (CADATH)

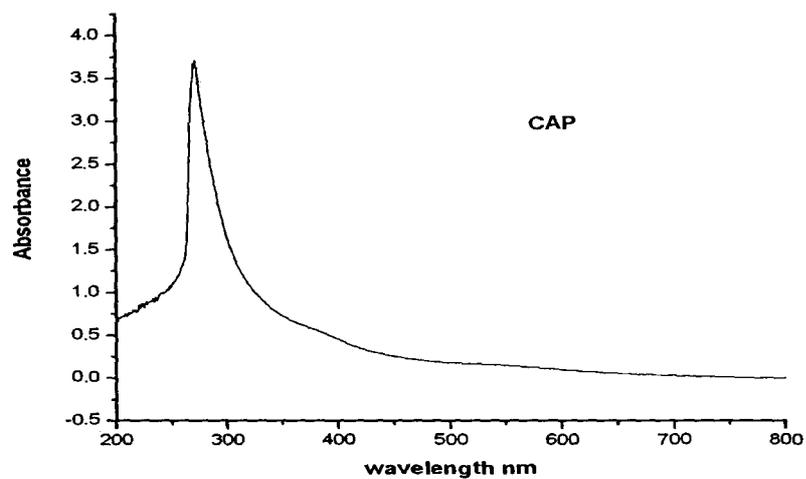


Figure 39: UV-Vis of cobalt L- Proline (CAP)

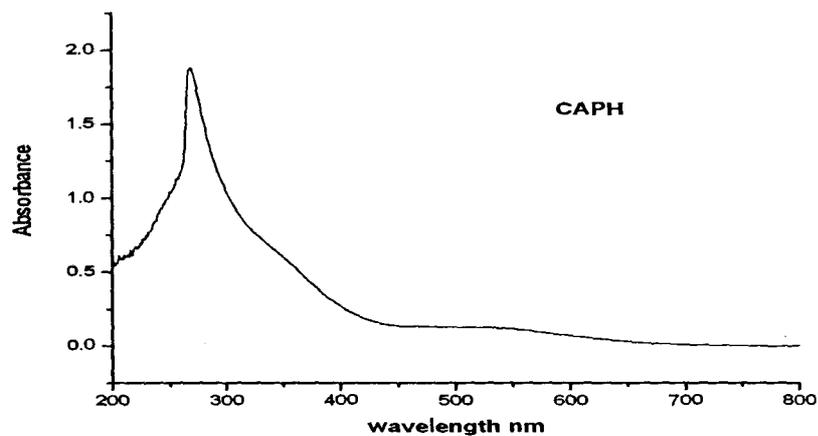


Figure 40: UV-Vis of cobalt L-Proline hydrazinate (CAPH)

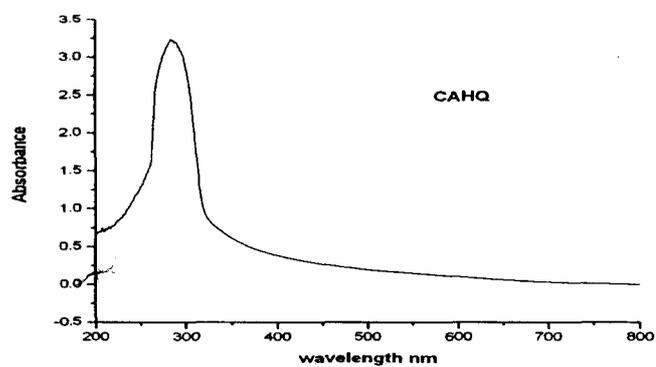


Figure 41: UV-Vis of cobalt hydroquinone (CAHQ)

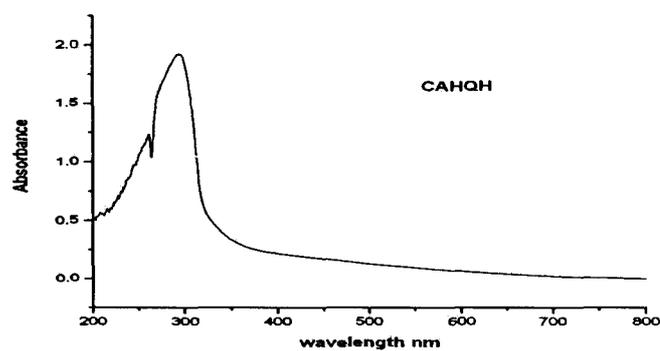


Figure 42: UV-Vis of cobalt hydroquinone hydrazinate (CAHQH)

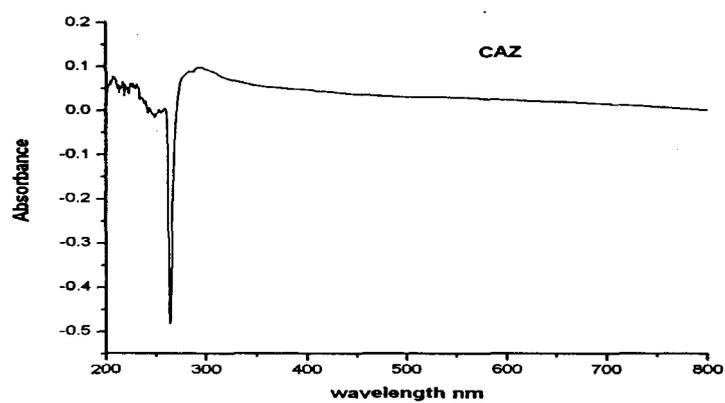


Figure 43 : UV-Vis of cobalt acetate carbohydrazide (CAZ)

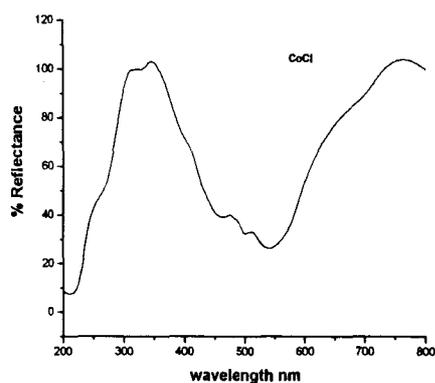
APPENDIX-IV**Ultra violet- Diffuse Reflectance Spectroscopy (UV-DRS) SPECTRA**

Figure 44: UV-DRS of cobalt chloride (CoCl)

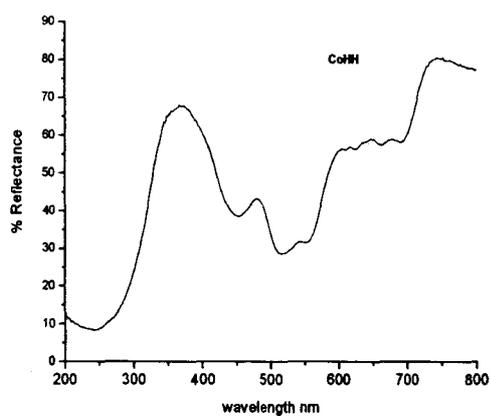


Figure 45: UV-DRS of cobalt chloride hydrate (CH)

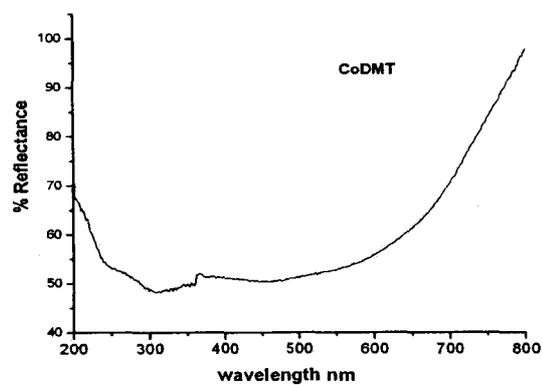


Figure 46: UV-DRS of cobalt chloride diaminotoluene (CDAT)

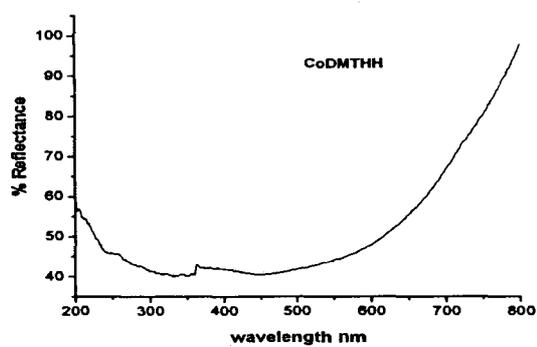


Figure 47: UV-DRS of cobalt chloride diaminotoluene hydrazinate (CDATH)

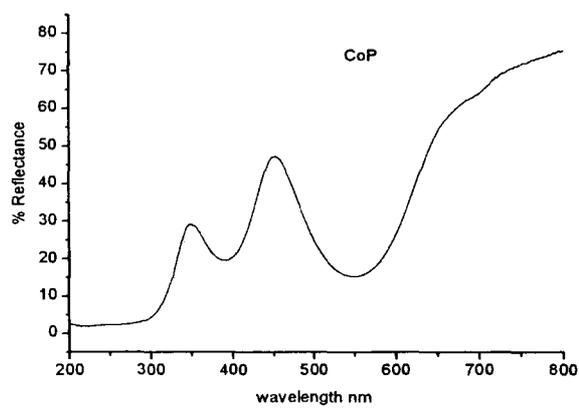


Figure 48: UV-DRS of cobalt L-Proline (CP)

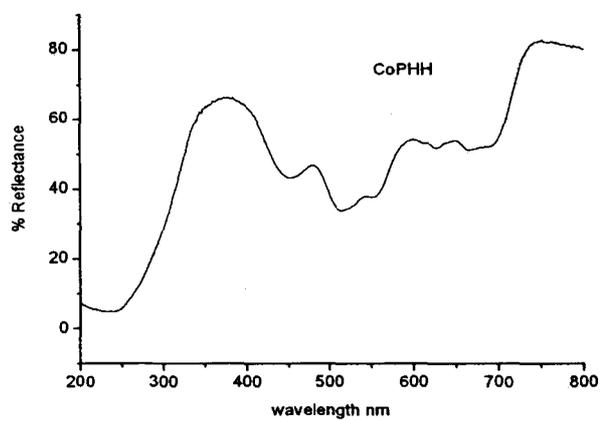


Figure 49: UV-DRS of cobalt L-Proline hydrazinate (CPH)

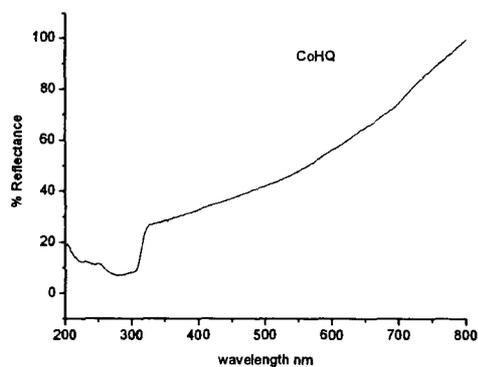


Figure 50: UV-DRS of cobalt hydroquinone (CHQ)

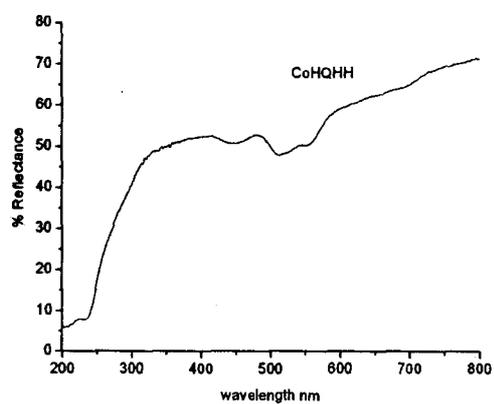


Figure 51: UV-DRS of cobalt hydroquinone hydrazinate (CHQH)

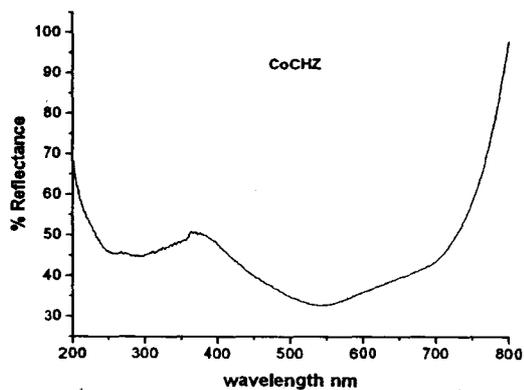


Figure 52: UV-DRS of cobalt chloride carbohydrazide (CZ)

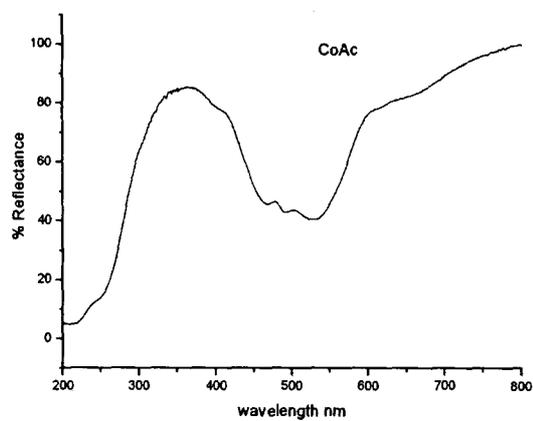


Figure 53: UV-DRS of cobalt acetate (CA)

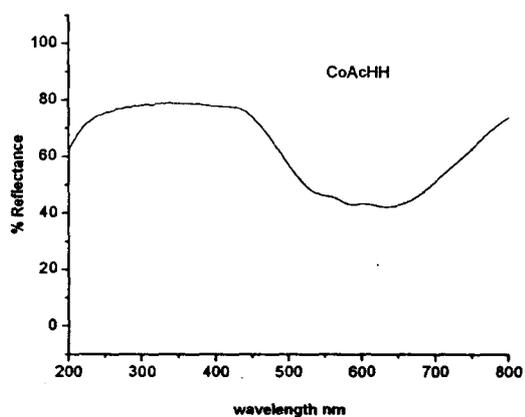


Figure 54: UV-DRS of cobalt acetate hydrazinate (CAH)

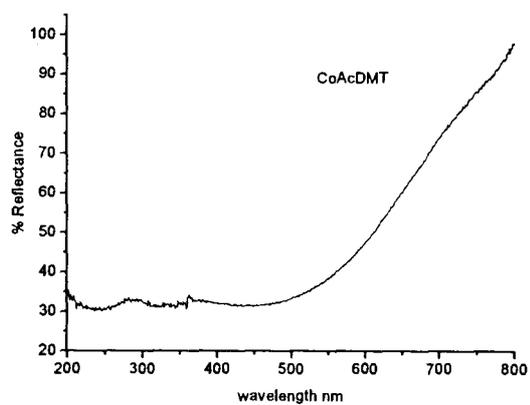


Figure 55: UV-DRS of cobalt acetate diaminotoluene (CADAT)

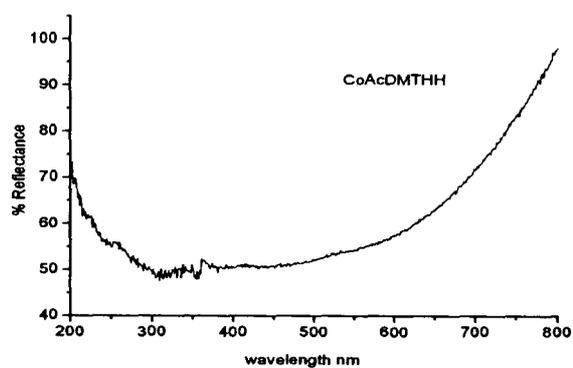


Figure 56: UV-DRS of cobalt acetate diaminotoluene hydrazinate (CADATH)

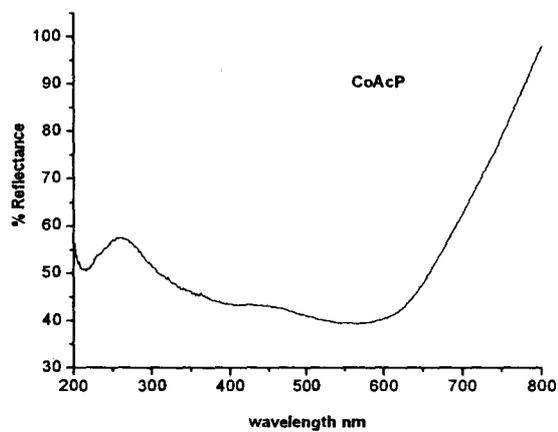


Figure 57: UV-DRS of cobalt L-Proline (CAP)

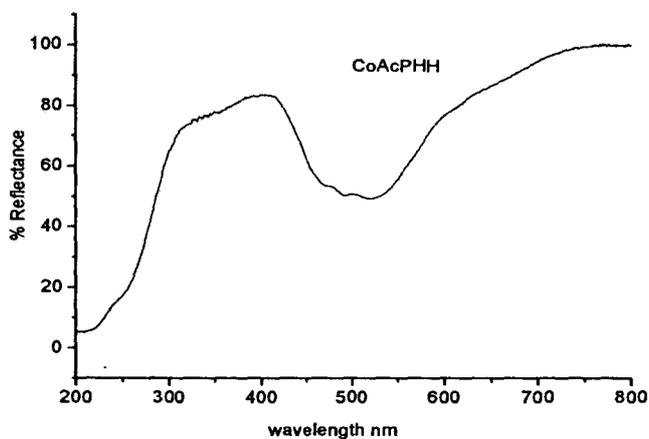


Figure 58: UV-DRS of cobalt L-Proline hydrazinate(CAPH)

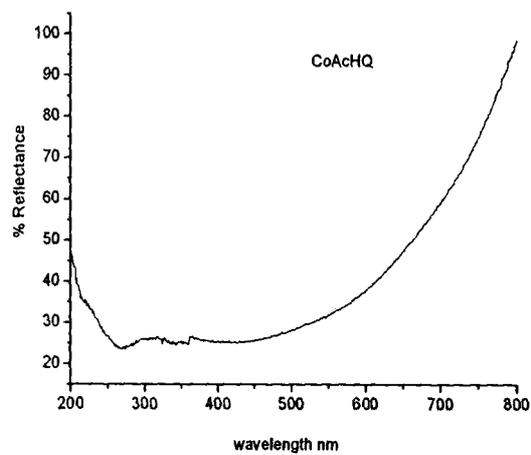


Figure 59: UV-DRS of cobalt hydroquinone (CAHQ)

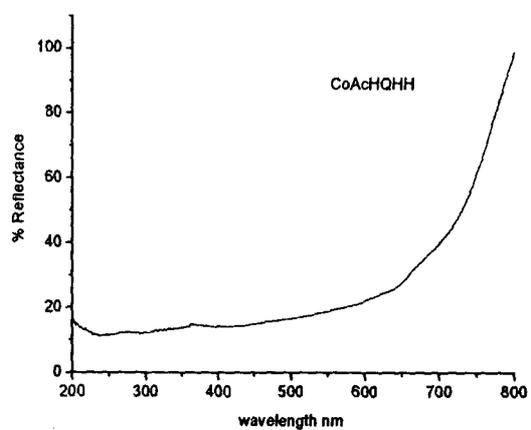


Figure 60: UV-DRS of cobalt hydroquinone hydrazinate (CAHQH)

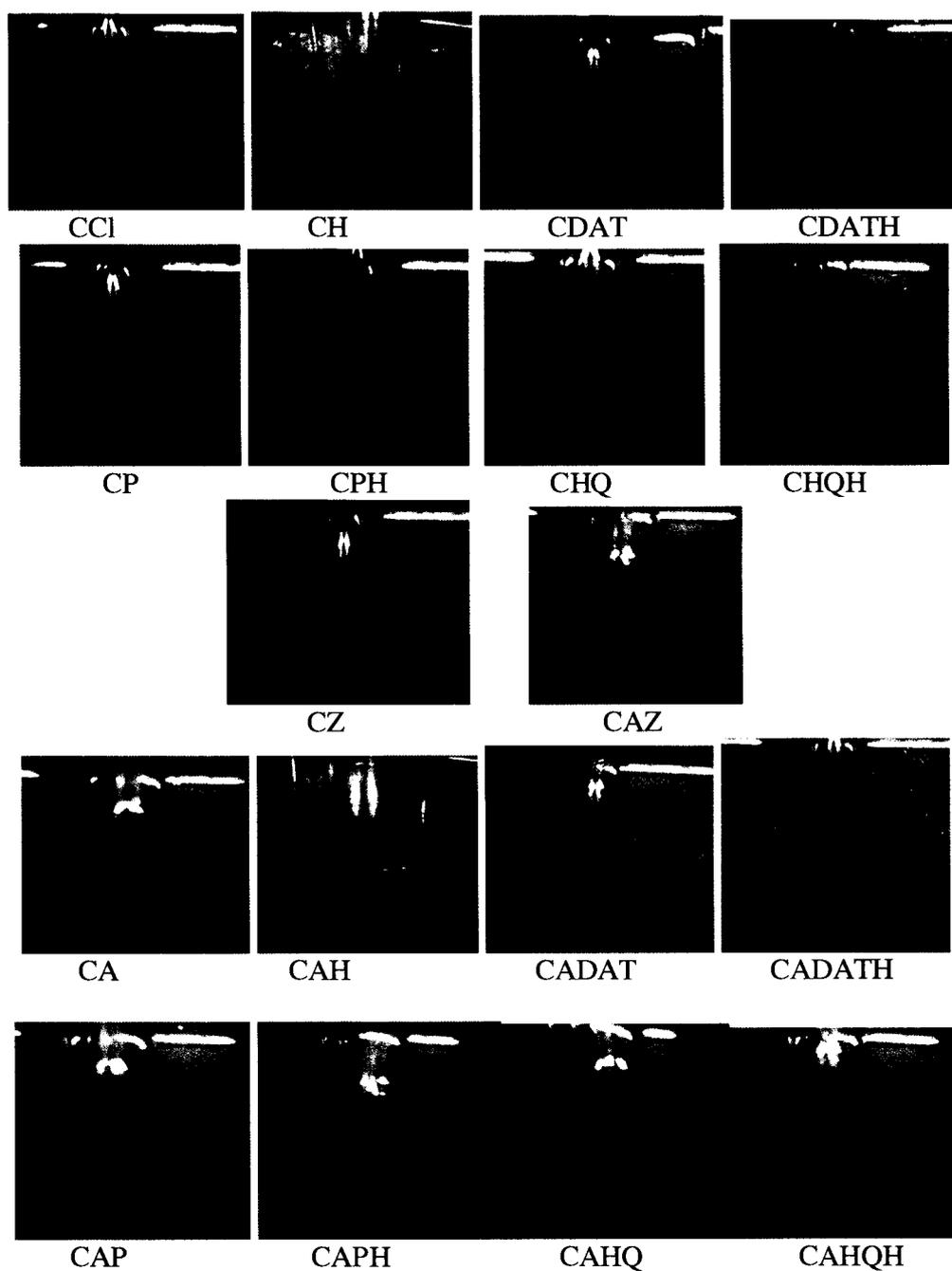


Figure 61: Different colors observed when colored Cobalt complexes were dissolved in DMF for UV-Vis

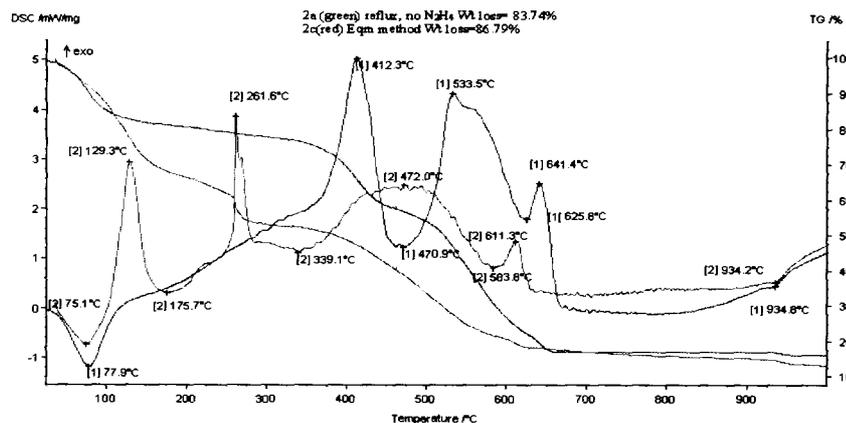
APPENDIX-V**Thermogravimetric (TG) and differential scanning calorimetric(DSC) /
(differential thermal analysis) (DTA) TRACES**

Figure 62: TG/DSC trace of Cobalt chloride diaminotoluene (CDAT) and its hydrazinate (CDATH)

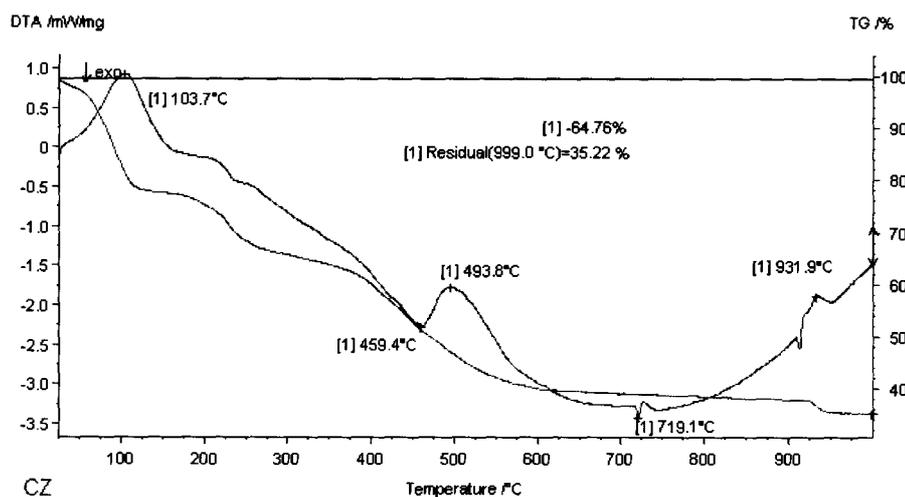


Figure 63: TG/DTA trace of Cobalt chloride carbohydrazide (CZ)

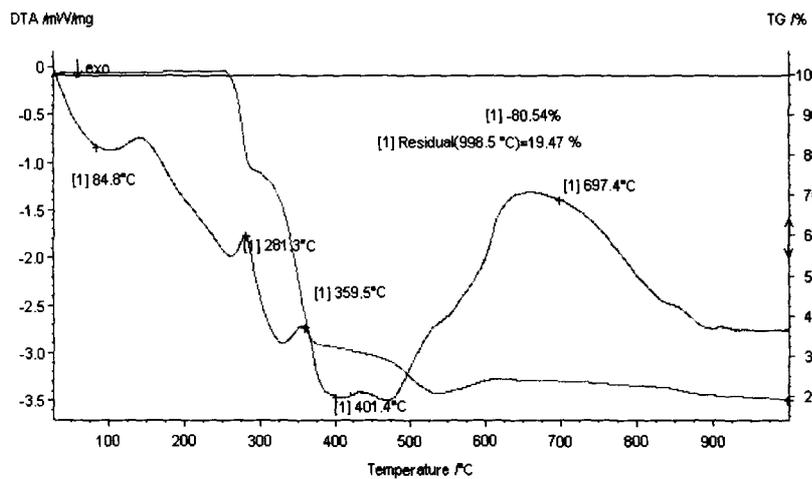
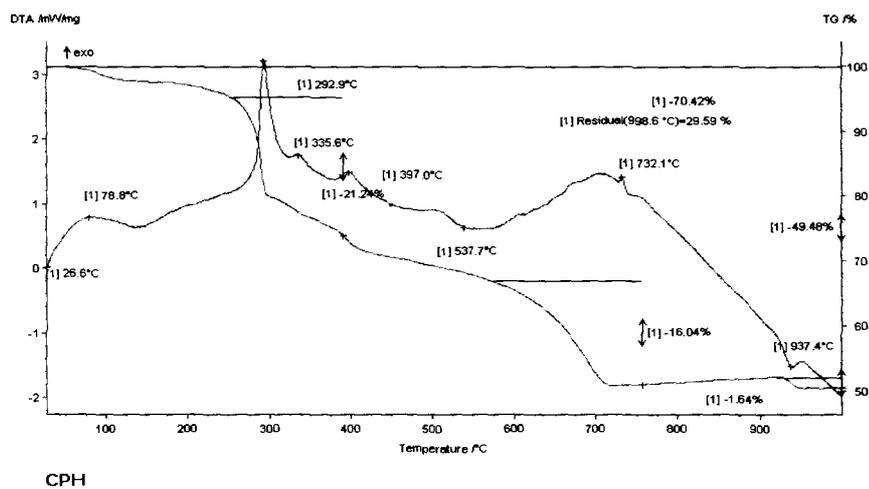


Figure 64: TG/DTA trace of Cobalt L-Proline (CP)



CPH

Figure 65: TG/DTA trace of Cobalt L-Proline hydrazinate (CPH)

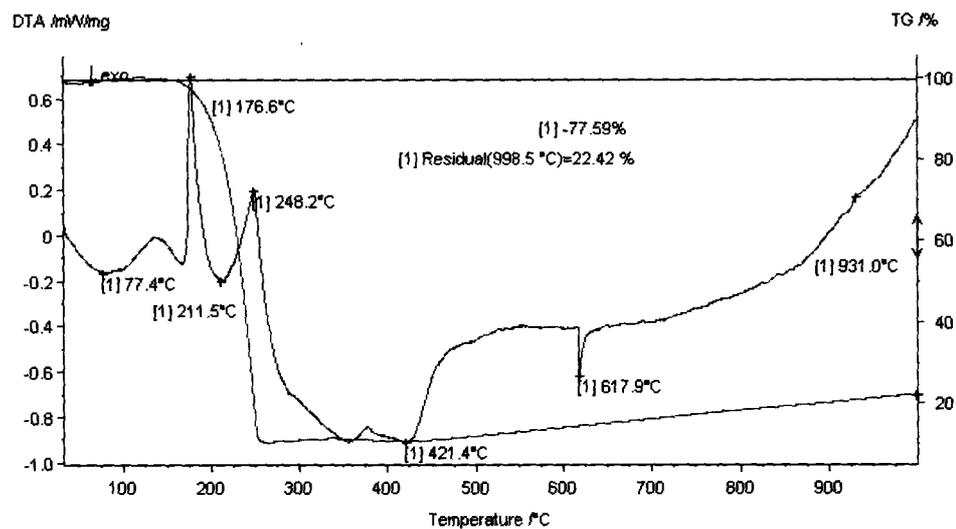


Figure 66: TG/DTA trace of Cobalt Hydroquinone (CHQ)

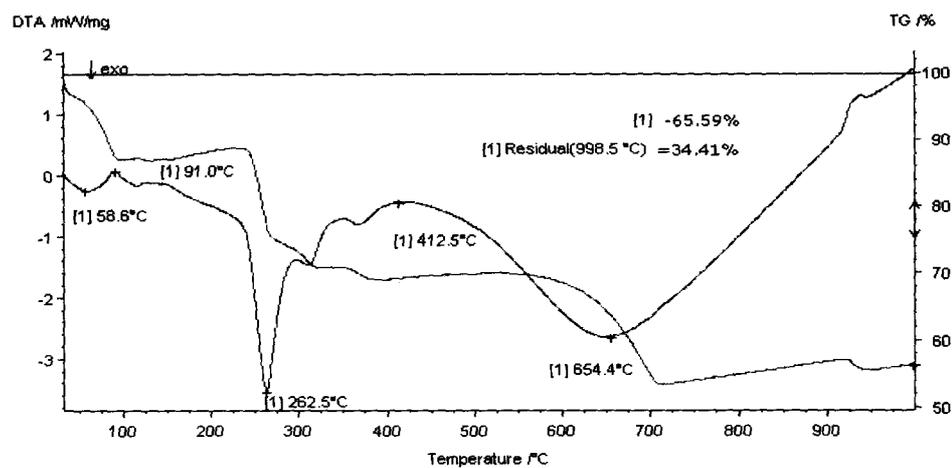


Figure 67: TG/DTA trace of Cobalt Hydroquinone hydrazinate (CHQH)

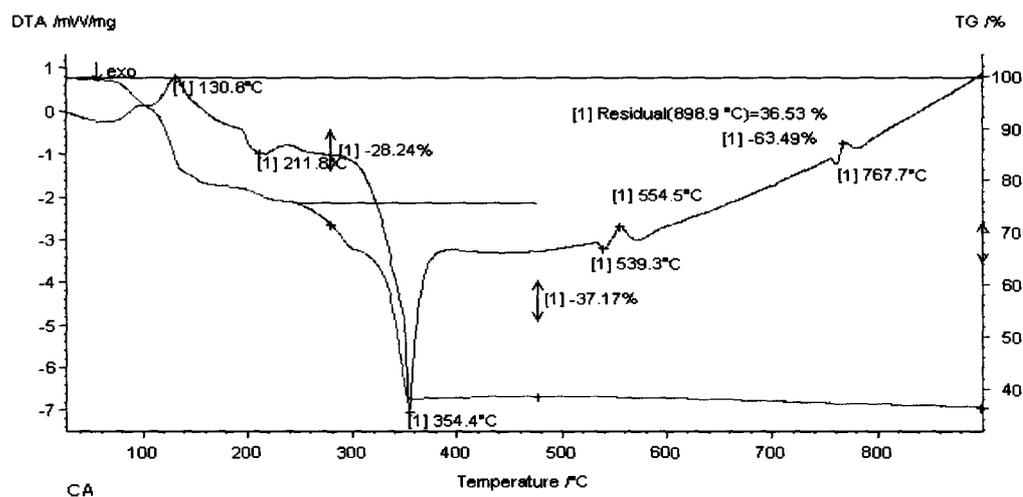


Figure 68: TG/DTA trace of Cobalt acetate (CA)

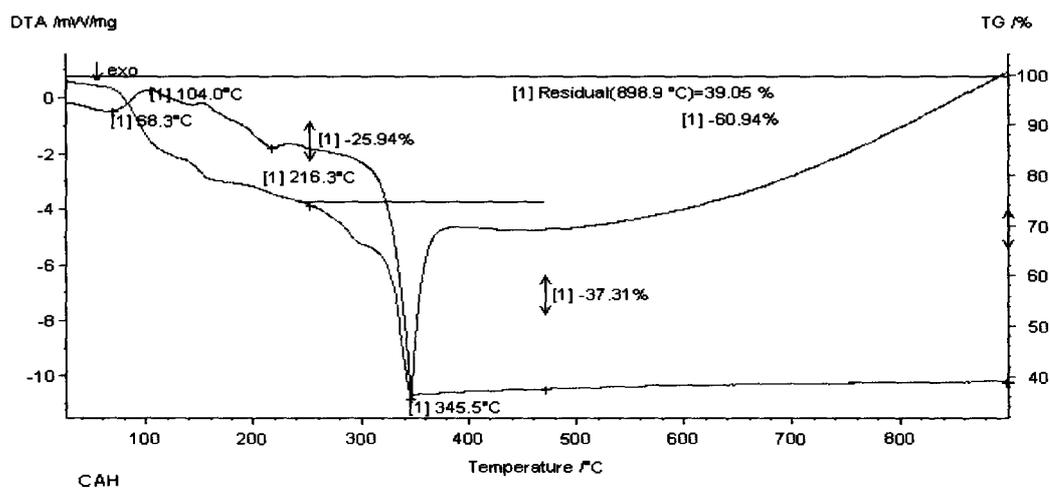


Figure 69: TG/DTA trace of Cobalt acetate hydrazinate (CAH)

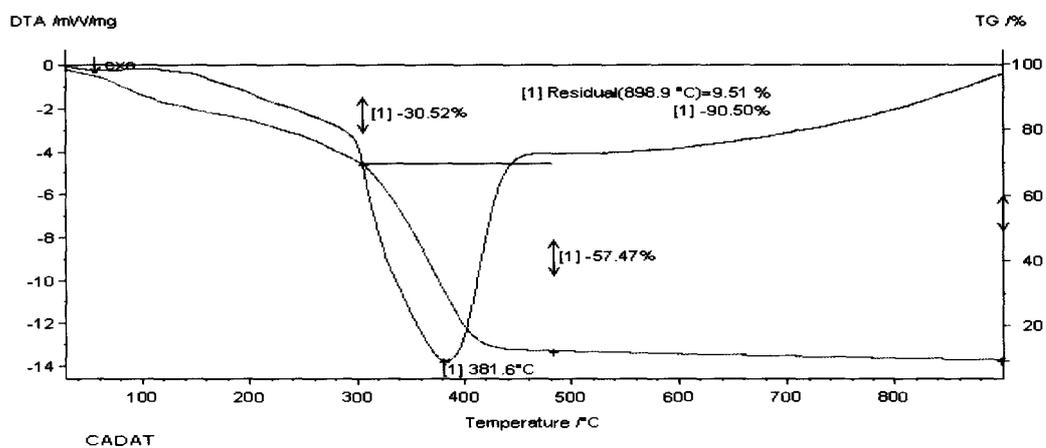


Figure 70: TG/DTA trace of Cobalt acetate diaminotoluene (CADAT)

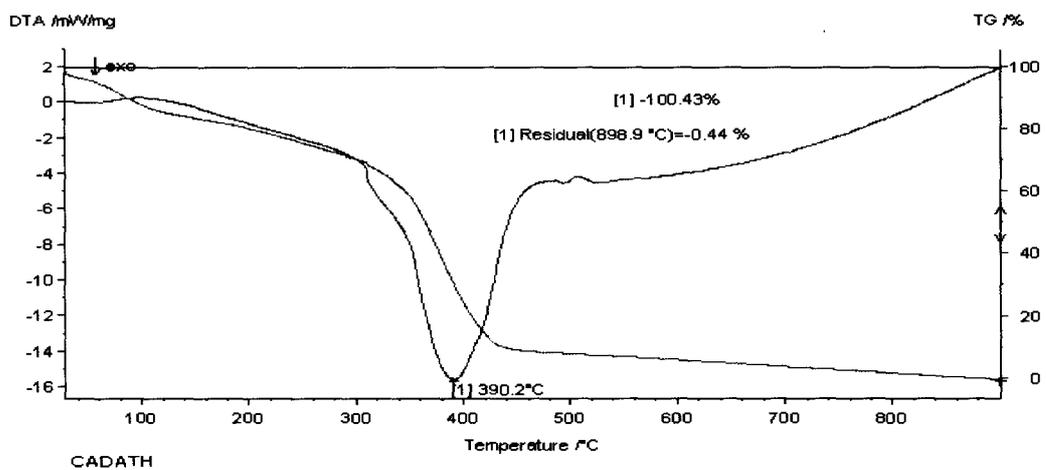


Figure 71: TG/DTA trace of Cobalt acetate diaminotoluene hydrazinate (CADATH)

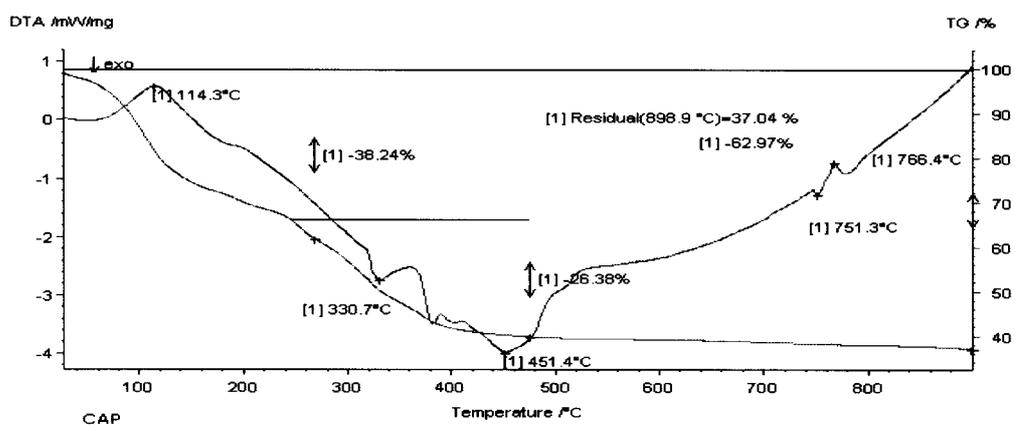


Figure 72: TG/DTA trace of Cobalt L-Proline (CAP)

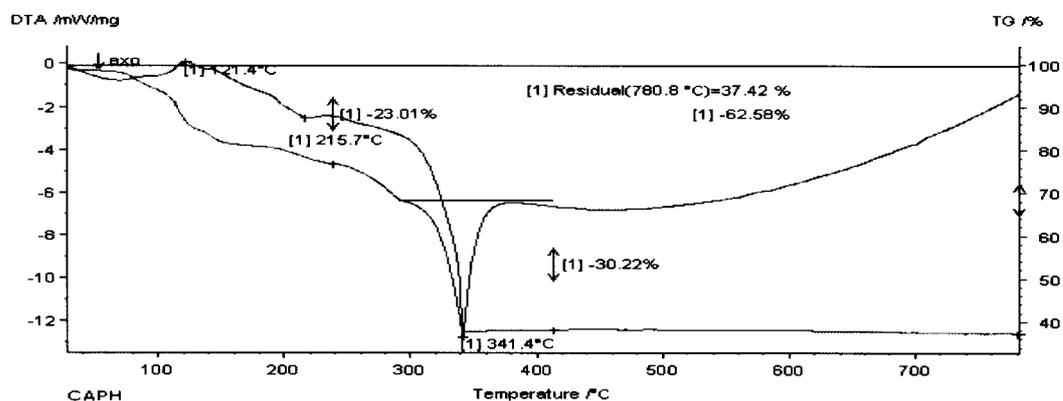


Figure 73: TG/DTA trace of Cobalt L-Proline hydrazinate (CAPH)

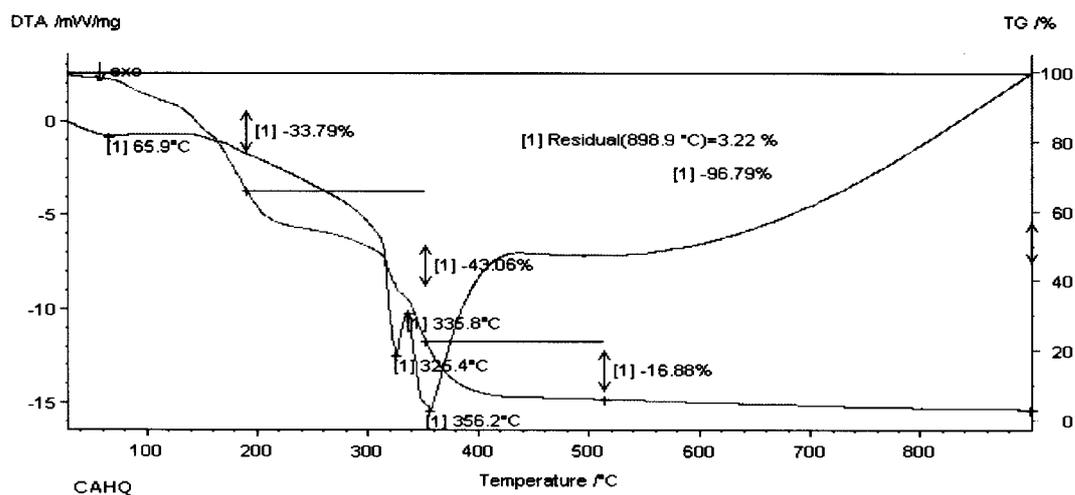


Figure 74: TG/DTA trace of Cobalt Hydroquinone (CAHQ)

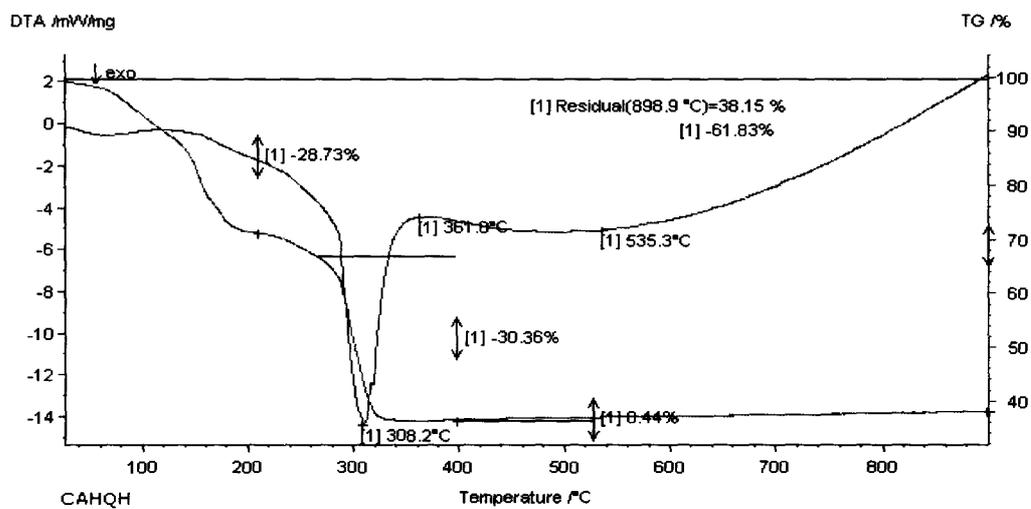


Figure 75: TG/DTA trace of Cobalt Hydroquinone Hydrazinate(CAHQH)

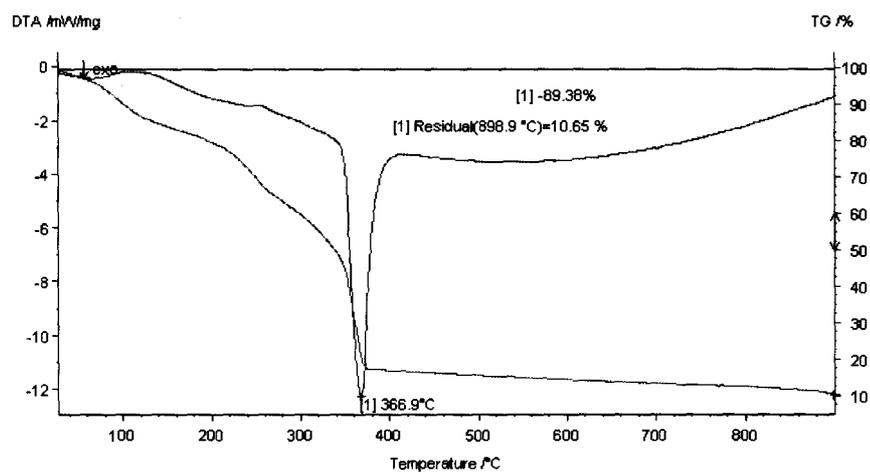


Figure 76: TG/DTA trace of Cobalt acetate Carbohydrazide (CAZ)

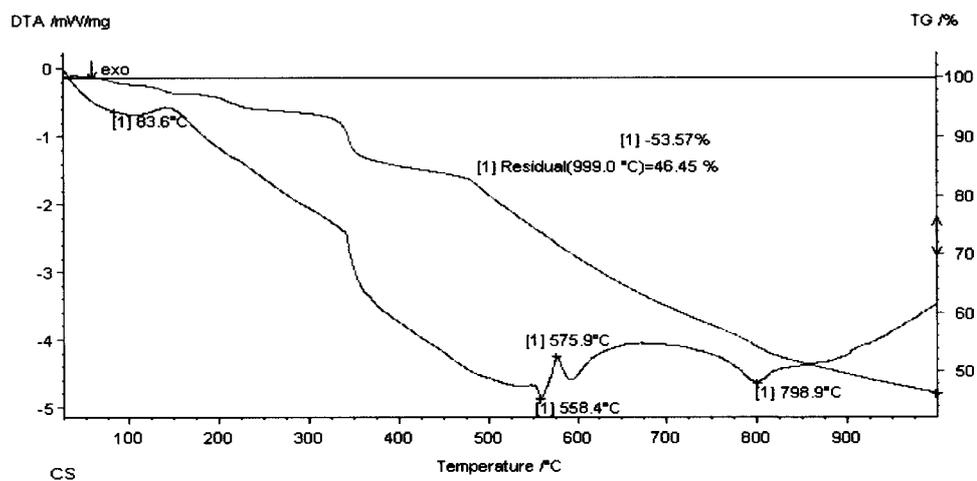


Figure 77: TG/DTA trace of Cobalt Salen (CS)

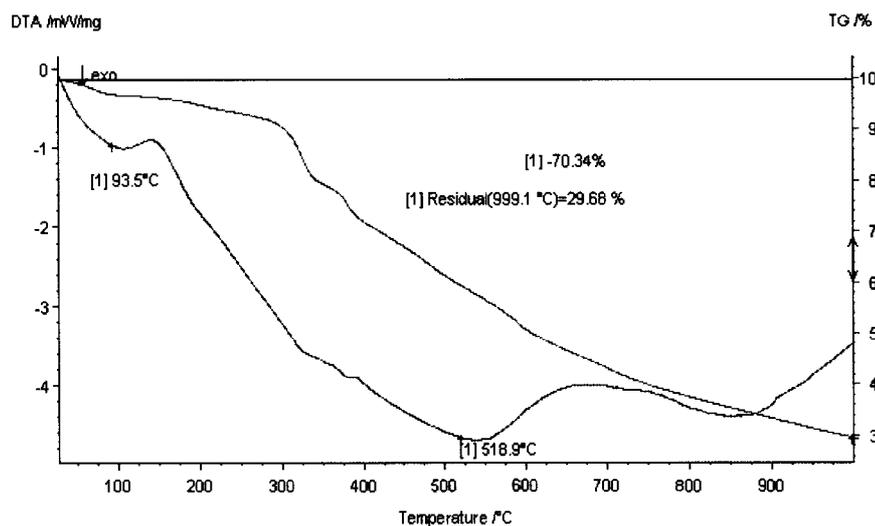


Figure 78: TG/DTA trace of Cobalt Salen hydrazinate (CSH)

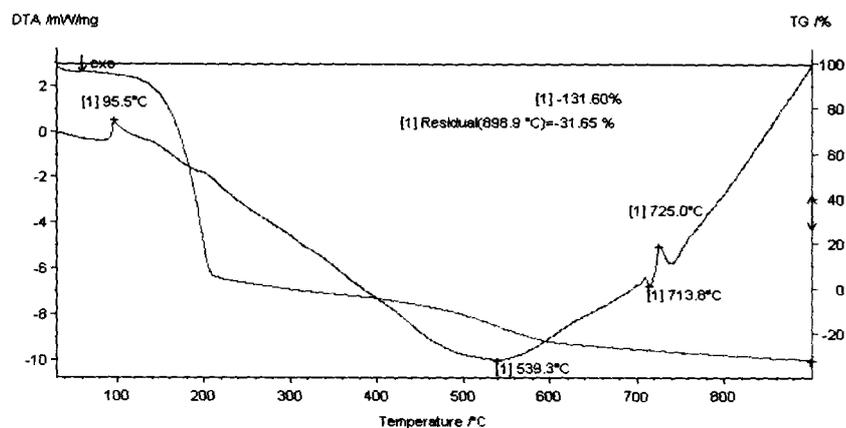


Figure 79: TG/DTA trace of diamino toluene hydrazinate (DATH)

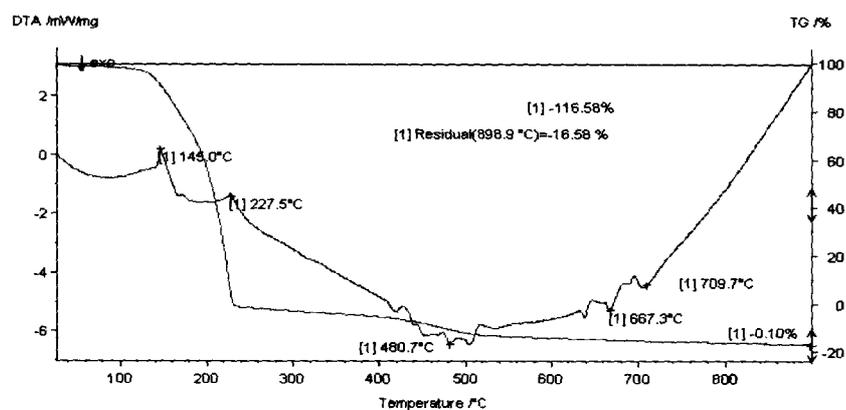


Figure 80: TG/DTA trace of Hydroquinone hydrazinate (HQH)

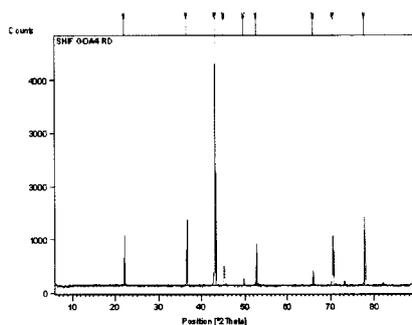
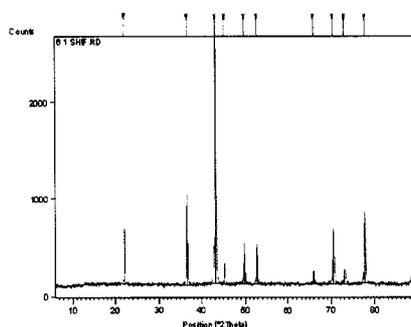
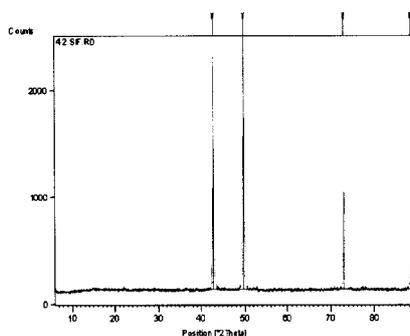
APPENDIX-VI**X-Ray Diffraction (XRD) SCANS OF OXIDES OF COBALT**700°C: Co_3O_4 900°C: Co_3O_4 1000°C: CoO

Figure 81: XRD Powder Pattern at 700 °C, 900 °C and 1000 °C

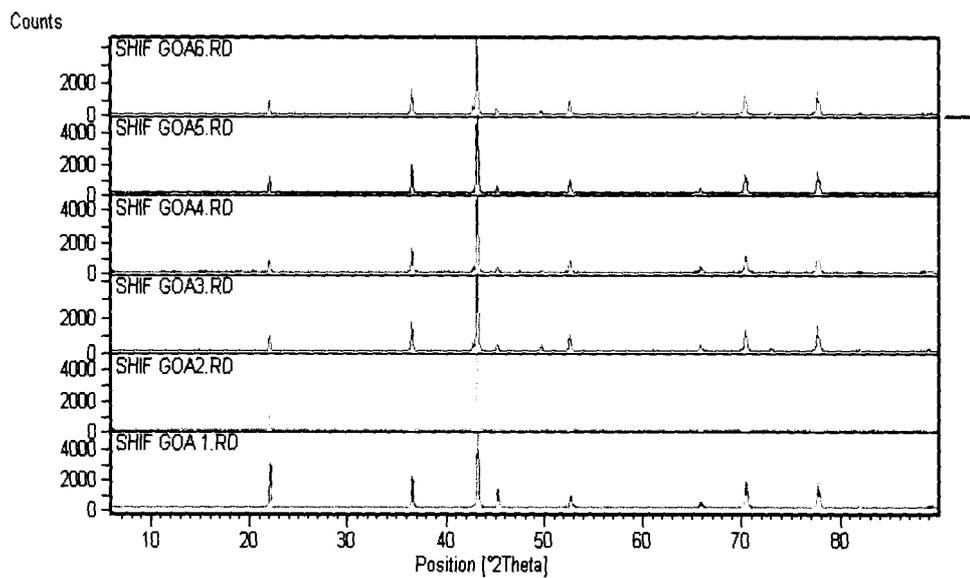


Figure 82: XRD Powder Pattern at 700 °C.

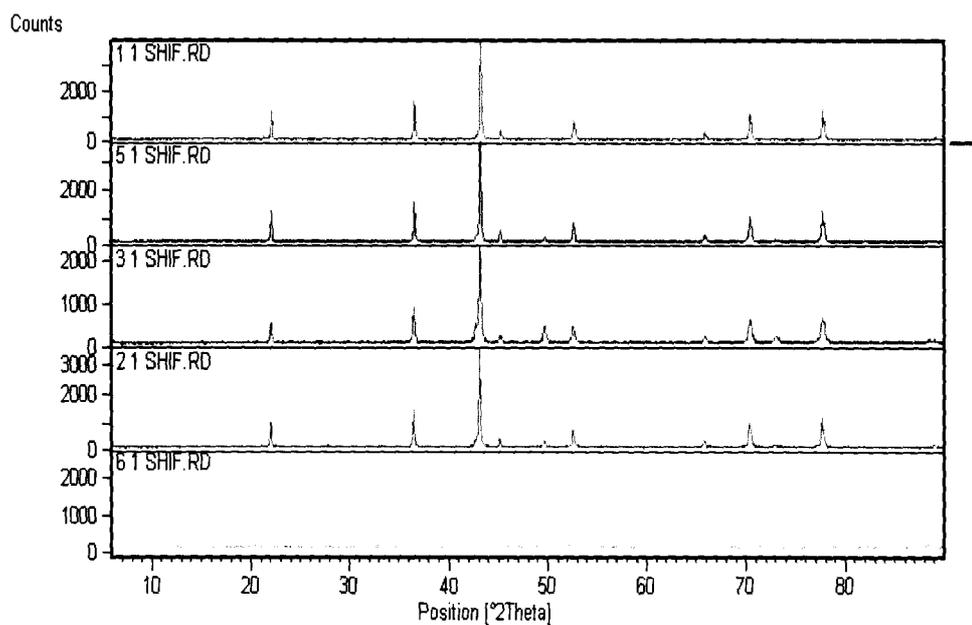


Figure 83: XRD Powder Pattern at 900 °C.

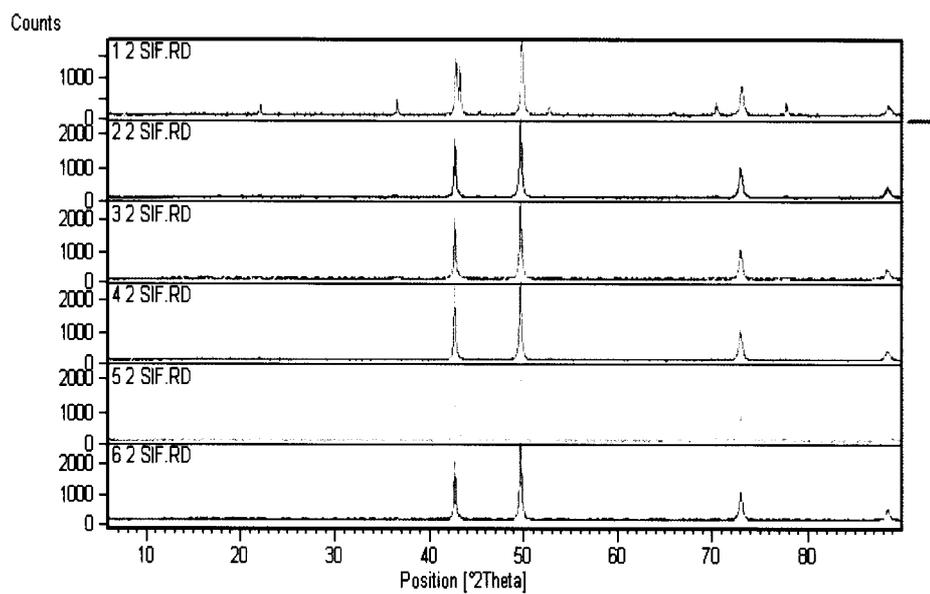


Figure 84: XRD Powder Pattern at 1000°C.

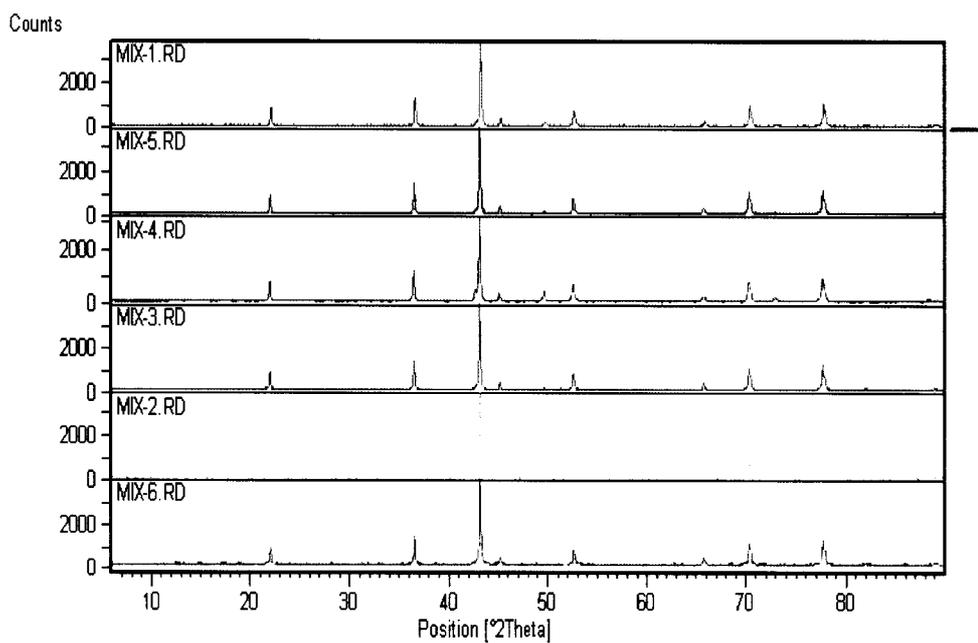


Figure 85: XRD Powder Pattern at 1200°C.

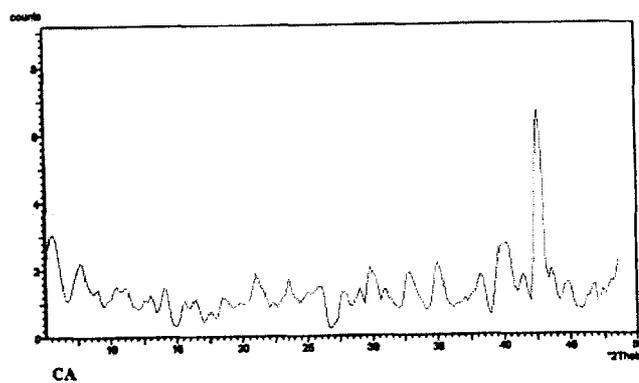
APPENDIX-VII**X-Ray Diffraction (XRD) SCANS OF PRECURSORS OF COBALT**

Figure 86: XRD scan of Cobalt acetate (CA)

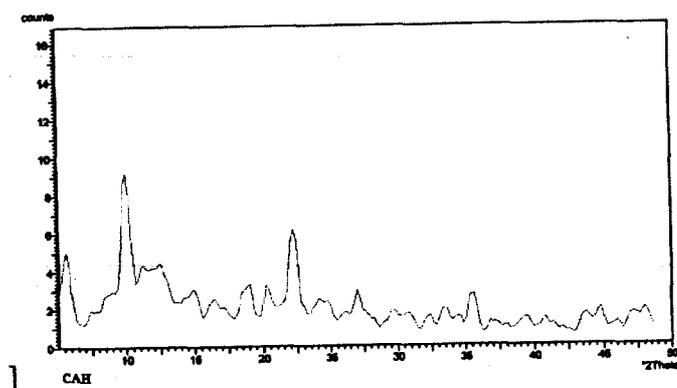


Figure 87: XRD scan of Cobalt acetate hydrazinate (CAH)

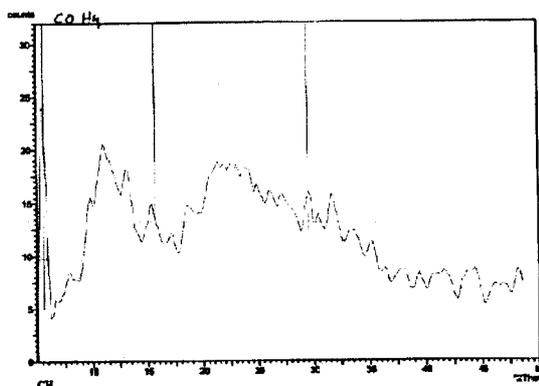


Figure 88: XRD scan of Cobalt chloride hydrazinate (CH)

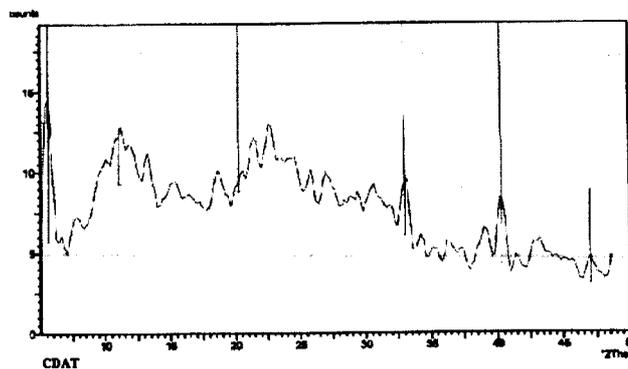


Figure 89: XRD scan of Cobalt chloride diamino toluene (CDAT)

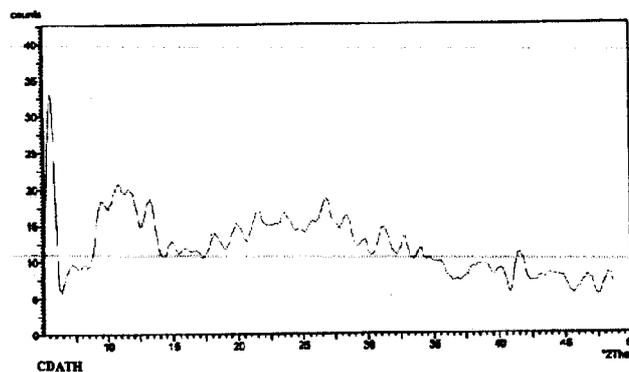


Figure 90: XRD scan of Cobalt chloride diamino toluene hydrazinate (CDATH)

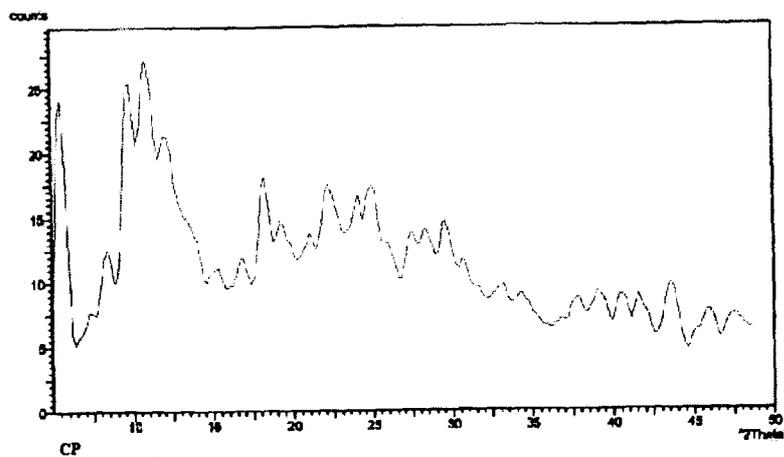


Figure 91: XRD scan of Cobalt L-Proline (CP)

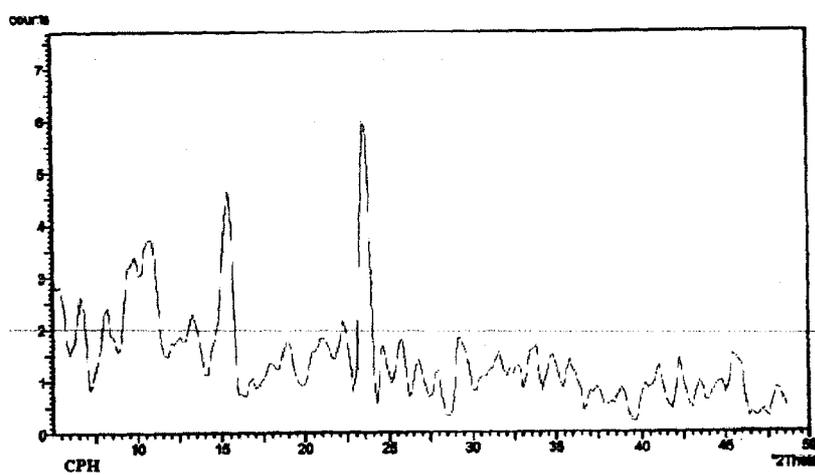


Figure 92: XRD scan of Cobalt L-Proline hydrazinate (CPH)

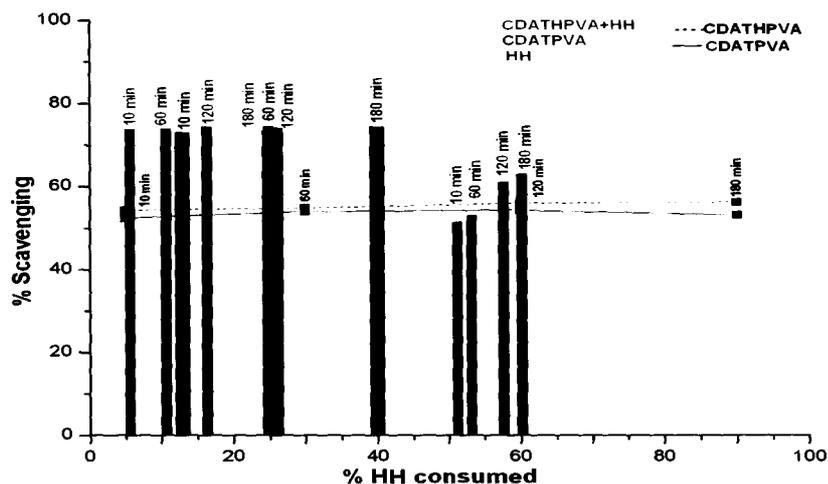
APPENDIX-VIII**PLOTS OF % OXYGEN SCAVENGING**

Figure 93: Relation between hydrazine hydrate consumption and oxygen scavenging action by polymer based cobalt complexes CDATH-PVA/CDATH-PVA and HH as a function of time

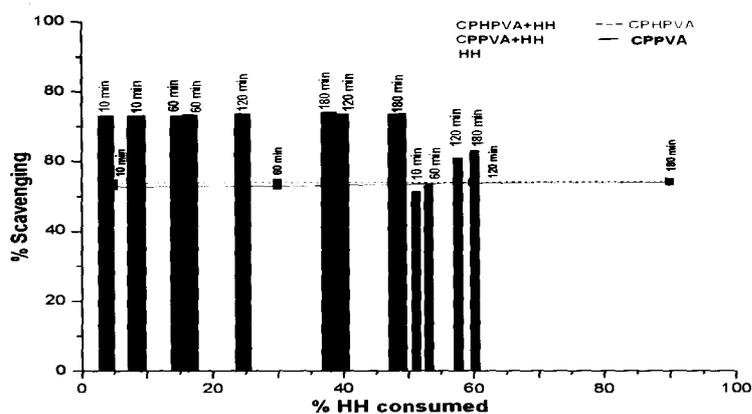


Figure 94: Relation between hydrazine hydrate consumption and oxygen scavenging action by polymer based cobalt complexes CP-PVA/CPH-PVA and HH as a function of time

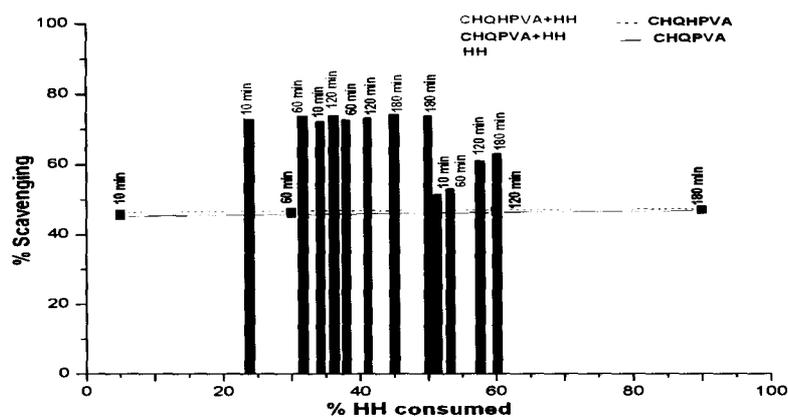


Figure 95: Relation between hydrazine hydrate consumption and oxygen scavenging action by polymer based cobalt complexes CHQ-PVA/CHQH-PVA and HH as a function of time

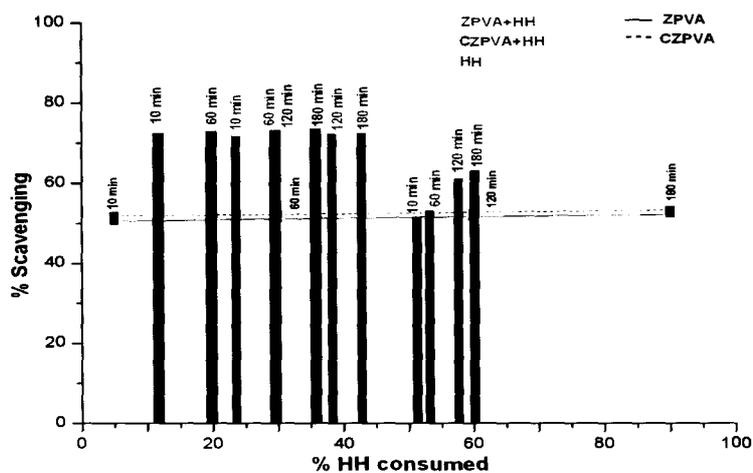


Figure 96: Relation between hydrazine hydrate consumption and oxygen scavenging action by polymer based cobalt complexes CZ-PVA/Z-PVA and HH as a function of time

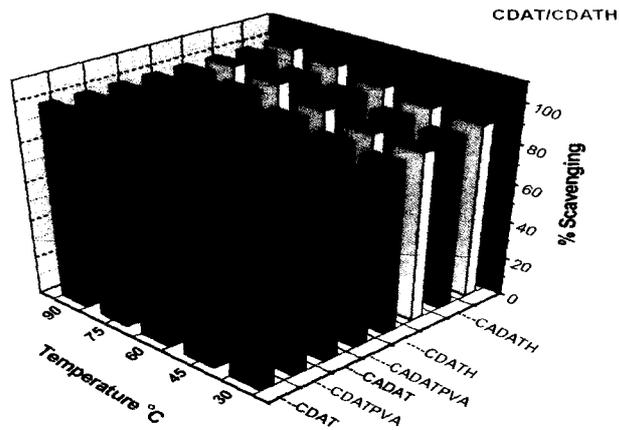


Figure 97: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CDAT/CADAT/CDATH/CADATH (3-D view)

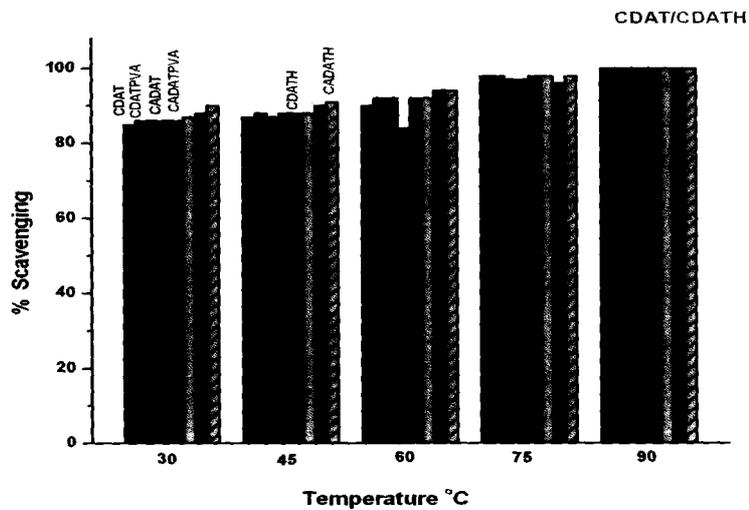


Figure 98: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CDAT/CADAT/CDATH/CADATH (2-D view)

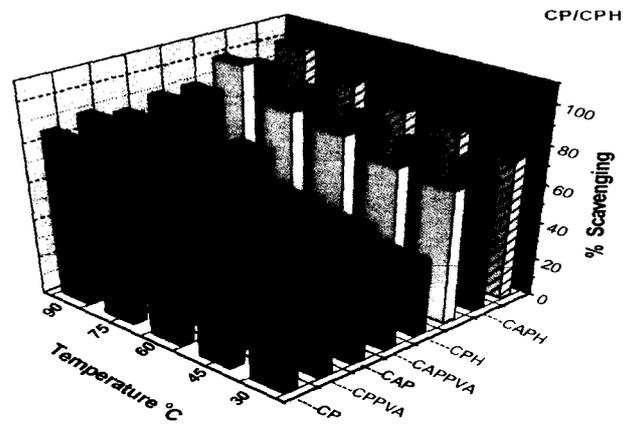


Figure 99: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CP/CAP/CPH/CAPH (3-D view)

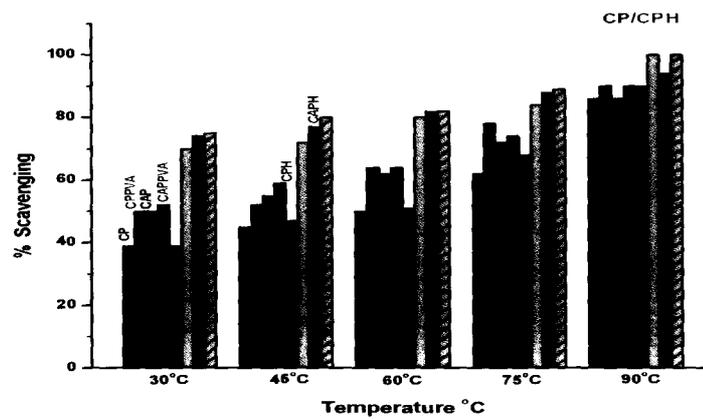


Figure 100: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CP/CAP/CPH/CAPH (2-D view)

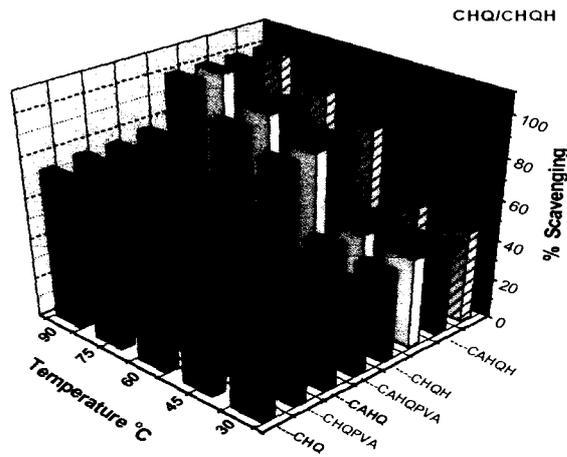


Figure 101: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CHQ/CAHQ/CHQH/CAHQH (3-D view)

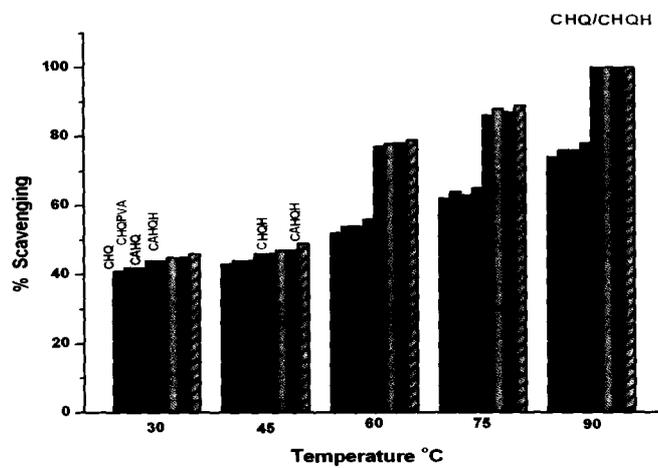


Figure 102: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CHQ/CAHQ/CHQH/CAHQH (2-D view)

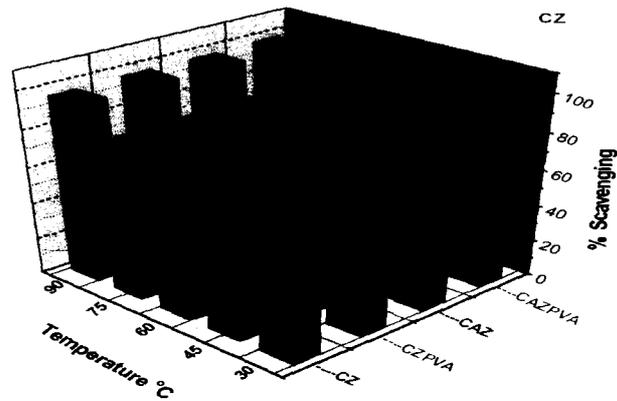


Figure 103: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CZ/CAZ (3-D view)

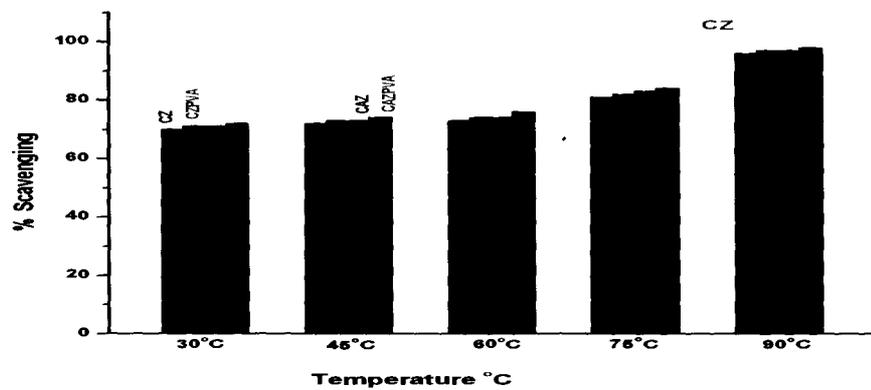


Figure 104: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for CZ/CAZ/ (2-D view)

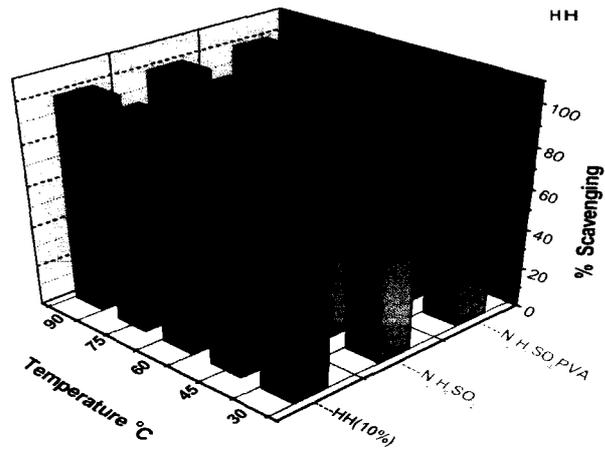


Figure 105: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for HH (3-D view)

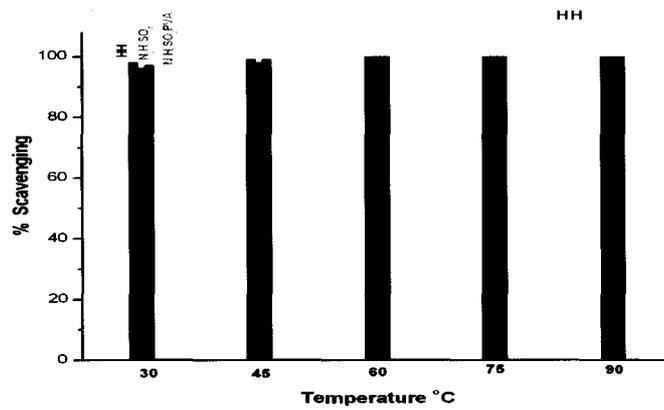


Figure 106: % Oxygen scavenging vs. Temperature of the Boiler feed water of 4-5 ppm dissolved oxygen for HH (2-D view)

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