SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III) AND CHROMIUM(VI) USING 2-[E)-[{3-[(2-HYDROXYBENZYLIDENE) AMINO]PHENYL}IMINO)METHYL]PHENOL

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DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY,

FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF NIGERIA, NSUKKA

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TITLE PAGE

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A PROJECT SUBMITTED TO UNIVERSITY OF NIGERIA, NSUKKA FOR THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY,

FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF NIGERIA, NSUKKA

DECEMBER, 2014

APPROVAL PAGE

This is to certify that the project entitled: Spectrophotometric Determination of Chromium(III) and Chromium(VI) Using 2-[(E)-[{3-[(2-Hydroxybenzylidene)amino]phenyl}imino)methyl] phenol carried out by IFEMELUMMA, OLUCHUKWU IFEOMA with registration number, PG/M.Sc/10/57760, met the requirements for award of Masters Degree in Industrial Chemistry, University of Nigeria, Nsukka and is approved for its contribution to scientific, literature and industrial presentation.

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Head of Department

DECLARATION

I hereby declare that this project contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources has been duly acknowledged by means of references.

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Ifemelumma, Oluchukwu Ifeoma, B.Sc (ESUTECH) Date

PG/M.Sc/2010/57760

Student

DEDICATION

This work is dedicated to the Almighty God for the opportunity and inspiration to carry out this work.

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My profound gratitude goes to God Almighty for His love and mercies that endures forever. I wish to appreciate my supervisor, Prof Pius Oziri Ukoha for taking pains to read through the work and for always being there for me.

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ABSTRACT

The Schiff base ligand, 2-[(E)-[{3--[(2-hydroxybenzylidene)amino]phenyl}imino)methyl]phenol was synthesized by condensing 1,3-diaminobenzene and 2-hydroxybenzaldehyde in absolute ethanol. Its Cr(III) and Cr(VI) complexes were equally synthesized. The ligand was characterized via UV, IR and NMR spectroscopy, whereas the complexes were characterized based on UV and IR spectroscopy and conductivity values. Stoichiometric studies indicated 1:1 metal to ligand ratio for both complexes. Cr(III) complex absorbed at 1042.56 cm^{-1} g(C-O), 532.37 cm^{-1} g(Cr-N) and 607.60 cm^{-1} g(Cr-O) while the Cr(VI) complex absorbed at 1182 cm^{-1} g(C-O), 749.37 cm^{-1} g(Cr-O) and 457 cm^{-1} for g(Cr-N). Based on UV, IR and NMR studies, the ligand coordinated to the metals using the nitrogen and oxygen atoms. Spectrophotometric determination of the metals using the ligand was done at 368 nm for Cr(III) and 465 nm for Cr(VI).Optimum conditions for complexation and stability were studied and it was shown that optimum pH for Cr(III) and Cr(VI) were 13.0 and 2.0 respectively. Very few ions such as Co^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+} and Zn^{2+} interfered with the determination. Beerôs law was obeyed between 0.02 to 0.14ppm for both metals. The method was successfully applied in the analysis of steel.

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CHAPTER ONE

INTRODUCTION

1.1 SPECTROPHOTOMETRY

Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength[1]. It is more specific than the general term electromagnetic spectroscopy in that spectrophotometry deals with visible light, near-ultraviolet, and near-infrared, but does not cover time-resolved spectroscopic techniques. Spectrophotometry is a very fast and convenient method of qualitative analysis, due to the fact that absorption occurs in less than one second and can be measured very rapidly. Molecular absorption is valuable for identifying functional groups in a molecule and for the quantitative determination of compounds containing absorbing groups[2,3]. A spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass or gases. However, they can also be designed to measure the diffusivity of any of the listed light ranges that usually cover around 200 ï 250 nm using different controls and calibrations[1] .

The most common spectrophotometers are used in the UV and visible regions of the spectrum and some of these instruments also operate into the near-infrared region as well. Visible region (400 ï 700 nm) spectrophotometry is used extensively in colorimetry science. Ink manufacturers, printing companies, textile, vendors and many more, need the data provided through colorimetry. They take readings in the region of every 5 ï 20 nanometers along the visible region and produce a spectral reflectance curve or a data stream for alternative presentations.

Spectrophotometeric method is undoubtedly the most accurate method for determining, among other things, the concentration of substances in solution, but the instruments are of necessity more expensive. A spectrophotometer may be regarded as a refined filter photoelectric photometer which permits the use of continuously variable and more nearly monochromatic bands of light. The essential parts of a spectrophotometer are (1) a source of radiant energy (2) a monochromator i.e. a device for isolating monochromatic light or, more accurately, narrow bands of radiant energy from

the light source (3) glass or silica cells for the solvent and for the solution under test and (4) a device to receive or measure the beams of radiant energy passing through the solvent[4].

Infrared (IR)[5] light is electromagnetic radiation with longer wavelengths than those of visible light, extending from the nominal red edge of the visible spectrum at 700 nm to 1mm. Infrared spectroscopy is very useful for obtaining qualitative information about molecules. For absorption in infrared region to occur, there must be a change in the dipole moment (polarity) of the molecule. Absorbing groups in the infrared region absorb within a certain wavelength region, and the exact wavelength will be influenced by neighbouring groups. Their absorption peaks are much sharper than the ultraviolet or visible regions and easier to identify. The most important use of infrared spectroscopy is in identification and structure analysis; it is useful for qualitative analysis of complex mixtures of similar compounds because some absorption peaks for each compound will occur at a definite and selective wavelength, with intensities proportional to the concentration of absorbing species.

Nuclear magnetic resonance spectroscopy[5] is a research technique that exploits the magnetic properties of certain atomic nuclei. It measures the absorption of electromagnetic radiation in the radiofrequency region of roughly 4 MHz to 750 MHz, nuclei of atoms rather than outer electrons are involved in the absorption process. It determines the physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of NMR and can provide detailed information about the structure, dynamics, reaction state and chemical environment of molecules. NMR is used to investigate the environment of molecules. NMR is used to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin.

1.1.1 Beer- Lambert's Law

In optics, the Beer-Lambert law, also known as Beerôs law or the Lambert- Beerôs law (named after August Beer, Johann Heinrich Lambert and Pierre Bouguer) relates the absorption of light to the properties of the material through which the light is travelling[6].

The law states that there is a logarithmic dependence between the transmission (transmissivity), T, of light through a substance and the product of the absorption coefficient of the substance, the light travels through the material (the path length), l. The absorption coefficient can, in turn, be written as a product of either a molar absorptivity (extinction coefficient) of the absorber, £ and the molar concentration, c of absorbing species in the material, or an absorption cross section, σ and the (number) density Nô of absorbers[6].

For liquids: $\frac{I}{I_0} = 10^{-\varepsilon c l}$

Whereas in biology and physics, they are normally written

$\frac{I}{I_0} = e^{-\sigma n l} = e^{-\alpha l}$

Where I_O and I are the intensities (power per unit area) of the incident light and the transmitted light respectively. Ŭ is cross section of light absorption by a single particle and n is the density of absorbing particles. The transmission (transmissivity) is expressed in terms of an absorbance which for liquids, is defined as[6]

$A = -\log_{10}\left(\frac{I}{I_0}\right)$

Whereas, for gases, it is usually defined as

$A_e = -\ln\left(\frac{I}{I_0}\right)$

This implies that absorbance becomes linear with the concentration according to[6]

$A = \varepsilon c l = \alpha l$

Historically, the Lambert law states that absorption is proportional to the light path length, whereas the Beer law states that absorption is proportional to the concentration of absorbing species in the material[6].

The modern derivation of the Beer-Lambert law combines the two laws and correlates the absorbance to both, the concentration as well as the thickness (path length) of the sample[6]

$\frac{I_0}{I} = e^{\varepsilon c l} = e^{\alpha l}$

This implies that

$$A = -\ln\frac{I_t}{I_0} = \varepsilon cl = kcl$$

And $A = -\log_{10}\frac{I_t}{I_0} = \frac{\varepsilon}{2.303}cl = \varepsilon cl = kcl$

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors.

1.2 Schiff Base Ligands

Schiff base (imine or azomethine)[7], named after Hugo Schiff [8], contains a carbon-nitrogen double bond,C=N, with the nitrogen[9] connected to an aryl or alkyl but not hydrogen[10]. Schiff bases are of general formula $R^1R^2C=NR^3$, where R is an organic side chain. R^3 is a phenyl or alkyl group that makes the Schiff bases a stable imine. Some restrict the term to the secondary aldimines (azomethines where the carbon is connected to a hydrogen atom, thus with the general formula $RHC=NR^1$ [11]

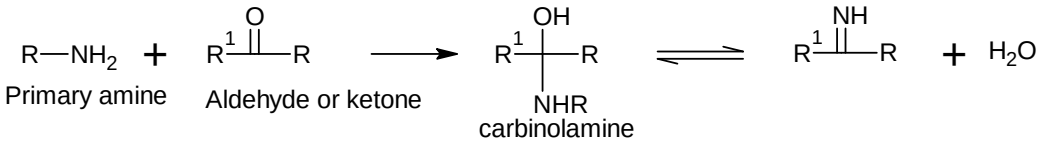
Schiff base compounds were reported for the first time by Hugo Schiff in 1864[8]. These bases are very efficient as ligands. Many Schiff bases have a second functional group, generally an OH, near the imine function. This proximity of the functional group permits the formation of five or six member chelate rings when coordinated with metal ions. Schiff bases have a diversified structure with nitrogen and oxygen donor systems being the most numerous. However, nitrogen and sulfur donor systems and only nitrogen systems have been studied. The presence of lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical importance and impart excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. This chelating ability of the Schiff bases combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry[12].

1.2.1 Preparation of Schiff bases [13]

A Schiff is the nitrogen analog of an aldehyde or ketone in which the C=O is replaced by a C=N-R group. It is usually formed by condensation of an aldehyde or ketone with a primary amine.

Schiff base that contain aryl substituents are more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehyde having effective conjugation are more stable [14-19].

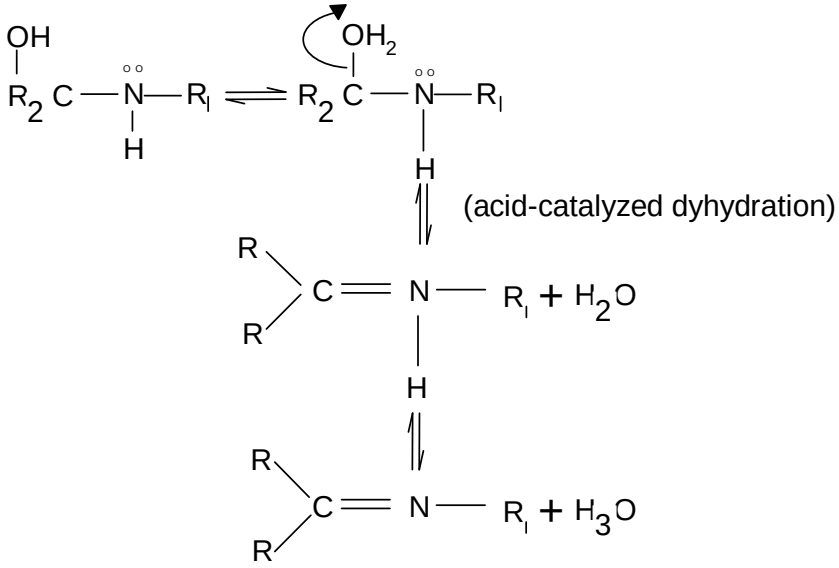
The formation of Schiff bases from aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating:



The formation is driven to completion by separation of the product or removal of water or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.

The mechanism of Schiff base formation is another variation on the theme of nucleophilic addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called a carbinolamine.

The carbinolamine loses water by either acid or base-catalysed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalysed dehydration.



Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and this is why the reaction is catalysed by acids[20]. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophilic, equilibrium is pulled to the left and carbinolamine formation occurs. Therefore, many Schiff bases syntheses are carried out at mildly acidic pH.

1.2.2 Uses of Schiff Bases

Schiff bases have wide application in food, dye, analytical chemistry, catalysis and agrochemical industries[21].

Schiff bases are widely used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers[22]. They are also used in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhanced selectivity and sensitivity[23,24]. Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties[25,26].

Schiff bases are widely used in analytical determination, using reaction of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with amino or carbonyl group). Schiff bases play important roles in coordination

chemistry as they easily form stable complexes with transition metal ions[27,28]. In organic synthesis; Schiff base reactions are useful in making carbon-nitrogen bonds.

1.2.3 Biological Importance of Schiff Bases

Schiff bases appear to be important intermediates in a number of enzymatic reactions involving interaction of the amino group of an enzyme, usually that of a lysine residue, with a carbonyl group of a substrate[29]. Stereochemical investigation[30] carried out with the aid of molecular models showed that Schiff bases formed between methylglyoxal and the amino group of the lysine side chains of proteins can bend back in such a way toward the N atom of peptide group that a charge transfer can occur between these groups and the oxygen atoms of the Schiff bases. Complexes of Co(II), Cu(II), Ni(II), Mn(II) and Cr(III) with Schiff bases derived from 2,6-diacetyl pyridine and 2-pyridine carboxaldehyde with 4-amino-2,3-dimethyl-1-phenyl-3-pyrozolin-5-one show antibacterial and antifungal activities against *Escherichia coli, Staphylocccus bacteaureus, Klebsiella pneumonia, Mycobacterium snegmatis, Pseudomonas aeruginosa, Enterococcus cloacae, Bacillus megaterium* and *Micrococcus leteus.* The results showed that the ligand had a greater effect against E. Coil than other bacteria while it has no activity against *S.aureus*. Metal complexes had greater effect than the ligand against almost all bacteria. Schiff bases derived from pyridoxal (the active form of vitamin B6) and amino acids are considered as very important ligands from biological point of view. Schiff bases are involved as intermediates in the processes of non-enzymatic glycosylations. These processes are normal during aging but they are remarkably accelerated in pathogeneses caused by stress, excess of metal ions or diseases such as diabetes, Alzheimerôs disease and atherosclerosis. Non-enzymatic glycosylation begins with an attack of sugar carbonyls or lipid peroxidation fragments on amino groups of proteins, aminophospholipids and nucleic acid, causing tissue damages by numerous oxidative rearrangements. One of the consequences is cataract of lens proteins[31]. Many biologically important Schiff bases have been reported in the literature. These possess antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [32-37]. Another important role of Schiff base structure is in transamination[38].

Transamination reactions are catalysed by a class of enzymes called transaminases. Transaminases are found in mitochondria and cytosal of eukaryotic cells.

1.2.4 Schiff Base Metal Complexes

Transition metals are known to form Schiff base complexes. Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Their metal complexes have been of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules[39]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities[40-41]. Schiff base metal complexes have occupied a central place in the development of coordination chemistry after the work of Jergensen and Werner[42]. Pfeiffer and his co-workers[43] reported a series of complexes derived from Schiff bases of salicylaldehyde and its substituted analogues. The configuration of the chelate group in the four coordinate complexes may be square-planar, tetrahedral, distorted tetrahedral or distorted trigonal pyramidal with the metal atom at the apex. The advantages of the salicyaldiimines ligand systems is the considerable flexibility of the synthetic procedures, which have resulted in the preparations of a wide variety of complexes with a given metal whose properties are often dependent on the ligand structure. A number of structural studies on the effect of the number of CH_2 groups between the two azomethine moieties in VO^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} complexes of tetradentate Schiff bases derived from salicyladehyde and a variety of diamine (1:2 ratio) have been reported[44-45]. It has been shown that an increase in the methylene chain length allows adequate flexibility for the complexes to change their structure from planar towards a distorted or pseudotetrahedral coordination depending on the magnitude. In addition, the longer chains cause the ligand field strength to decrease[46-48]. Metal

complexes of this type have been prepared for the series n=2 to 10 for the bivalent cobalt, nickel, copper, zinc and manganese. For n=2 most divalent first-row transition metals are expected to form square-planar complexes. The v stretching frequencies fall in the range 861-994cm^{-1} and the effective magnetic moments at room temperature of the complexes are between 1.64 and 1.81 BM. The complexes with [(n=2, R_1=R_2=H), (R_1= H, R_2=CH_3), (R_1=R_2=CH_3)] are green and their spectroscopic and magnetic properties suggest that they have tetragonal pyramidal structures. A corresponding complex (R_1 = R_2 = H, n = 3) is orange-yellow and its x-ray structure shows that it is polymeric, having a distorted octahedral geometry.

In general, Co(II) complexes have a higher tendency to assume a tetrahedral configuration than the corresponding Ni(II) complexes. The complexes of Cr(III), Fe(III), Co(III) and Ni(II) ions with a Schiff base derived from 4-dimethylaminobenzaldehyde and primary amines have been prepared and investigated using different physio-chemical techniques, such as elemental analysis molar conductance measurements, and infrared spectra. The analytical data showed formation of the complexes and a square planar geometry was suggested for Co(II) and Ni(II) complexes and an octahedral structure for Cr(III) and Fe(III) complexes. Nair, *et al* synthesized two Schiff bases from 5-ethyl-2,4-dihydroxyacetophenone[49]. Their copper, nickel, iron and zinc complexes were screened for antibacterial activity against some clinically important bacteria, such as Pseudomonas aeruginosa, Proteus vulgaris, Proteus mirabilis, Klebsiella pneumoniae and Staphylococcus aureus.

The metal complexes showed differential effects on the bacterial strains investigated and the solvent used, suggesting that the antibacterial activity is dependent on the molecular structure of the compound, the solvent used and the bacterial strain under consideration.

1.3 Chromium

1.3.1 Determination of Chromium

Chromium is found throughout the environment in 3 major oxidation states: chromium(0), chromium(III) and chromium(VI)[50]. The most stable form, chromium(III), occurs naturally in the environment, while chromium(VI) and chromium(0) are generally produced by industrial

processes[51]. The trivalent and hexavalent states of chromium are the most biologically significant. Chromium in biologic tissues is almost always trivalent and helps to maintain the normal metabolism of glucose, protein and fat[51,52]. However, trivalent chromium may be harmful if ingested in large amounts. Chromium(VI) is a strong oxidizing agent and highly toxic to humans and animals due to its carcinogenic and mutagenic properties[51]. Hence, the determination of chromium in environmental and biologic samples is of great interest. There are many sensitive techniques for chromium determination, such as ICP ï MS[53-55], ICP-AES[56,57], NAA[58-60],UV-visible[56,61] and AAS[56,62,63].

On the other hand, the application of kinetic catalytic methods for trace analysis allows one to achieve detection limits and sensitivity comparable with the above mentioned instrument techniques and offers simple and low-cost equipment[64]. Moreover, catalytic methods for chromium determination take a very small place among the many sensitive methods reported for the determination of chromium. Most catalytic spectrophotometric methods for chromium determination reported so far are based on its catalytic effect on a given redox reaction[61,65]. The oxidants most frequently used are hydrogen peroxide, chlorate, bromate or ceric ions and most of the substrates used are organic compounds: aromatic amines, phenols and their derivatives[61,65-69] .

1.3.2 Uses

- **Metallurgy**[70] : The strengthening effect of forming stable metal carbides at the grain boundaries and the strong increase in corrosion resistance made chromium an important alloying material for Stainless steel is formed when chromium is added to iron in sufficient concentrations[71]. The relative high hardness and corrosion resistance of unalloyed chromium makes it a good surface coating with unparalleled combined durability[72].
- **Dye and pigment**[70]: lead chromate, $PbCrO_4$ was used as a yellow pigment shortly after its discovery. Chromium oxides are also used as a green colour in glass making and as a glaze in ceramics[73]. It is also the main ingredient in IR reflecting paints, used by the armed forces to paint vehicle, to give them the same IR reflectance as green leaves.

- **Synthetic ruby and the first laser**[70]: Natural rubies are aluminium oxide crystals that are colored red due to chromium(III) ions. A red-colored artificial ruby may also be achieved by dropping chromium(III) into artificial aluminium oxide crystals, thus making chromium a requirement for making synthetic rubies[74].
- **Wood preservative**[70]: chromium(IV) salts are used for the preservation of wood. Chromate copper arsenate is used in timber treatment to protect wood from decay fungi, wood attacking insects, including termites and marine bores[75].
- **Tanning**[70]: Chromium(III) salts, especially chrome alum and chromium(III) sulfate are used in the tanning of leather. The chromium(III) stabilizes the leather by cross linking the collages fibres[76].
- **Refractory material**[70]: the high heat resistivity and high melting point makes chromite and chromium(III) oxide a material for high temperature refractory applications, like blast furnaces cement kilns, molds for the firing of bricks and as foundry sands for the casting of metals[77].
- **Catalysts**[70]: Several chromium compounds are used as catalysts for processing hydrocarbons. For example the Philips catalysts for the production of polyethylene are mixtures of chromium and silicon dioxide or mixtures of chromium and titanium and aluminum oxide[78].
- Chromium(IV) oxide is used to manufacture magnetic tape used in high performance audio tape and standard audio cassettes[79]. Chromic acid is a powerful oxidizing agent and is a useful compound for cleaning laboratory glassware of any trace of organic compounds.

1.4 Statement Of the Problem

Chromium(VI) is very toxic and have accumulative effects. The determination of Cr(VI) in environmental samples plays an important role in the monitoring of environmental pollution and the associated health hazards to both terrestrial and aquatic lives.

Different classical and instrumental techniques for the determination of Chromium are very expensive, readily unavailable and require high cost of maintenance. Instrumental methods like

atomic absorption spectrophotometry is very sensitive and highly selective in metal determination, but cannot give information about Cr(III) and Cr(VI) as found in their various compounds[69,70]. Atomic absorption spectrophotometry does not take cognizance of complexation studies of ions present in complexes as do the ultraviolet/visible spectrophotometry. Only UV spectrophotometry can give information about the ions present in metals already determined by AAS. Cr(III) and Cr(VI) can be determined spectrophotometrically by forming light absorbing colouredï complexes with organic reagents. This method is cost-effective, rapid and its sensitivity and selectivity can be enhanced by masking other ions present in the sample of a given analyte. This research work is inspired by a serious need to search for more reagents and also establish the optimum and fundamental conditions of complex formation needed for application in the determination of metal ions.

1.5 Aims And Objectives

Spectrophotometric determination of chromium(III) and chromium(VI) ions requires the formation of stable chelates with a light absorbing reagent that can be absorbed in the UV /visible region of the electromagnetic spectrum. Therefore, the main aim of the present work were to ascertain the possibility of direct determination of Cr(III) and Cr(VI) in steel with the Schiff base ligand derived from 1, 3 ï diamino benzene and salicyaldehyde. The specific objectives were to:

(a) synthesize a Schiff base derived from 1,3ï diamino benzene and salicyaldehyde.

(b) synthesize Cr(III) and Cr(VI) complexes of the ligand

(c) characterize the ligand and the metal complexes on the basis of melting point, electronic spectra, infrared spectra, nuclear magnetic resonance (^{1}H and ^{13}C) spectra.

(d) conductivity test of the ligand and the complexes

(e) propose structures for the synthesized ligand and complexes on the basis of their spectral data, as precursors for further structural studies.

(f) determine Cr(III) and Cr(VI) by looking at the following parameters below:

i. the composition of the complexes

ii. the effect of time on the formation of the complexes

iii. the effect of the concentration of the reagent on the formation of the complexes

iv. the effect of temperature on the formation of the complexes

v. the effect of pH on the formation of the complexes

vi. the effect of some interfering ions on the formation of the complexes

vii. Calibration curve

(g) application/direct determination of Cr(III) and Cr(VI) in standard steel to ascertain the possibility of the determination of the ions.

CHAPTER TWO

2.0 LITERATURE REVIEW

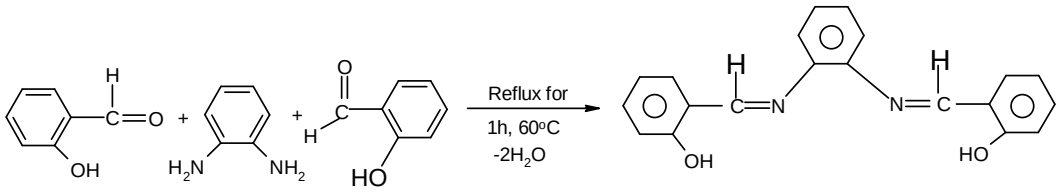
2.1 Catalytic Spectrophotometric Determination of Chromium

Stoyanova[50] reported the catalytic spectrophotometric determination of chromium using sulfanilic acid. In this work, the catalytic effect of Cr(III) and Cr(VI) on the oxidation of sulfanilic acid with hydrogen peroxide was exploited in the spectrophotometric determination of the metal ions. The slope of the curve increased abruptly above pH 5, and the buffer of pH 6.6 provided the highest sensitivity in the determination of Cr(III) and Cr(VI). The optimal concentration of sensitivity was 0.004 mol dm^{-3}. The concentration of hydrogen peroxide was 0.56 mol dm^{-3}. The optimum temperature for the determination was 50^0C. The influence of the reaction parameters (acidity, temperature, reagent concentration) on the reaction rate was studied in the presence and absence of Cr(VI) to establish the optimum reaction conditions. This showed the dependence of the initial reaction rate on the acidity. The wavelength of maximum absorption under the optimum condition was 360 nm. The absorption spectra of the reaction for Cr(III) and Cr(VI) catalysed reactions were similar.

2.2 Spectrophotometric Determination Of Trace Level Chromium Using Bis (Salicylaldehyde) OrthophenyleneDiamine In Non-ionic Micellar Media

Soomro and Co-workers[80] reported the spectrophotometric determination of chromium using bis(salicylaldehyde)orthophenyldiamine. The ligand reacted with chromium(VI) in slightly acidic micellar medium to form a yellow-orange chelate with a molar ratio of 2:3. The molar absorptivity of the Cr(VI) complex formed in the presence of nonionic Triton X-100 surfactant was found to be almost ten times higher than that observed in aqueous solution. The maximum absorbance was obtained at 482 nm and remained constant for over 24 h. The average molar absorptivity coefficient and Sandellôs sensitivity were found to be 3.5 X 10^5 dm^3 mol^{-1} and 5 mg cm^{-2} of Cr(VI) respectively. Linearity range was found between 0.01 ï 12.0 mg $dm^{-3}$of Cr(VI) with correlation coefficient value of 0.9987. They also found that over 50 cations, anions and complexing agents do not interfere in the

determination. The ligand was synthesized by refluxing 1, 2-diaminobenzene and salicyclaldehyde at 60^0C for 1 h.



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2.3 Spectrophotometric Determination of chromium(III) and chromium(VI) in sea water.

Tsunenobu and co-workers[81] reported the determination of chromium by spectrophotometric method with diphenylcarbazide (DPC). Chromium(VI) reacts with DPC to form reddish violet complex. The reaction was selective for chromium and very sensitive. One tenth to five microgram of chromium could be determined with an error of ± 2%. The procedure was as follows: to a sample solution containing 0.1-5 µg of chromium,1 cm^3 of 1 M- H_2SO_4 and 0.5 cm^3 of 0.01 M-$KMnO_4$ solution was added and warmed in boiling water for 40 min to oxidize chromium(III) to chromium(VI). After cooling, a few drops of 4%-NaN_3 solution was added and warmed again at 60^0C for 3 min to reduce excess $KMnO_4$. The mixture was cooled in ice water and 2 cm^3 of 0.25%-DPC solution was added and made up to 25 cm^3. After standing for 20 min, the absorbance was measured at 540 nm against the reagent blank, using 5 cm cell. Molar extinction coefficient of Cr (VI)-DPC complex was affected by the purity and the amount of the reagent, it was estimated to be 34400 at 540 nm.

2.4 Determination of Hexavalent Chromium in drinking water by ion Chromatography with post-column derivatization and UV-visible spectroscopic Detection.

Zaffiro et al [82] reported the determination of hexavalent chromium in drinking water by the use of ion chromatography with post-column derivatization and UV-visible spectroscopy. The samples were preserved with a combined buffer/dechlorinating reagent which complexed free chlorine and increased the pH to a value greater than eight. CrO_4^{2-} was separated from other matrix components on an anion exchange column. CrO_4^{2-} was derivatized with 1,5-diphenylcarbazide in a post-column reactor and was detected spectrophotometrically at a wavelength of 530 nm. Cr(VI) was qualitatively

assayed via retention time and the concentration of CrO_4^{2-} in the sample was calculated using the integrated peak area and the external standard.

2.5 Determination of Cr(VI) in Environmental Sample by Evaluating Cr(VI) impact in a contaminated Area.

Pranvera Lazo [83] reported the determination of Cr(VI) in environmental samples via 1,5-diphenylcarbazide, in water, sediment and soil samples based on conventional spectrophotometric methods for coloured Cr(VI)-1,5-diphenylcarbazide complex measured at 540 nm in acid solution. An optimization procedure was employed for determining the proper optimum operating conditions for both instrumental system and chemical variables. The operating conditions obtained were as follows:

- 5 mg/L Cr(VI) -1,5-diphenylcarbazide (2 cm^3, 0.5%) solution measured in different condition of acid solution caused constant absorption for 0.1 to 0.5 M H_3PO_4/and or H_2SO_4 medium (t=20 min, λ=540 nm).
- after the variation of quantity of diphenylcarbazide, the maximum absorption was found for 0.5 to 4 cm^3 0.5% 1, 5-diphenylcarbazide at λ = 542 nm (0.5 mg/L Cr(VI) standard solution in 0.2 M H_3PO_4 solution and measured after 20 min).
- the absorbance of standard solution via the time, using 1 cm^3 1,5-diphenylcarbazide 0.5, 0.1 M H_3PO_4/and or H_2SO_4 was stable after 7 min.
- selectivity of the method was investigated through the interferences of Fe(III). Cr(VI) absorb on ə=373 nm, whereas Cr(VI)-1,5-diphenylcarbazide complex have a strong absorption on ə=542 nm, interfered from the presence of Fe(III). For Fe/Cr ratio smaller than 500 in 0.2 M H_3PO_4 and smaller than 10 in 0.2 M H_2SO_4 medium, the interference of Fe(III) was negligible.
- the interference of Fe^{3+} was totally negligible by using 1.5 cm^3 5% NaF and 0.2 M H_3PO_4 medium.

The optimal conditions of Cr(VI)-1,5-diphenylcarbazide measurements was: H_3PO_4 0.2 M solution, adding 1.5 cm^3 5% NaF and 1 cm^3 0.5% 1.5-diphenylcarbazide, time of measurements after 7 min in

λ = 542 nm. Avoiding the analyte, interference blank solution was measured in the same time with samples.

Linearity of the response of the sample was investigated through the linearity of calibration line, obtained from five standard solution, which showed a linear regression coefficient greater than 0.99 ($y = 0.7991x + 0.0011$ with $R^2 = 0.9995$). Beerôs law was obeyed in the concentration range 0.05-5 mg/l of Cr(VI) and limit of detection was 4.7 µg/L (1=1 cm), which is low enough to allow determination of Cr(VI) also in water samples.

2.6 Indirect Extraction - Spectrophotometric Determination of chromium.

Telepcakova *et al* [84] reported the indirect extraction ï spectrophotometric determination of chromium. The appropriate volumes of 1 mol dm^{-3} sulfuric acid, Cationic Yellow 42(CY42) were pipette to 0.6 cm^3 of 10^{-4} mol dm^{-3} $K_2Cr_2O_7$. This was diluted with water until the volume of the solution was 5 cm^3. After adding each reagent, it was mixed thoroughly and then left to stand in the dark for 3 min. Then the formed ion was extracted in a test tube at room temperature by 5 cm^3 of toluene for 30 s. After equilibrium was established, the organic phase was separated and absorbance of the organic phase was measured at 430 nm against toluene. A reagent blank was prepared similarly but without chromium.

The analytical approach for determination of chromium was dependent on two reactions which must be quantitative. First, chromium in hexavalent state must oxidize an equivalent amount of iodide ions. It is known that Cr(IV) and iodide ion react quantitatively in an acid medium as follows:

$$2CrO_4^{2-} + 6I^- + 16H^+ \longleftrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$$

In the presence of an excess iodide ion, the liberated iodine forms triiodide ion, which combines with a cationic dye ion extracted into organic phase formed by solvent (S_{org}).

$$I_2 + I^- \longleftrightarrow I_3^-$$

$$I_3^- + CY42^+_{aq} + S_{org} \longleftrightarrow CY42^+I^-_{3org}$$

2.7 Sensitivity Determination of Hexavalent Chromium in Drinking Water

Lipika and co-worker[85] reported the sensitive determination of hexavalent chromium in drinking water using anion exchange chromatography. The work described the modification of the conditions described in Environmental Protection Agency(EPA) [86-88] method 218.6, including use of the column in the 2 mm format and a smaller reaction coil to increase method sensitivity. The modified method used Dionex IonPac AG7 guard (2 x 50 mm) and Dionex Ionpac AS7 analytical columns (2x250 mm), an eluent of 250 mM ammonium sulfate/100 mM ammonium hydroxide at a flow rate of 0.36 cm^3/min, a 1000 µL injection volume, and postcolumn reaction with 2 mM diphenylcarbazide/10% methanol/1 N sulfuric acid (using a 125 µL reaction coil) followed by visible absorbance detection at 530 nm. This modified method permits method detection limit(MDL) for chromate of 0.001 µg /L resulting in a quantitation limit of 0.003 µg/L.

2.8 Determination of Dissolved Hexavalent Chromium in Drinking Water, Ground Water and Industrial Waste Water Effluents by Ion Chromatography [86]

The method presented here provided a sensitive and selective means of determining Cr(VI) as the chromate anion CrO_4^{2-} down to the 1-mg/L level in a variety of environmental matrices. An aqueous sample was injected onto a high capacity anion exchange column where Cr(IV) as CrO_4^{2-} was retained and then eluted with an alkaline sulfate eluent. After this separation, a diphenylcarbazide colour reagent was added to the eluent stream, which then flowed through a photometric detector. The reagent formed a colour complex with Cr(IV), which was detected by absorbance at 530 nm.

CHAPTER THREE

3.0 EXPERIMENTAL

3.1 Apparatus

Meter E. 2000 weighing balance.

Jenway 3510 pH meter.

Gallenkamp(England) melting point model.

LF-90, WTW (model) ï conductivity meter.

A Jenway 6305 UV/visible spectrophotometer.

UV-2012PC spectrophotometer.

Infrared-Schimadzu model spectrophotometer .

^{1}HNMR-mercury-2000BB spectrophotometer.

^{13}C NMR-Mercury-2000BB spectrophotometer.

3.2 Preparation of Stock Solutions

i. 0.01 M 2-[(E)-[{3-[(2-hydroxybenzylidene)amino]phenyl}imino)methyl]Phenol(H_2BPMP) stock solution was prepared by dissolving 3.1636 g dried sample in analytical grade ethanol in a 1dm^3 volumetric flask.

ii. 0.01 M Cr(III) solution: The stock solution was prepared by dissolving 4.00143 g of $Cr(NO_3)_3.9H_2O$, in distilled water in a 1 dm^3 volumetric flask and made up to mark using distilled water.

iii. 0.050 M borax: 0.728 g of borax ($Na_2BO_7.5H_2O$) was accurately weighed, dissolved in distilled water and made up to mark in a 50 cm^3 volumetric flask.

iv. 0.05 M HCl: 4.35 cm^3 of 37 % hydrochloric (S.G 1.18) was made up to mark in 100 cm^3 volumetric flask with distilled water. The acid was standardized by titrating 50 cm^3 with 25 cm^3 of 0.050 M borax, lower concentrations were obtained by diluting as required.

v. 1 M KCl: The stock solution was prepared by dissolving 74.5 g of KCl in a beaker with 200 cm^3 distilled water and thereafter the solution was transferred into a 1 dm^3 volumetric flask and the flask was made up to mark with distilled water.

vi. 0.50 M NaOH: The stock solution of NaOH was prepared by weighing 0.021 g of 96% NaOH and dissolved in warmed distilled water and made in a 100 cm^3 volumetric flask. The sodium hydroxide solution was standardized by titrating 50 cm^3 with 25 cm^3 of 0.05 M oxalic acid, and lower concentrations obtained by diluting as required.

vii. 1 M KH_2PO_4: 1 M KH_2PO_4 was prepared by dissolving 136 g of KH_2PO_4 in a beaker with 200 cm^3 distilled water and thereafter the solution was transferred into a 1dm^3 volumetric flask and was made up to mark with distilled water.

viii. 1 M H_3BO_3 was prepared by dissolving 62 g of H_3BO_3 in a beaker with 200 cm^3 distilled water and thereafter the solution was transferred into a 1dm^3 volumetric flask and was made up to mark**.**

3.3 Preparation of Buffer Solutions

Clark and Lubbôs procedure[89] was used to prepare standard buffer solution covering the pH range 1-13 with standard solution of the following acid/salt systems; hydrochloric acid, potassium chloride, hydrochloric/potassium hydrogen phthalate, potassium hydrogen phthalate/sodium hydroxide, and boric acid/sodium hydroxide. The Jenway 3510 pH meter was used and were prepared as follow in Table 3.1.

3.4 Synthesis of the Ligand(HBAPP)

Synthesis of the HBAPP was carried out according to reported method[90]. An aliquot of 1,3-Diaminobenzene(5.41 g ,0.05 mole) was dissolved in 50 cm^3 of absolute ethanol and 2 cm^3 of 1.0 M NaOH was added and stirred to dissolve. 2-hydroxybenzaldehyde (10.44 g, 0.1 mole) was added to the resulting solution at room temperature. The reaction mixture was refluxed for 2 h at 60-65^oC. There was a colour change from green to orange yellow. The mixture was cooled and the product

formed was collected, recrystallized with cold ethanol (98%) and kept in a dessicator over fused $CaCl_2$.

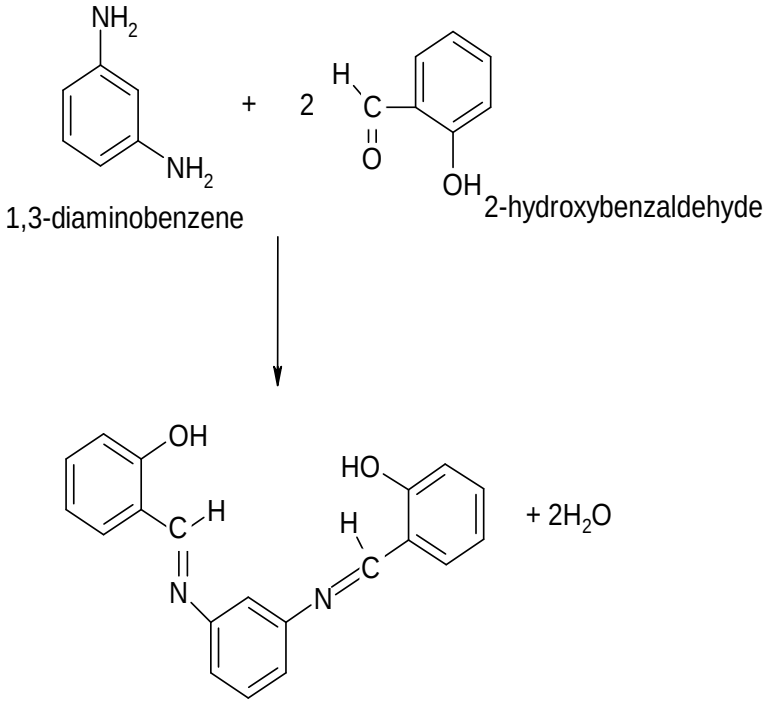
Table 3.1: Preparation of Buffer Solution

pH Value	Procedure
1.00	25 cm^3 of 0.2 M KCl was mixed with 67.0cm^3 of 0.2 M HCl, diluted and made up to 100 cm^3 with distilled water
2.00	25 cm^3 of 0.2 M KCl was mixed with 6.5 cm^3 of 0.2 M HCl, diluted and made up to 100 cm^3 with distilled water
3.00	50 cm^3 of 0.1 M KH phthalate was mixed with 22.3 cm^3 of 0.2 M HCl, diluted and made up to 100 cm^3 with distilled water
4.00	50 cm^3 of 0.1 M KH phthalate was mixed with 3.0 cm^3 of 0.1 M NaOH, diluted and made up to 100 cm^3 with distilled water
5.00	50 cm^3 of 0.1 M KH phthalate was mixed with 22.6 cm^3 of 0.1 M NaOH, diluted and made up to 100 cm^3 with distilled water
6.00	50 cm^3 of 0.1 M KH_2PO_4 was mixed with 5.6 cm^3 of 0.1 M NaOH, diluted and made up to 100 cm^3 with distilled water
7.00	50 cm^3 of 0.1 M KH_2PO_4 was mixed with 29.1 cm^3 of 0.1 M NaOH, diluted and made up to 100 cm^3 with distilled water
8.00	50 cm^3 of 0.1 M with respect to both KCl and H_3BO_3 was added to 3.8 cm^3 of 0.1 M NaOH and diluted and made up to 100 cm^3 with distilled water
9.00	50 cm^3 of 0.1 M with respect to both KCl and H_3BO_3 was added to 20.8 cm^3 of 0.1 M NaOH and diluted and made up to 100 cm^3 with distilled water
10.00	50 cm^3 of 0.1 M with respect to both KCl and H_3BO_3 was added to 43.7 cm^3 of 0.1 M NaOH and diluted and made up to 100 cm^3 with distilled water
11.00	50 cm^3 of 0.05 M Na_2HPO_4 was mixed 4.1 cm^3 of 0.1 M NaOH and was diluted to 100 cm^3 with distilled water
12.00	25 cm^3 of 0.2 M KCl was mixed with 6.0 cm^3 of 0.2 M NaOH and was diluted to 100 cm^3 with distilled water
13.00	25 cm^3 of 0.2 M KCl was mixed with 66.0 cm^3 of 0.2 M NaOH and was diluted to 100 cm^3 with distilled water

3.5 Synthesis of Chromium(III) and Chromium(VI) Complexes of HBAPP

Cr(III) and Cr(VI) complexes of the ligand were synthesized according to literature[50]. In each case, a solution of the ligand (1.5818 g ,0.005 mole) in absolute ethanol (25 cm^3) was reacted with 1 g (0.0025 mole) solution of Cr(III) in distilled water (25 cm^3) and 0.485475 g of Cr(VI) in distilled water (25 cm^3) respectively. The reaction mixtures were refluxed at 60^oC for 1 h. There was observable colour change from black to brown and yellow to brownish yellow respectively. The

mixtures were then cooled and the residue formed collected by filtration. The residue was recrystallized from absolute ethanol and kept in dessicator over fused calcium chloride.



Scheme 1: Formation of 2-[(E)-[{3--[(2-hydroxybenzylidene) amino] phenyl} imino) methyl] phenol(H_2BPMP)

3.5.1 Determination of the Stoichiometry of the Complexes by Slope-Ratio Method.

The experiment was performed as described in literature[80] as follows: Two sets of solution were prepared for two sets of observation. For the first set, a fixed (excess) concentration of the metal ion under study was reacted with varying concentrations of the ligands. About 1.0×10^{-3} M solution of Cr(III) and Cr(VI) respectively were fixed, the ligand concentration varied from 1.0×10^{-5} M to 8.0×10^{-5} M concentrations. For the second set, the reverse was the case; a fixed (excess) concentration of the ligand was reacted with varying amount of the metal ion under study. The absorbance at maximum wavelength (λ_{max}) were measured and plotted against corresponding concentration for the two sets of observation and the stoichiometry determined by comparing the slopes of the plots.

3.6 General Procedure for the Complexation Studies

3.6.1 Effect of Time on the Formation of the Complexes

Aliquots of 0.0005 M solution of the Cr(III) and Cr(VI) respectively were reacted with 0.0005 M solution of the ligand. The absorbances were taken at different intervals between 5 and 80 min and a plot of absorbance versus time was obtained.

3.6.2 Effect of Temperature on the Formation of the Complexes

Aliquots of 0.0005 M solution of the ligand was reacted with 0.0005 M solution of Cr(III) and Cr(VI) respectively according to stoichiometry. Cr(III) complex was allowed to form for 10 min, while Cr(VI) complex was allowed to form for 40 minutes at different temperatures (30 ï 80^{o}C) in a thermostated water bath. The absorbances were taken at the λ_{max} for each complex and plotted against the corresponding temperature.

3.6.3 Effect of Concentration of Reagent on the Formation of the Complexes

Different amounts of 0.01 M stock solution of the ligand (reagent) ranging from 1.0×10^{-5} to 8.0×10^{-5} M solution were reacted with a fixed amount of 5.0×10^{-5} M solution of the metal ion under study. The mixture was allowed to react for a given time, and the absorbances taken at the λ^{max} of the complex. The absorbances were plotted against the various concentrations of the reagent.

3.6.4 Effect of pH on the Formation of the Complexes

Ligand solutions 0.0005 M solution were reacted with 0.0005 M solution of Cr(III) and Cr(VI) respectively over the pH range of 1-13. The mixtures were allowed to react for 40 min for Cr(III) and for 10 min in the case of Cr(VI) complex at 60^{0}C and 50^{0}C for Cr(III) and Cr(VI) complexes respectively. The absorbances were taken at the λ_{max} of the complexes under study and plotted against the pH.

3.6.5 Effect of Interfering Ions on the Formation of the Complexes

A given amount of the metal ion under study was taken with different amounts of foreign ions. The mixture was buffered and appropriate amount of the ligand solution was added, as required by the

stoichiometry of the complex. It was allowed to react at a given temperature for a given time, and absorbance taken at the λ_{max} of the complex under study. The absorbance was compared with the absorbance of the complex in the absence of foreign ions and percentage interference calculated.

3.6.6 Calibration Curve-Beer's Law

Different concentrations of the metal ions under study were pipetted into separate test tubes, and made up to volume with the appropriate buffer, and then the ligand was added according to the stochiometry of the complex. The concentration range was 0.02 ï 0.14 ppm for both Cr(III) and Cr(VI) complexes. The reactions were allowed to come to completion at the predetermined times. The final absorbances were plotted against the various metal ions concentration to obtain the standard curves.

3.7 Determination of Chromium in Alloy

3.7.1 Determination of Chromium in Alloy with Flame Atomic Absorption Spectrophotometry

An aliquot of 1.0 g of a given alloy was taken to which 25-30 cm^3 of aqua regia was added and the mixture was heated gently until the alloy decomposed completely. Then concentrated HCl was added in installments of 4.0 cm^3. The solution was evaporated to dryness. The residue was dissolved in 10 M HCl (20 cm^3) and diluted to one litre to give 1000 ppm solution. Using dilution method, lower concentration of the solution was obtained by dilution. Chromium concentration was determined in the solutions of the alloys using AAS method and the results obtained were compared with the results obtained with the UV method.

3.7.2 Determination of Chromium in Alloys with UV Spectrophotometry

An aliquot of the solutions already determined by AAS was taken and the content of the metal ion under study was determined as follows; In a test tube were placed an aliquot of standard solution of the alloys, a small amount of masking agent and a given volume of the required buffer solution was added. The test tube was kept at a given temperature in a thermostated water bath for a given time. Then a given amount of the ligand was added, the mixture was homogenized by shaking and

transferred into a $5cm^3$ constant temperature cell of the spectrophotometer. The absorbance was taken at the λ_{max} of the complex under study, after a given time and the concentration of the metal ion was extrapolated from the standard curve.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The tetradentate 2-[(E)-[{3--[(2-hydroxybenzylidene)amino]phenyl}imino)methyl]phenol was synthesized from the starting materials; 1,3-diaminobenzene and 2-hydroxybenzaldehyde in a single step. The complexes of Cr(III) and Cr(VI) were synthesized by reacting ethanol solution of the ligand with aqueous solution of the corresponding metal ion.

4.1 Physical Characterization and Molar Conductivity Data of the Ligands and Its Cr(III) and Cr(VI) Complexes

Soomro et al[72] earlier reported that Cr(VI) complex of Salicyaldehydeorthophenylenediamine gave a orange-yellow chelate which is in agreement with the results in Table 4.1

Table 4.1: Physical Data of the Ligands and Its Complexes

Compound	Colour	Texture	Melting point (^oC)	%Yield	Molar Conductivity ($MScm^{-1}$)
Ligand	Orange- yellow	Crystalline	146-150^oC	69.80	1.6
Cr(III) complex	Brown	Crystalline	290-300^oC	37.85	1.1
Cr(VI) complex	Brownish- yellow	Powdery	145-150^oC	21.10	2.5

Table 4.1 shows the molar conductivity values of 10^{-4}M aqueous solutions of the ligand and the complexes at room temperature. Cr(III) have the lowest value, suggesting that it is non-ionic. The molar conductivity of Cr(VI) is almost double the others because of the charge in its structure.

4.2 Spectroscopic Characterization of the Ligand and its Cr(III) and Cr(VI) Complexes.

4.2.1 Electronic Spectral Data of the Ligand and Its Complexes

The electronic spectra of the ligand and its complexes are presented in Table 4.2. From Table 4.2, three absorption bands ranging from weak to strong intensities were recorded for the ligand. In the ligand, 271.4 and 329.4 nm is assigned to ´ ï ´* transition and 360 nm is assigned to n ï ´* transition. The Cr(III) complex absorbed at 366.2 nm which is likely due to intraligand ´ ï ´*

transition. The bands at 447 and 482 nm with low intensities are likely due to d-d transition of Cr(III). Cr(VI) is a d^o and lacks the capacity for d-d transition. Therefore, the band formed at 394.2 nm with high intensity is likely due to ligand to metal charge transfer from the filled antibonding orbitals of the ligand to the d orbital of the metal. The same reason could be adduced for the band at 464 nm but with limited probability. The UV spectrum of the ligand and complexes are showed in Figures 4.26, 4.27 and 4.28 respectively as Appendix B.

Table 4.2: Electronic Spectra

Compound	Wavelength	Absorbance	Molar absorptivity $Lmol^{-1}cm^{-1}$
Ligand	271.4 329.4 360	2.261 1.968 1.229	4522 3936 2458
Cr(III) complex	366.2 447.2 482.6	0.102 0.058 0.031	204 116 62
Cr(VI) complex	394.2 464.6	1.728 0.478	3456 956

4.2.2 Infrared Spectra

The IR spectra of the ligand and the complexes are as presented in Table 4.3. The band at 3500 in the ligand is as a result of the presence of phenol while the absence of the band in the complexes was as a result of deprotonation during the complexing with the metals. The peaks at 1615, 1606 and 1593.25 are assigned to C=N of the ligand, Cr(III) and Cr(VI) complex respectively. The band at 1275 and 1355.0 cm^{-1} and 1392cm^{-1} is assigned to C-H in plane Aromatics. The bands at 532 and 457cm^{-1} is assigned to metal ï nitrogen stretch of Cr(III) and Cr(VI) respectively while 607.60cm^{-1} and 749.37cm^{-1} is assigned to metal-oxygen stretch of Cr(III) and Cr(VI) respectively. The spectra assignment agreed with the structure. The IR spectra of the ligand and the complexes are shown in Figures 4.29, 4.30 and 4.31 respectively in Appendix B

Table 4.3: Infrared Spectral Data of the Ligand and Its Complexes

Ligand	Cr(III) complex	Cr(IV) complex	Assignments
3500			v(O-H) phenol
3056.31	3138.29	3050.52	v(C-H) aromatic
2718.76	1932.74	2745	v(C-H) methane
1615.44	1606.76	1593.25	v(C=N)
1479.04		1478	v(C=C) of aromatic
1275.95	1355.04	1392	v(C-H) in plane Aromatic
1192.05	1042.56	1182	v(C-O) of phenols
1107.18		1272	v(C-O) of phenols
818.81	838.10	895	v(C-H)out of plane
	607.60	749.37	v(M-O)
	532.37	457	v(M-N)

4.2.3 ^{1}H and ^{13}C NMR Spectra of the Ligand

NMR data of the ligand are given in Tables 4.4 and 4.5 respectively. The **^{1}H, ^{13}C NMR** and the APT spectras are shown in Figure 4.32, 4.33 and 4.34 respectively in Appendix B

Table 4.4: ^{1}HNMR Spectral of the Ligand in $CDCl_3$ relative to TMS (ppm)

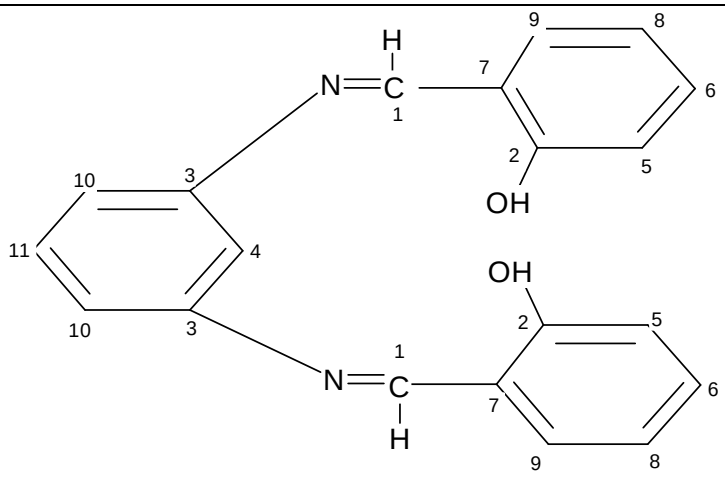
Peaks(ppm)	**Assignment**
13(2H,s)	Aromatic amines proton
10(2H,s)	Phenolic proton
8.85(1H,s)	Aromatic proton
7.408-7.029(2H,d)	Aromatic proton
6.93-6.883(2H,t)	Aromatic proton

s ï singlet, m ï multiplet, d-doublet, t-triplet

The peak at ŭ 10 is assigned to the phenolic proton. The peak for aromatic region appears between 6.883-8.85 ppm. The spectra are in agreement with the assigned structure.

4.2.4 ^{13}C NMR

Table 4.5: ^{13}CNMR Spectral Data of the Ligand

^{13}C(ppm)	Structure Showing Carbon Numbering
C_1 163.717	
C_2 161.345	
C_3 142.544	
C_4 133.392	
C_5 132.367	
C_6 127.725	
C_7 119.716	
C_8 119.233	
C_9 118.998	
C_{10} 117.549	

The Carbon-13 NMR spectrum is complimentary to the ^{1}HNMR peaks of ligand, and the assignment were made in accordance to what have been obtained for salicylaldehyde Schiff base. In exception of the C=N that appeared at 163ppm, the rest peaks were assigned to aromatic carbon keeping in mind its agreement with Attached Proton Test (APT) peaks. 161 ppm is assigned to C_2 because of the presence of a higher electronegative oxygen atom which cause deshielding. This is supported by the APT which appeared facing down as expected for C or CH_2 carbons.

4.2.5 APT (Attached Proton Test)

The APT reveals 6 (six) even carbon and seven odd carbon which agreed with the peaks at 77.714, 77.069 and 76.440 were probably due to the solvent ($CDCl_3$). As shown in Table 4.5, four carbon atoms numbered 10, two carbon atoms numbered 9, two carbon atoms numbered 8, two carbon

atoms numbered 7, two carbon atoms numbered 5, two carbon atoms numbered 3, two carbon atoms numbered 1 are equivalent. The great number of equivalent carbon atoms is as a result of the fact that the ligand is symmetrical.

4.3 STIOCHIOMERY OF THE COMPLEXES

4.3.1 Metal-Ligand Mole Ratio of Cr(III) Complex

Figs 4.1 and 4.2 show the results obtained with slope ratio method, for Cr(III) ion and the ligand respectively. The ratio of the slopes of the two plots show that Cr(III) ion to ligand mole ratio obtained is 1:1. The values used in plotting the graphs below are found in Tables 4.10 and 4.11.

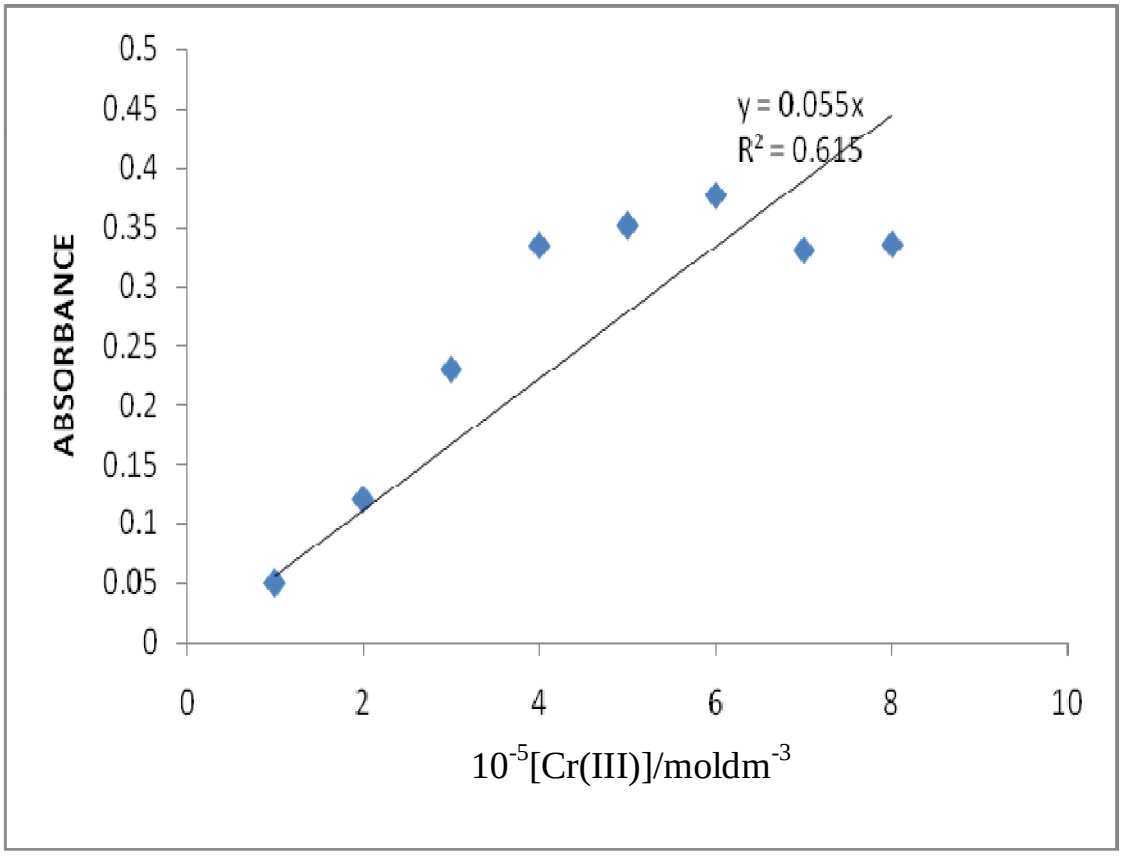


Fig4.1 Slope-ratio plot for Cr(III) complex at fixed ligand concentration ($1.0X10^{-3}M$)

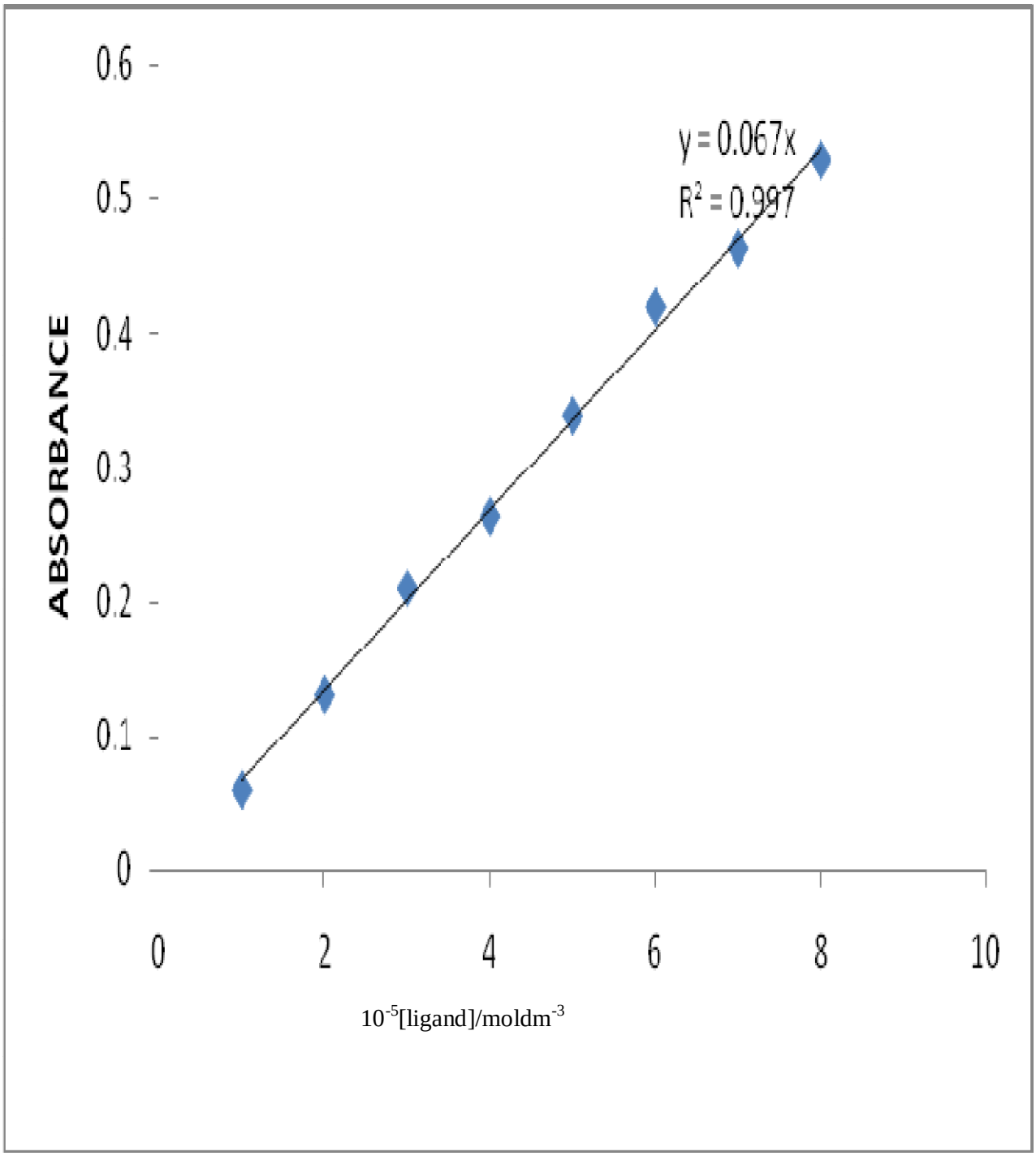


Fig4.2 Slope-ratio plot for Cr(III) complex at fixed metal concentration ($1.0x10^{-3}$)

4.3.2 Metal-Ligand Mole Ratio of Cr(VI) Complex

Figures 4.3 and 4.4 show the formation of the result obtained with the slope ratio method for Cr(VI) ion and the ligand respectively. The ratio of the slopes of the two plots show that Cr(VI) ion to ligand

mole ratio is 1:1. The values used for plotting the graphs on Figures 4.3 and 4.4 respectively are found in Table 4.12 and 4.13 respectively.

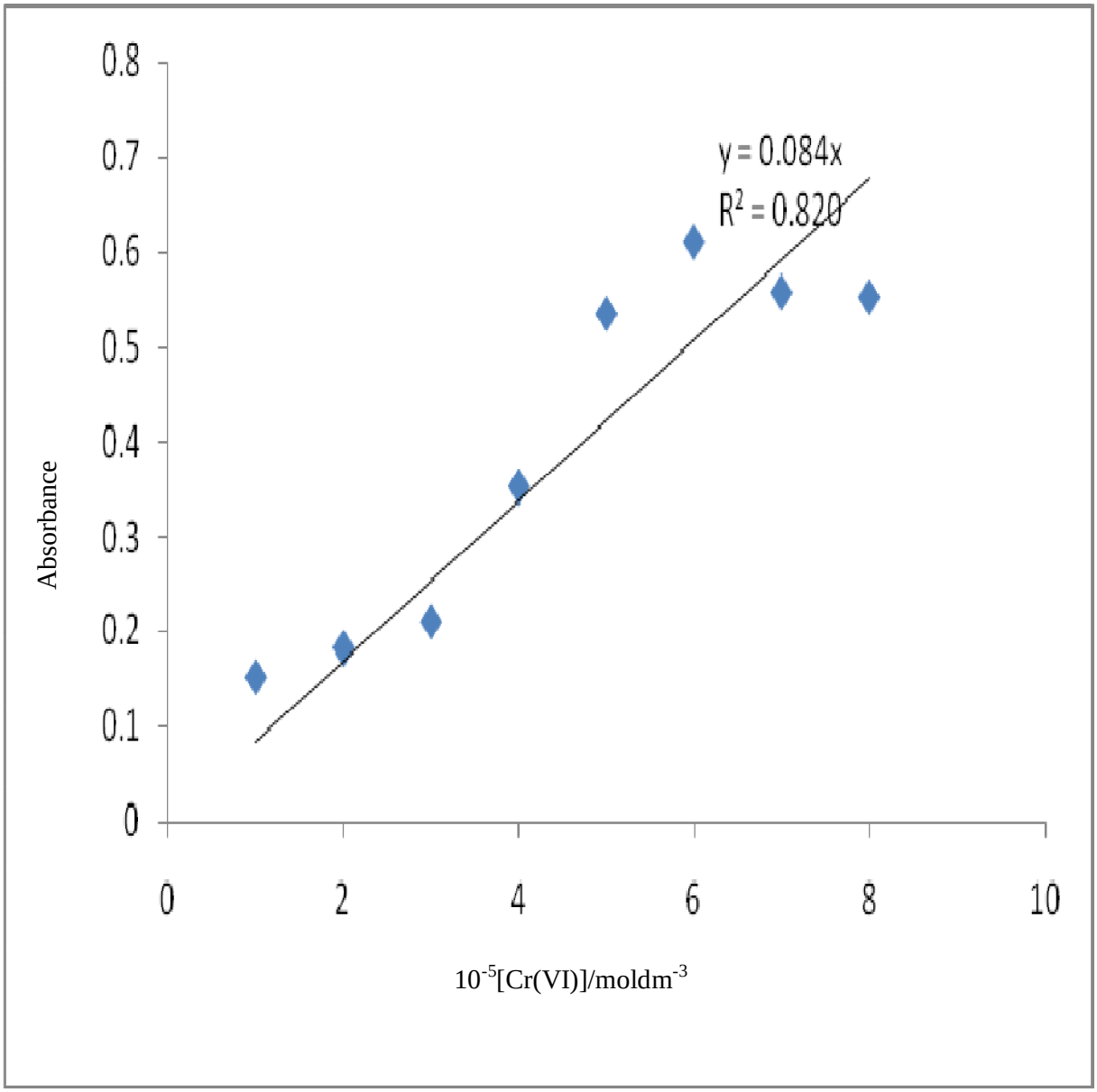


Fig 4.3 Slope-ratio plot for Cr(VI) complex at fixed ligand concentration ($1.0x10^{-3}$)M

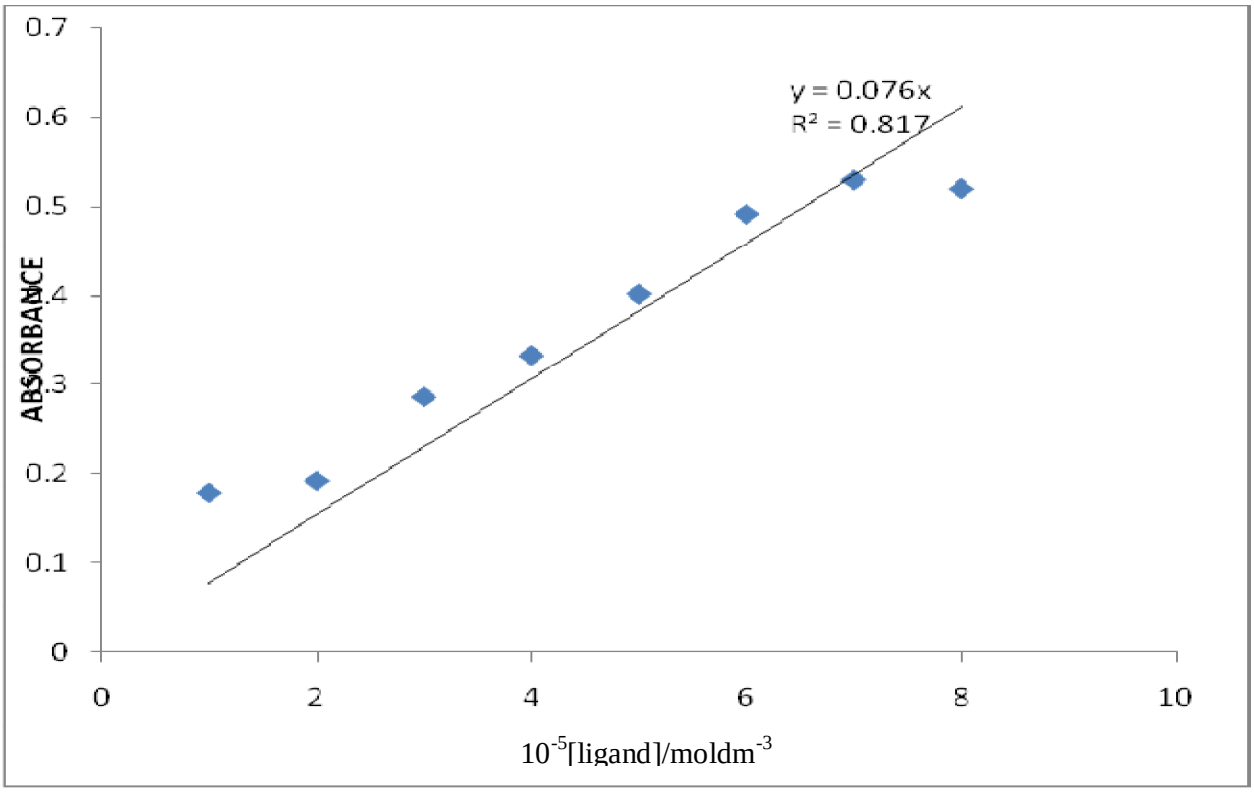
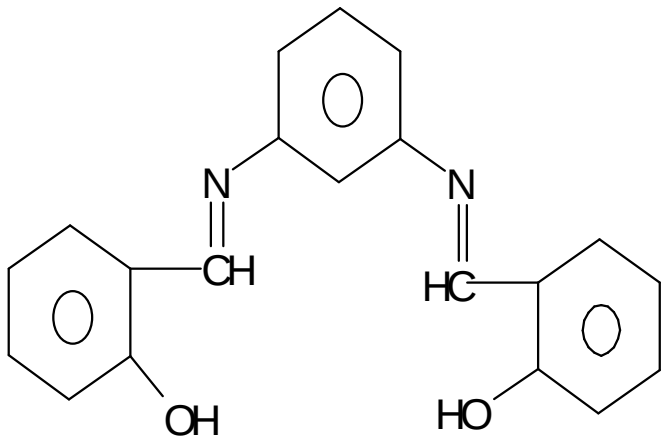


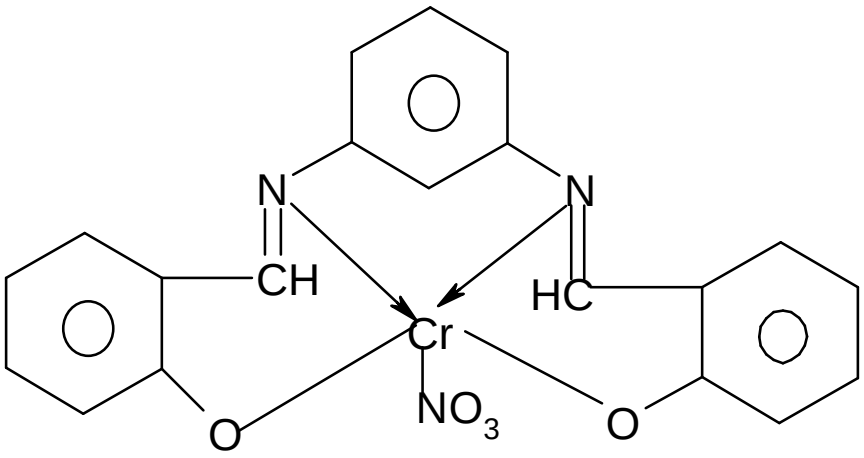
Fig4.4 Slope-ratio plot for Cr(VI) complex at fixed metal concentration ($1.0X10^{-3}M$)

4.3.3 Molecular Formulae and Structures of the Ligand and Its Complexes

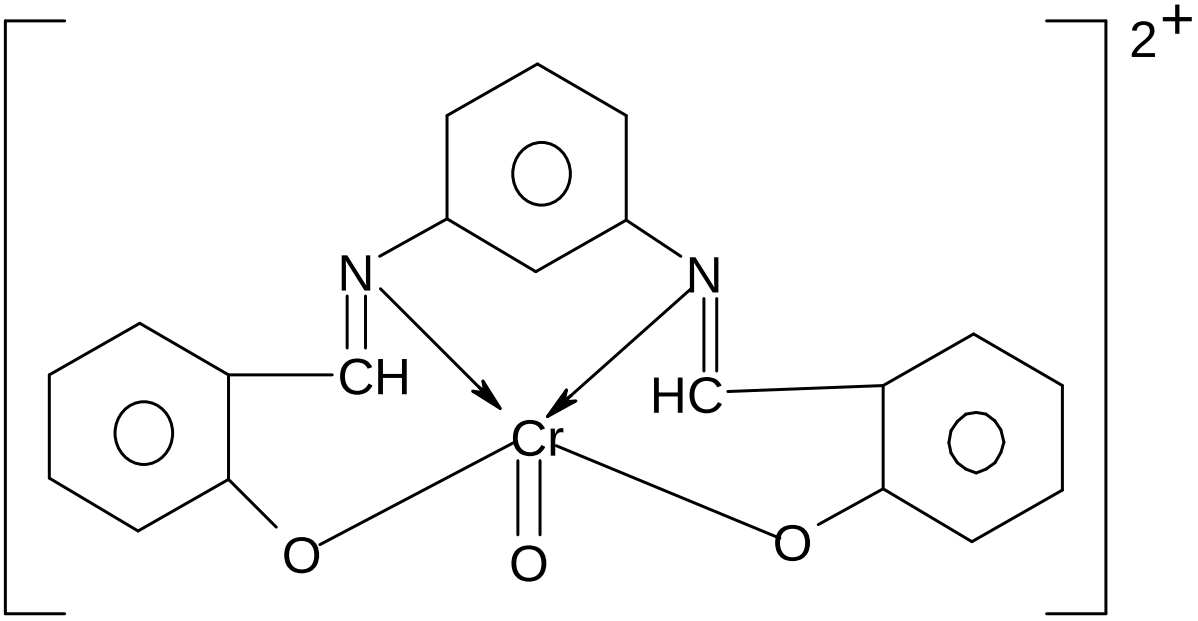
Based on the various spectral data obtained, the structures suggested for the ligand and the complexes are given in Scheme 2- 4.



Scheme 2: The ligand:2-[(E)-[{3--[(2-hydroxybenzylidene) amino]phenyl}imino) methyl]phenol (H_2BPMP)



Scheme 3: 2-[(E)-[{3-[(2-hydroxybenzylidene)amino]phenyl}imino)methyl]phenolCr(III) complex(Cr(NO_3)BMP)



Scheme 4: 2-[(E)-[{3-[(2-hydroxybenzylidene)amino]phenyl}imino)methyl]phenolCr(VI) Complex(Cr(O)BPMP)

The structures in Schemes 3 and 4 for Cr(III) and Cr(VI) complexes respectively indicate that the metal-ligand mole ratio is 1:1. The ligand is tetradentate and coordinates through the azomethine nitrogens and the phenolic oxygen atoms to the metal center giving a square pyramidal geometry

with =O occupying the apical site in the Cr(O)BPMP complex and NO_3 occupying the apical site in the Cr(NO_3)BPMP.

This complexation results in a chelate thereby leading to increased stability of the complex. The disappearance of OH band in the complexes is as a result of coordination with deprotonation of the phenolic oxygen.

4.4 Complexation Studies

4.4.1 Effect of Time on the formation of the Complexes

Fig 4.5 shows the variation of absorbance with time for the formation of the Cr(III) complex.

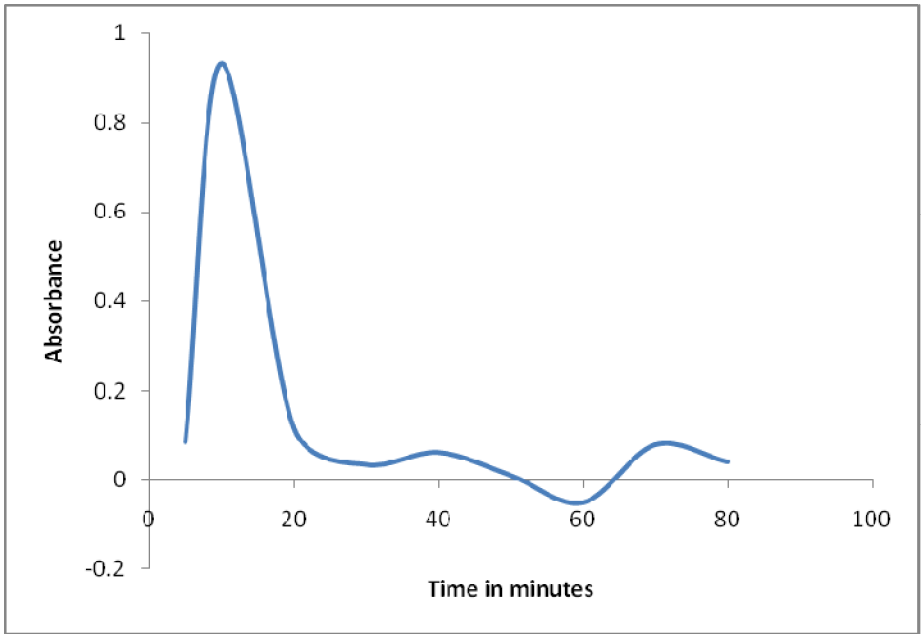


Fig 4.5: Effect of Time on the formation of Cr(III) complex

The highest absorbance of 0.932 was obtained after 10 min of the reaction. Therefore, 10 min was taken as the maximum time required for the reaction to come to completion under the prevailing conditions and was used throughout in the determination of Cr(III) ion.

Fig 4.6 shows the variation of absorbance with time for the formation of the Cr(VI) complex. The highest absorbance of 0.37 was obtained after 40 min of the reaction. Therefore 40 min was

taken as the maximum time required for the reaction to come to completion under the prevailing conditions and was used throughout in the determination of Cr(VI) ion.

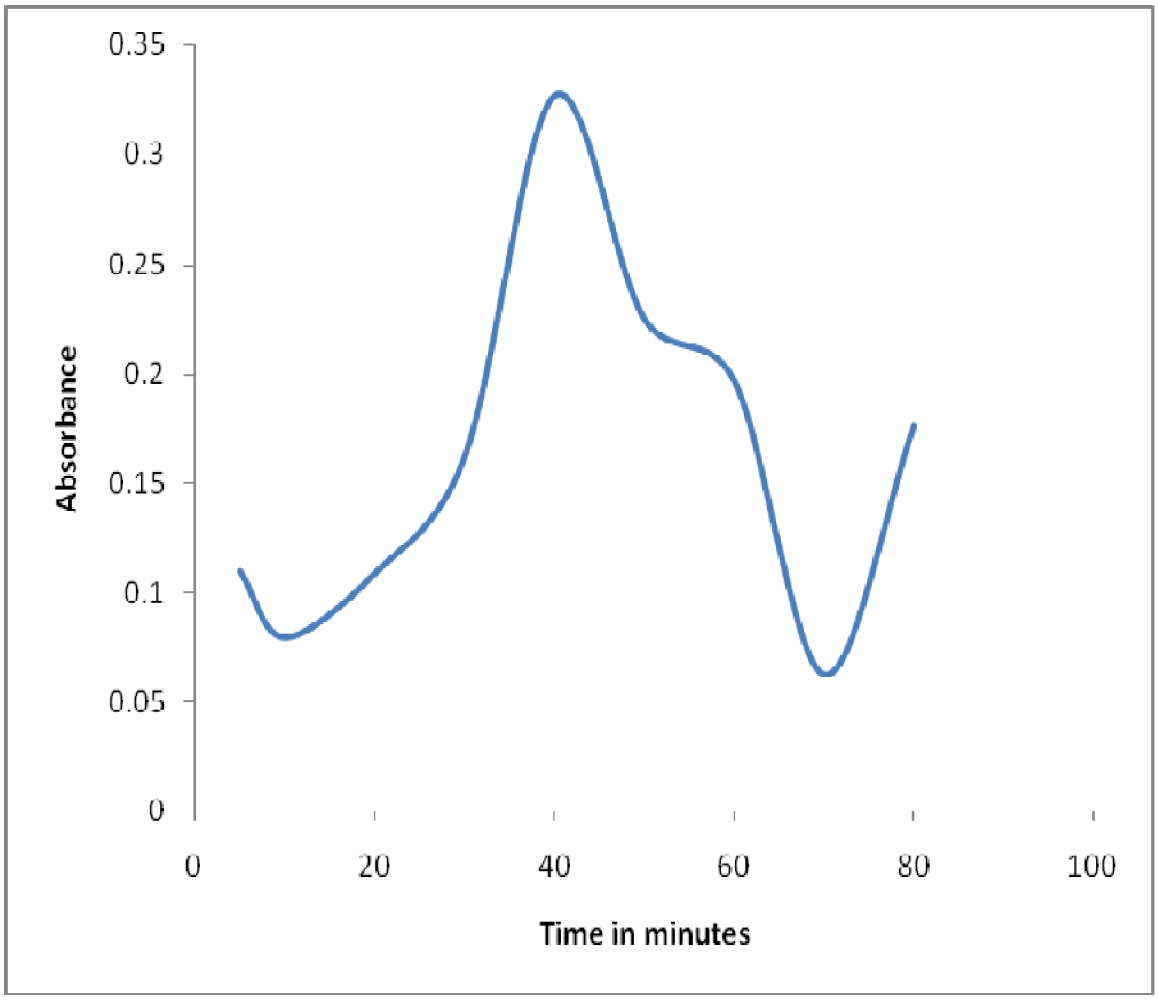


Fig4.6: Effect of Time on the formation of Cr(VI)complex

4.4.2 Effect of the concentration of the reagent on the formation of the complexes

From the results shown in Table 4.15, plots of absorbance versus concentration of Cr(III) and Cr(VI) complexes is shown in Figure 4.7 and 4.8 respectively.

The highest absorbance of 1.0 was obtained at $1x10^{-5}$ M. Therefore $1x10^{-5}$ M was taken as the maximum concentration required for the reaction to come to completion under the prevailing conditions for Cr(III) complex. The highest absorbance of 0.2 was obtained at $7x10^{-5}$ M. Therefore $7x10^{-5}$ M was taken as the maximum concentration required for the reaction to come to completion.

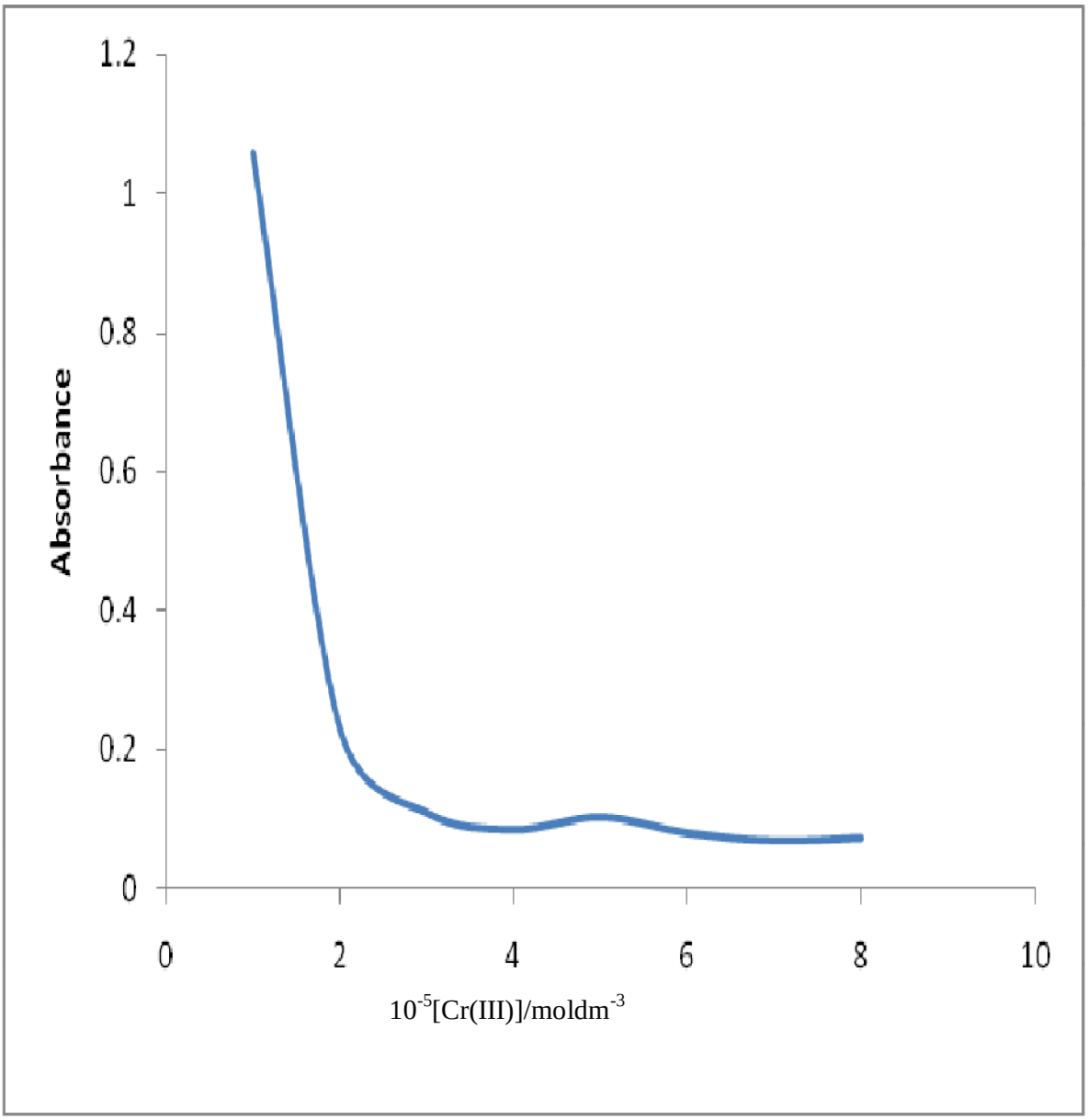


Fig4.7: Effect of concentration on the formation of Cr(III) complex

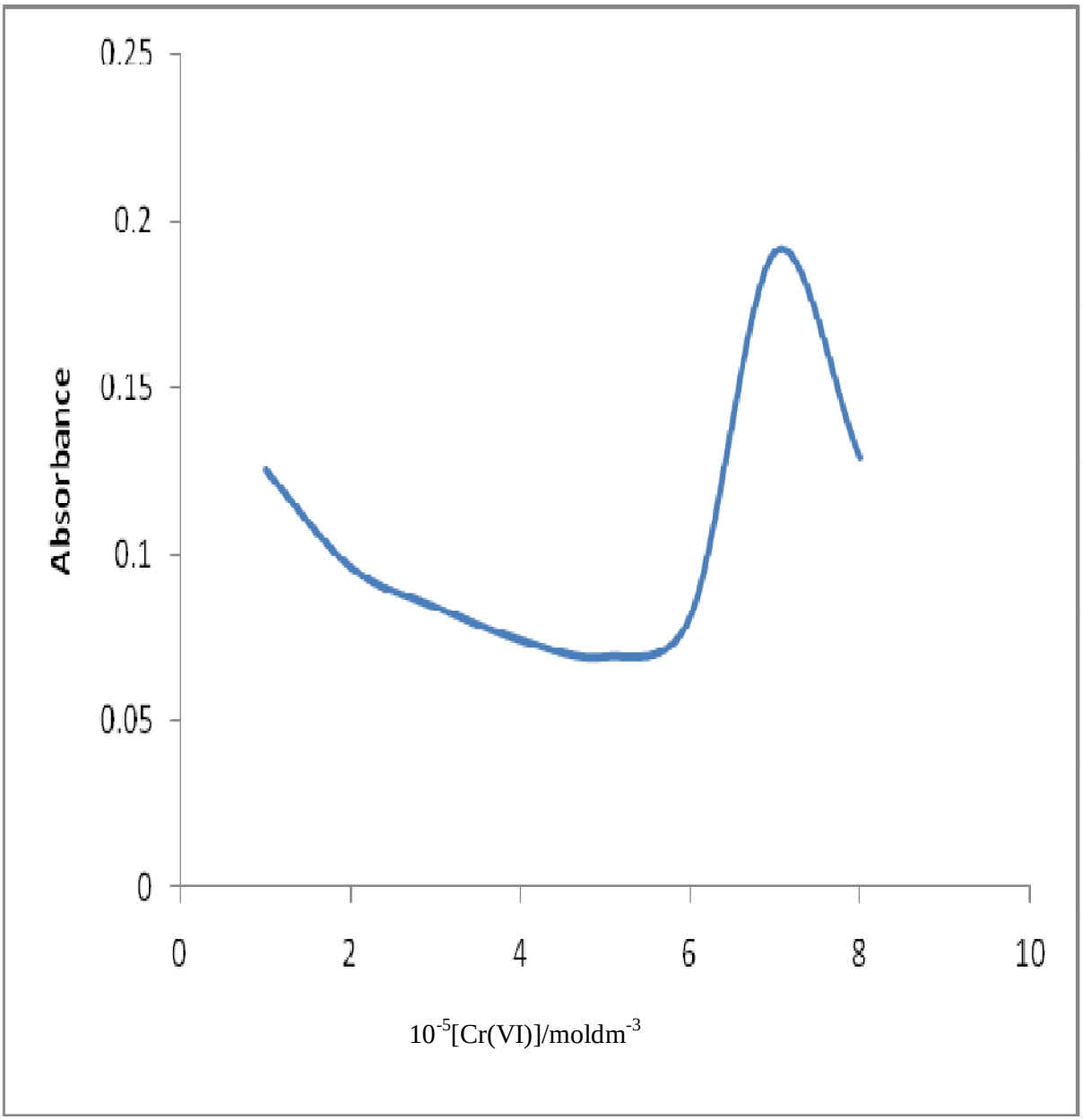


Fig4.8: Effect of concentration on the formation of Cr(VI) complex

4.4.3 Effect of temperature on the formation of the complexes

The values used for the plots on Figures 4.9 and 4.10 respectively are found in Table 4.16. Figure 4.9 shows the variation of absorbance with temperature for the formation of the Cr(III) complex.

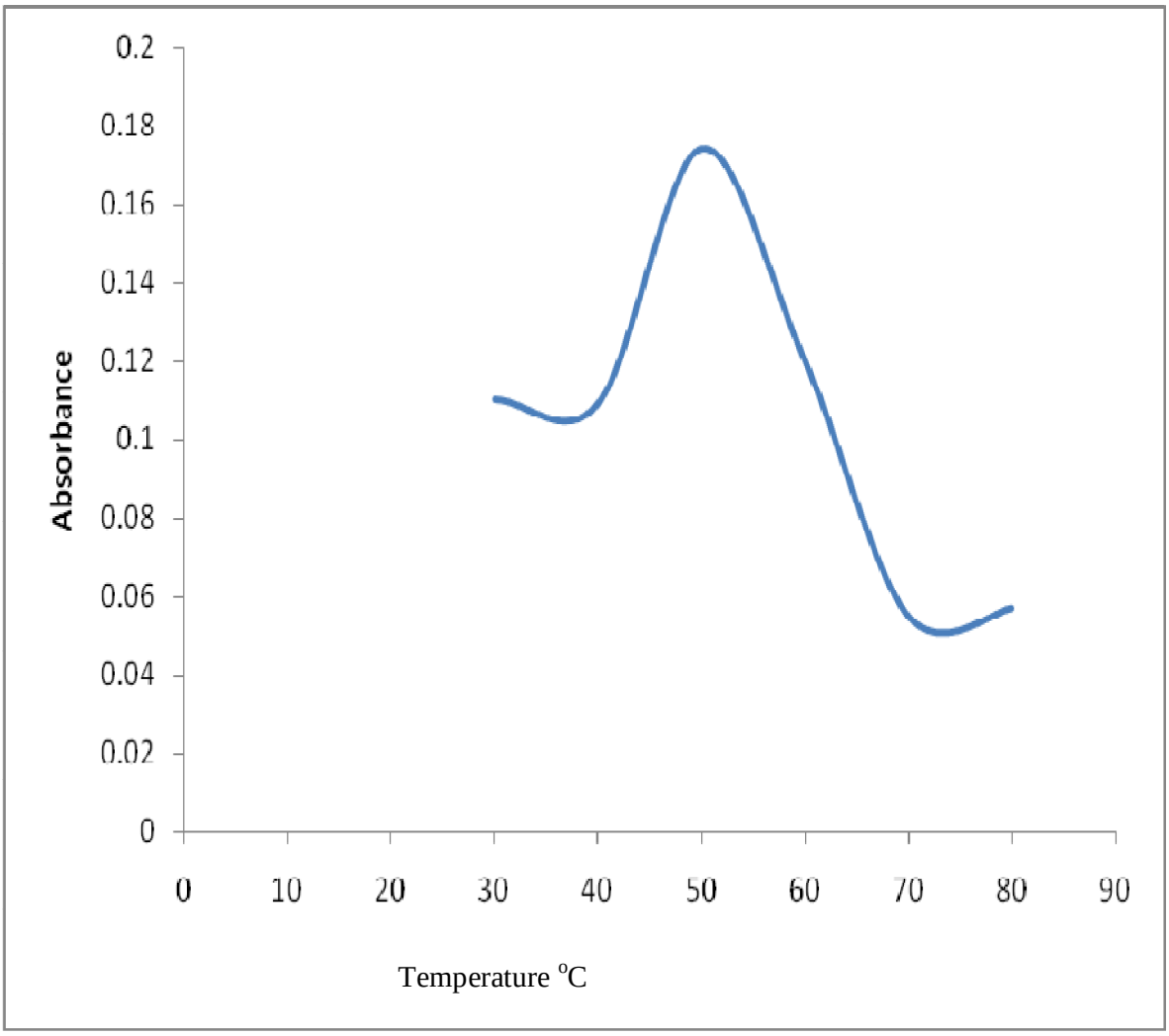


Fig4.9: Effect of Temperature on the formation of Cr(III)complex

In Figure 4.9, the highest absorbance of 0.544 was obtained at 60^0C. Therefore, 60^0C is taken as the optimum temperature required for the formation of Cr(III) complex under the prevailing conditions and was maintained throughout the determination of Cr(III) ions.

Figure 4.10 shows the variation of absorbance with temperature for the formation of the Cr(VI) complex. In Figure 4.10, the highest absorbance of 0.174 was obtained at 50^0C. Therefore 50^0C is as the optimum temperature required for the formation of Cr(VI) complex at the prevailing conditions. However, between the temperature range of 30^0 ï 70^0C, 50^0C was established as the fundamental condition and was maintained throughout in the determination of Cr(VI).

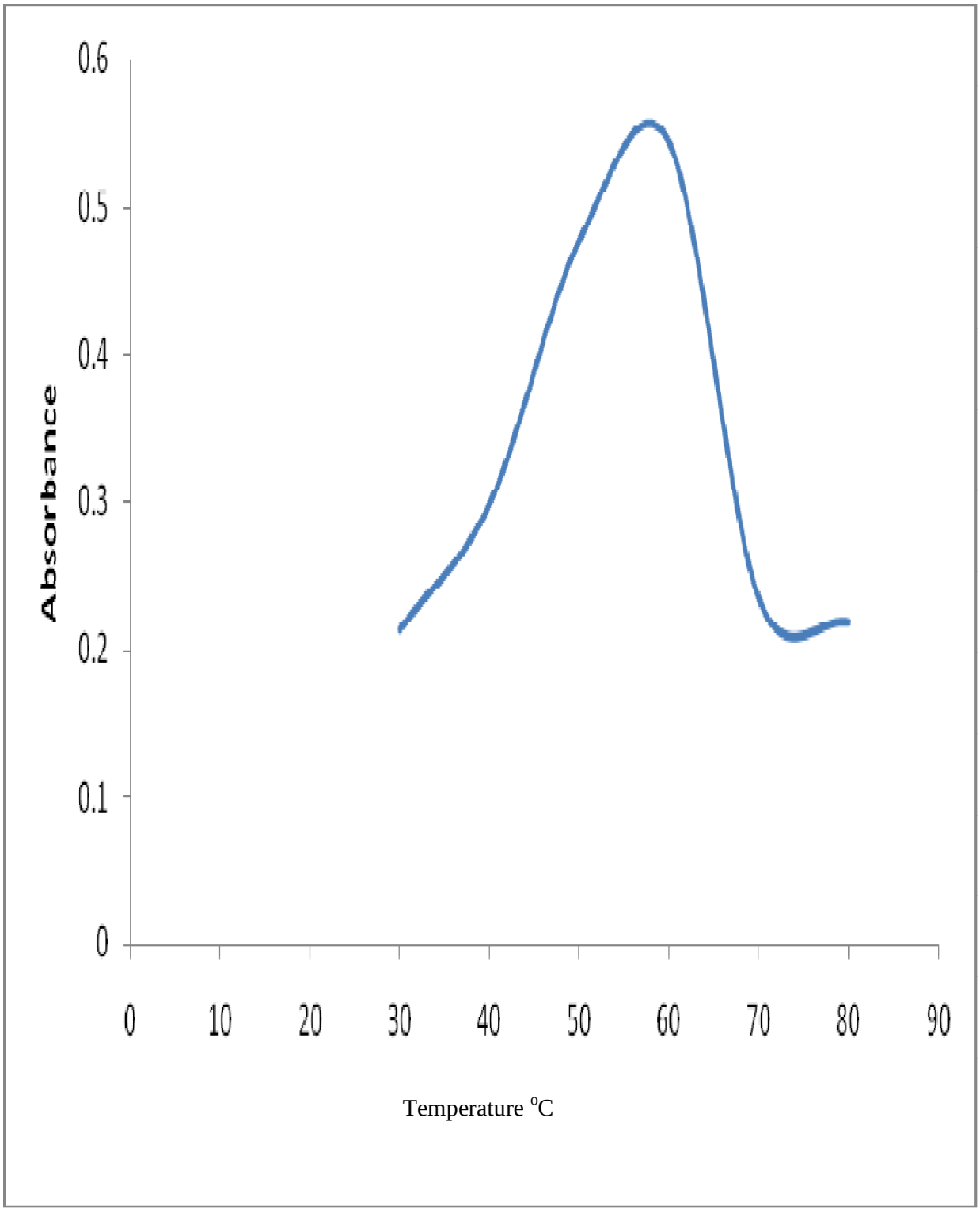


Fig4.10: Effect of Temperature on the formation of Cr(VI)complex

4.4.4 Effect of pH on the absorbance of the complexes

The values used for the plots in Figures 4.11 and 4.12 are found in Table 4.17. Figure 4.11 shows the variation of absorbance with pH for the formation of the Cr(III) complex. In Figure 4.11, the highest absorbance of 0.915 for the formation of Cr(III) complex was obtained at pH 13.0. Therefore, the pH 13.0 is taken as the fundamental condition for the determination of Cr(III) with the ligand. Figure 4.12 shows the variation of absorbance with pH for the formation of the Cr(VI) complex. In figure 4.12, the highest absorbance of 0.171 was obtained at pH2.0. Therefore, pH 2.0 is taken as the optimum pH for the formation of Cr(VI) complex under prevailing conditions and was maintained throughout in the determination of Cr(VI), this is in agreement with literature[91]

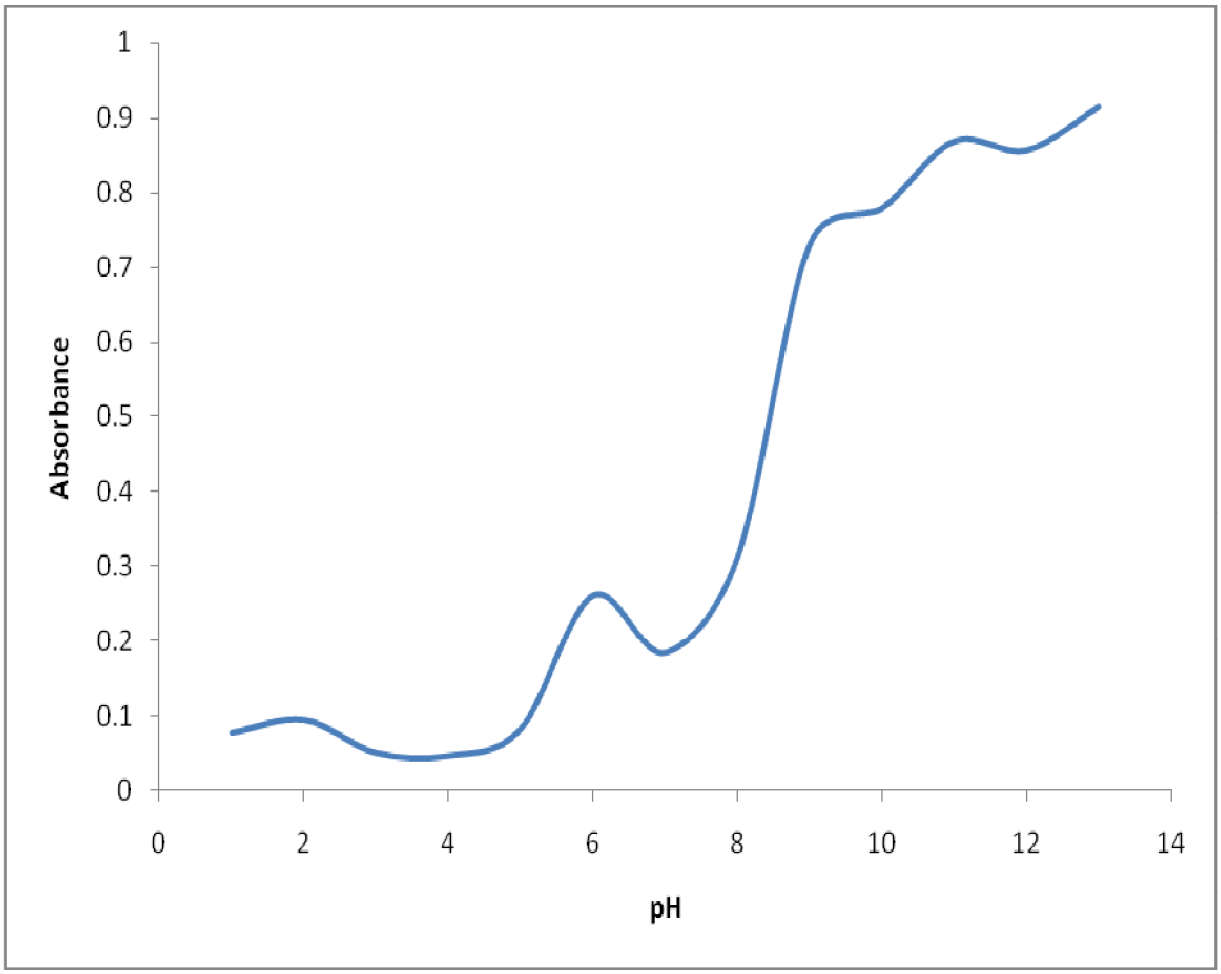


Fig4.11: Effect of pH on the formation of Cr(III)Complex

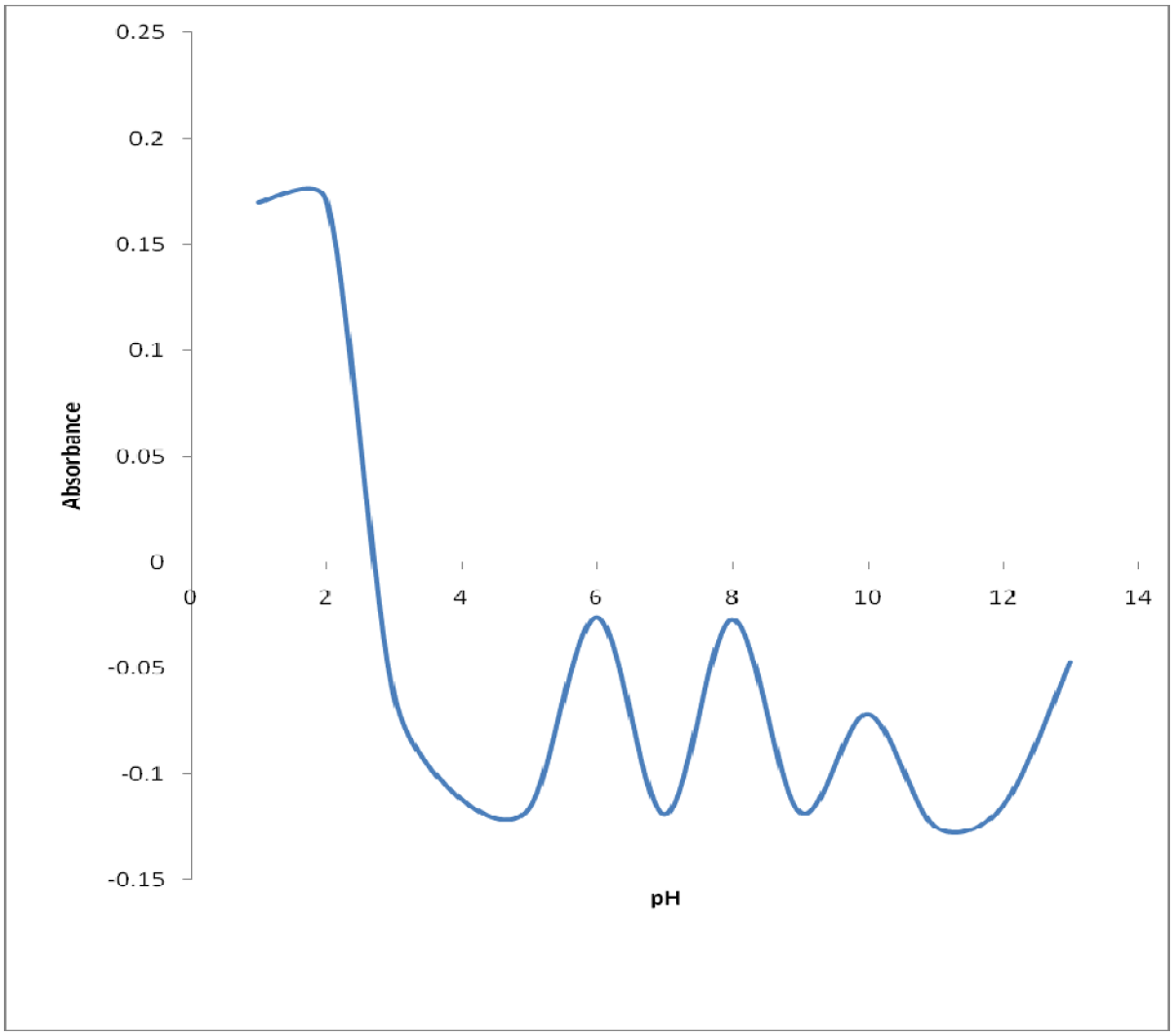


Fig4.12: Effect of pH on the formation of Cr(VI) Complex

4.4.5 Effect of interfering ions on the formation of Cr(II) and Cr(VI) complexes.

The selectivity of the proposed method was investigated by determining the effect of interfering ions on the formation of Cr(III) and Cr(VI) complexes. A fixed concentration of the metal ion under study in the presence of a series of other ions was used to fix the limiting value of concentration of the foreign ion which caused some error in absorbance corresponding to twice the standard deviation of the absorbance of the complexes.

Cr(III) complex

Cr(III) ion (1.14) was determined in the absence of foreign ions. The mean absorbance for five determinations is ±0.595. The interference levels in the absorbance of 1.14ppm Cr(III) complex with various proportions of foreign ions are shown in Table 4.6

Table 4.6. Effect of some interfering ions on Cr(III) determination.

Ion Added	Concentration (ppm)	Absorbance	Interference level (%)
Mg^{2+} added as MgO	0.8	0.458	-23.03%
	1.2	0.448	-24.71%
	1.6	0.446	-25.04%
	2.0	0.379	-36.30%
	2.4	0.445	-25.21%
	2.8	0.497	-16.47%
	3.2	0.578	-2.857%
Fe^{3+} added as $FeCl_3.6H_20$	0.8	1.082	81.8%
	1.2	1.777	198.7%
	1.6	1.910	221%
	2.0	1.917	222%
	2.4	1.859	212%
	2.8	0.760	27.7%
	3.2	0.642	7.9%
Zn^{2+} added as Zn0	0.8	0.451	-24.2%
	1.2	0.474	-20.3%
	1.6	0.505	-15.1%
	2.0	0.496	-16.6%
	2.4	0.545	-8.4%
	2.8	0.531	-10.8%
	3.2	0.492	-17.3%

In general, the interfering ions form complexes with the ligand. Magnesium and zinc ions interfered with the complexation of Cr(III) with the ligand and this is shown by the interference level which is negative. In the case of Fe(III), the interference was positive as shown from the percentage interference level. The interference of Fe(III) can be eliminated with ascorbic acid. The interference of all these ions can be reduced by pre-extraction with potassium cyanide.

Cr(VI) Complex

Cr(VI) ion(1.14 ppm) was determined in the absence of foreign ions. The mean absorbance for five determinations is 0.287 nm. The interference levels in the determination of 1.14 ppm Cr(VI) ion with

various proportions of foreign ions are shown in Table 4.7. From the Table 4.7, there was as interference but the ions interfered by suppressing the absorbance.

Table 4.7 Effect of some interfering ions on Cr(VI) determination.

Ion Added	Concentration (ppm)	Absorbance	Interference level (%)
Co^{2+} added as $CoCl_2$	0.8	0.006	-97.9%
	1.2	0.191	-33.4%
	1.6	0.242	-15.7%
	2.0	0.115	-59.9%
	2.4	0.087	-69.7%
	2.8	0.068	-76.3%
	3.2	0.175	-39.02%
Cu^{2+} added as $CuS0_4$	0.8	0.080	-72.1%
	1.2	0.091	-68.3%
	1.6	0.074	-74.2%
	2.0	0.078	-72.8%
	2.4	0.097	-66.2%
	2.8	0.100	-65.2%
	3.2	0.208	-27.5%
Mn^{2+} added as $MnCl_2.4H_20$	0.8	0.132	-54%
	1.2	0.134	-53.3%
	1.6	0.146	-49.1%
	2.0	0.134	-53.3%
	2.4	0.154	-46.3%
	2.8	0.149	-48.1%
	3.2	0.130	-54.7%

4.5. Calibration curve for the Determination of Cr(III) and Cr(VI) complexes

The calibration curve was constructed to validate the linearity of the Cr(III) and Cr(VI) complexes.

4.5.1 Cr(III) Complex

The calibration curve of Cr(III) shows a good linear relationship. Beerôs law is obeyed between concentration ranges of 0.02 to 0.14 ppm. The calibration curve which was constructed under the prevailing conditions is shown in Figure 4.13.

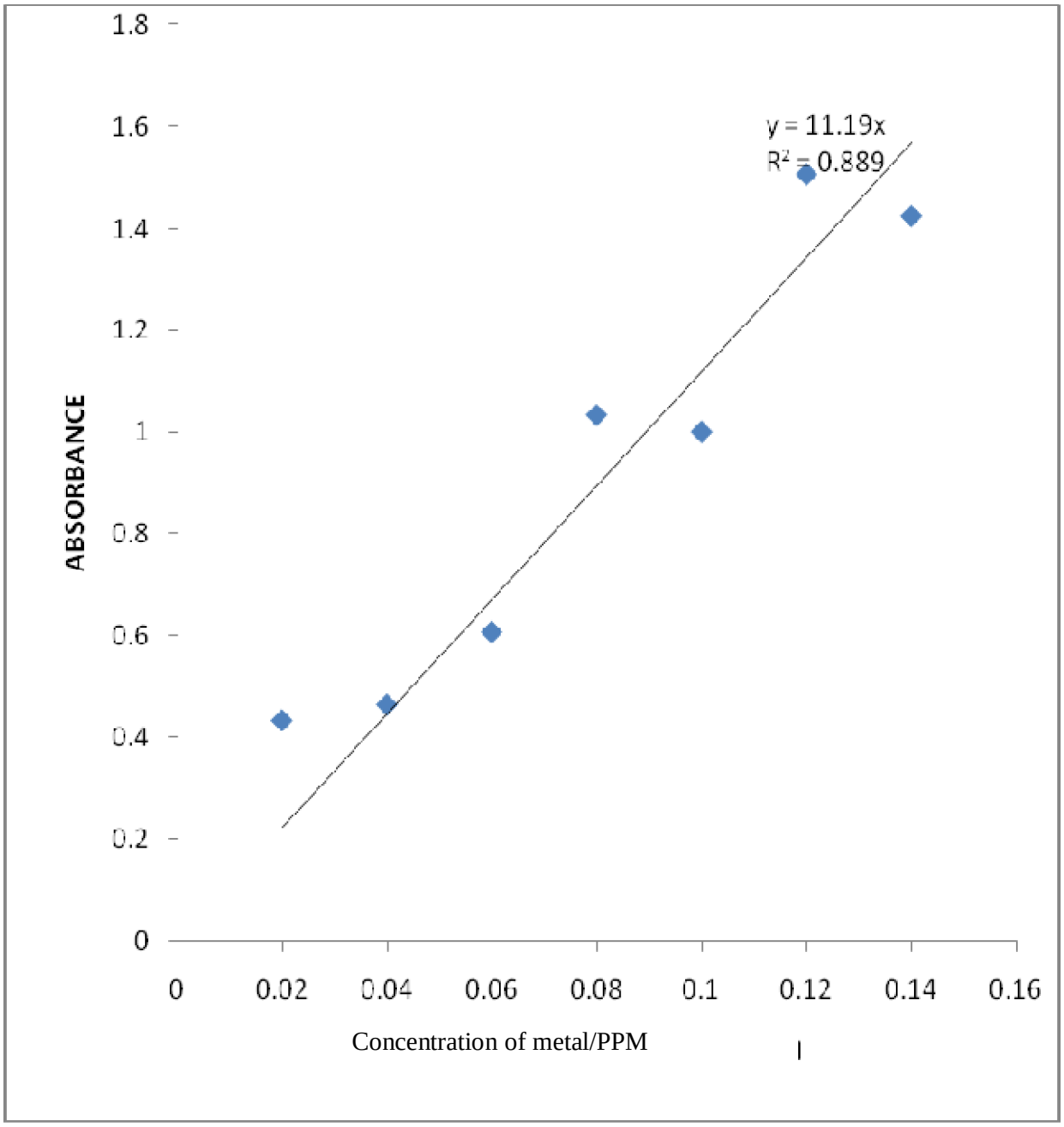


Fig. 4.13 Calibration curve of Cr(III) complex

4.5.2 Cr(VI) complex

The calibration curve constructed for Cr(VI) complex shows adherence to Beerôs law over the concentration range of 0.02 to 0.14 ppm. The plot is shown in Figure 4.14

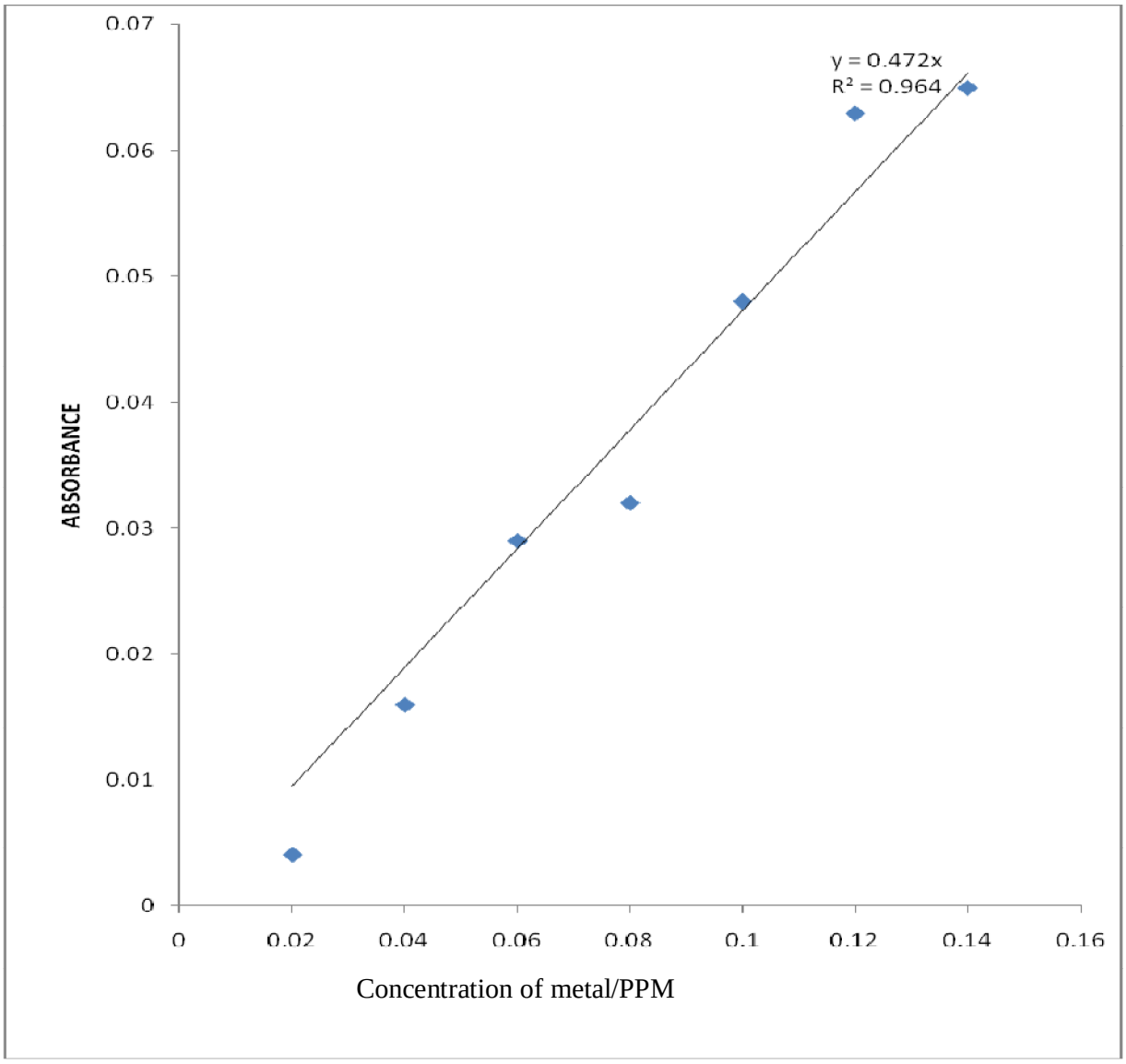


Fig4.14 Calibration Curve of Cr(VI) Complex

4.6 Application using steel solution

Using AAS the concentration of chromium in the steel solution is 3.7 ppm. Fe(III) was extracted from the steel solution with $3.1x10^{-3}$ M solution of KCN at room temperature. The same concentration of KCN was also used to mask Cu(II), Ni(II), Mn(II), Mg(II) and several other ions.

In the calibration curve the Beer Lambert law was obeyed between 0.00002 to 0.00008 M or 0.02 to 0.08 ppm. An equimolar concentration of the chromium in steel and the ligand being 0.37 ppm were prepared.

4.6.1 Determination of Cr(III) in the steel solution.

The determination was done based on established condition: ɔ= 366 nm, pH= 13, T=60^{0}C and t=10 min.

Table 4.8: Determination of Cr(III) in the steel solution.

S/No	Vol of steel (cm^3)	Vol of KCN (cm^3)	Vol of Buffer (cm^3)	Vol of Ligand (cm^3)	Absorbance			Mean Aborbance
1	0.2	0.4	4.2	0.2	0.130	0.137	0.133	0.133
2	0.4	0.4	4.2	0.4	0.236	0.243	0.239	0.239
3	0.6	0.4	3.8	0.6	0.397	0.389	0.395	0.394
4	0.8	0.4	3.0	0.8	0.644	0.645	0.656	0.658
5	1.0	04	2.6	1.0	0.752	0.776	0.772	0.767

4.6.2: Determination of Cr(VI) in steel solution

The determination was done based on established condition: ɔ= 465 nm, pH= 2, T=50^{0}C and t=40 min.

Table 4.9: Determination of Cr(VI) in the steel solution.

S/No	Vol of Steel (cm^3)	Vol of KCN (cm^3)	Volume of Buffer (cm^3)	Volume of Ligand (cm^3)	Absorbance			Mean absorbance
1	0.2	0.4	4.2	0.2	0.150	0.145	0.152	0.144
2	0.4	0.4	3.8	0.4	0.146	0.150	0.152	0.149
3	0.6	0.4	3.4	0.6	0.155	.0.153	0.150	0.153
4	0.8	0.4	3.0	0.8	0.170	0.172	0.168	0.170
5	1.0	0.4	2.6	1.0	0.166	0.171	0.178	0.172

4.7 Conclusion

In conclusion, the synthesis of 2-[(E)-[{3--[(2-hydroxybenzylidene) amino] phenyl}imino)methyl] phenol and its Cr(III) and Cr(VI) complexes were successful. The optimum condition for the complexation of the ligand and Cr(III) and Cr(VI) ions were established using the effect of time, effect of concentration, effect of temperature, pH and interfering ions. The Beer-Lambert plot of the complexes showed good linearity relationship. The application of the new method was validated using steel solution.

4.8 Recommendation

I recommend that the mass spectrograph and single crystal of these complexes be generated to enable the X-ray diffraction study to fully elucidate the structures. It is also important that the biological activities of the complexes be evaluated for possible serendipitous pharmaceutical breakthrough.

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APPENDIX A

Table 4.10: Result of slope-Ratio plot for Cr(III) complex-fixed ligand(1.0X 10^{-3} M)

CONCENTRATION OF Cr(III); X 10^{-5}M	ABSORBANCE
1.0	0.050
2.0	0.120
3.0	0.230
4.0	0.334
5.0	0.351
6.0	0.376
7.0	0.330
8.0	0.335

Table 4.11: Result of Slope- Ratio plot for Cr(III) complex- fixed metal(1.0 X10^{-3} M)

CONCENTRATION OF LIGAND ; X 10^{-5} M	ABSORBANCES
1.0	0.059
2.0	0.130
3.0	0.209
4.0	0.263
5.0	0.338
6.0	0.419
7.0	0.463
8.0	0.529

Table 4.12: Result of Slope-Ratio plot for Cr(VI) complex; fixed ligand(1.0 X 10^{-3} M)

CONCENTRATION OF Cr (VI) ; X10^{-5} M	ABSORBANCES
1.0	0.152
2.0	0.182
3.0	0.200
4.0	0.352
5.0	0.535
6.0	0.610
7.0	0.558
8.0	0.553

Table 4.13: Result of Slope- Ratio plot for Cr (VI) complex; fixed metal(1.0 X^{-3}M)

CONCENTRATION OF LIGAND ; $x10^{-5}$ M	ABSORBANCES
1.0	0.178
2.0	0.192
3.0	0.286
4.0	0.333
5.0	0.402
6.0	0.492
7.0	0.530
8.0	0.520

Table 4.14:Variation of absorbances with time for the formation of the complexes

TIME(MINUTES)	ABSORBANCE FOR Cr(III) COMPLEX	ABSORBANCES FOR Cr(VI) COMPLEX
5.00	0.084	0.110
10.00	0.934	0.080
20.00	0.117	0.109
30.00	0.034	0.162
40.00	0.061	0.327
50.00	0.010	0.225
60.00	-0.051	0.197
70.00	0.078	0.063
80.00	0.040	0.176

TABLE 4.15: Variation of absorbances with reagent concentration for the formation of complexes.

CONCENTRATION OF METAL; X 10^{-5} M	ABSORBANCE FOR Cr(III) COMPLEX	ABSORBANCE FOR Cr(VI) COMPLEX
1.0	1.058	0.125
2.0	0.231	0.096
3.0	0.111	0.084
4.0	0.087	0.074
5.0	0.1O5	0.069
6.0	0.O82	0.081
7.0	0.071	0.191
8.0	0.075	0.129

TABLE 4.16: Variation of absorbances with temperature for the formation of the complexes.

TEMPERATURE (^{O}C)	ABSORBANCE OF Cr(III) COMPLEX	ABSORBANCE OF Cr (VI) COMPLEX
30	0.213	0.110
40	0.298	0.109
50	0.477	0.174
60	0.544	0.120
70	0.234	0.055
80	0.218	0.057

TABLE 4.17: Variation of absorbances with pH for the formation of the complexes.

PH	ABSORBANCE OF Cr(III) COMPLEX	ABSORBANCE OF Cr(VI) COMPLEX
1.0	0.078	0.170
1.0	0.095	0.171
3.0	0.051	-0.063
4.0	0.047	-0.112
5.0	0.083	-0.116
6.0	0.261	-0.026
7.0	0.184	-0.119
8.0	0.311	-0.027
9.0	0.731	-0.118
10.0	0.779	-0.072
11.0	0.868	-0.125
12.0	0.856	-0.115
13.0	0.915	-0.047

TABLE 4.18: Results of calibration curves for Cr(III) and Cr(VI) complexes

CONCENTRATION(PPM)	ABSORBANCE OF Cr(III) COMPLEX	ABSORBANCE OF Cr(VI) COMPLEX
0.02	0.434	0.004
0.04	0.465	0.016
0.06	0.608	0.029
0.08	1.034	0.032
0.10	1.001	0.048
0.12	1.507	0.063
0.14	1.426	0.065

APPENDIX B

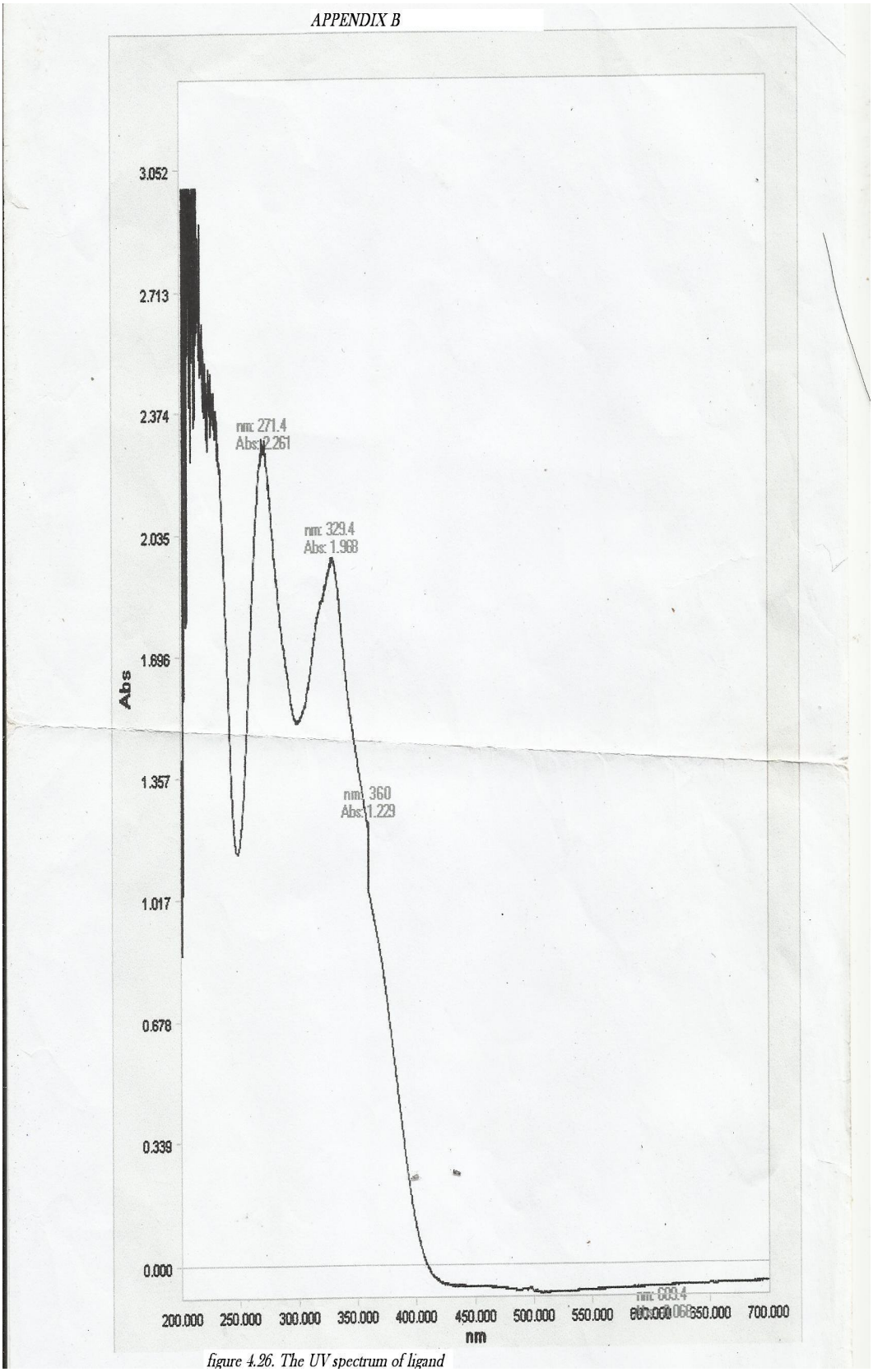


figure 4.26. The UV spectrum of ligand

APPENDIX B

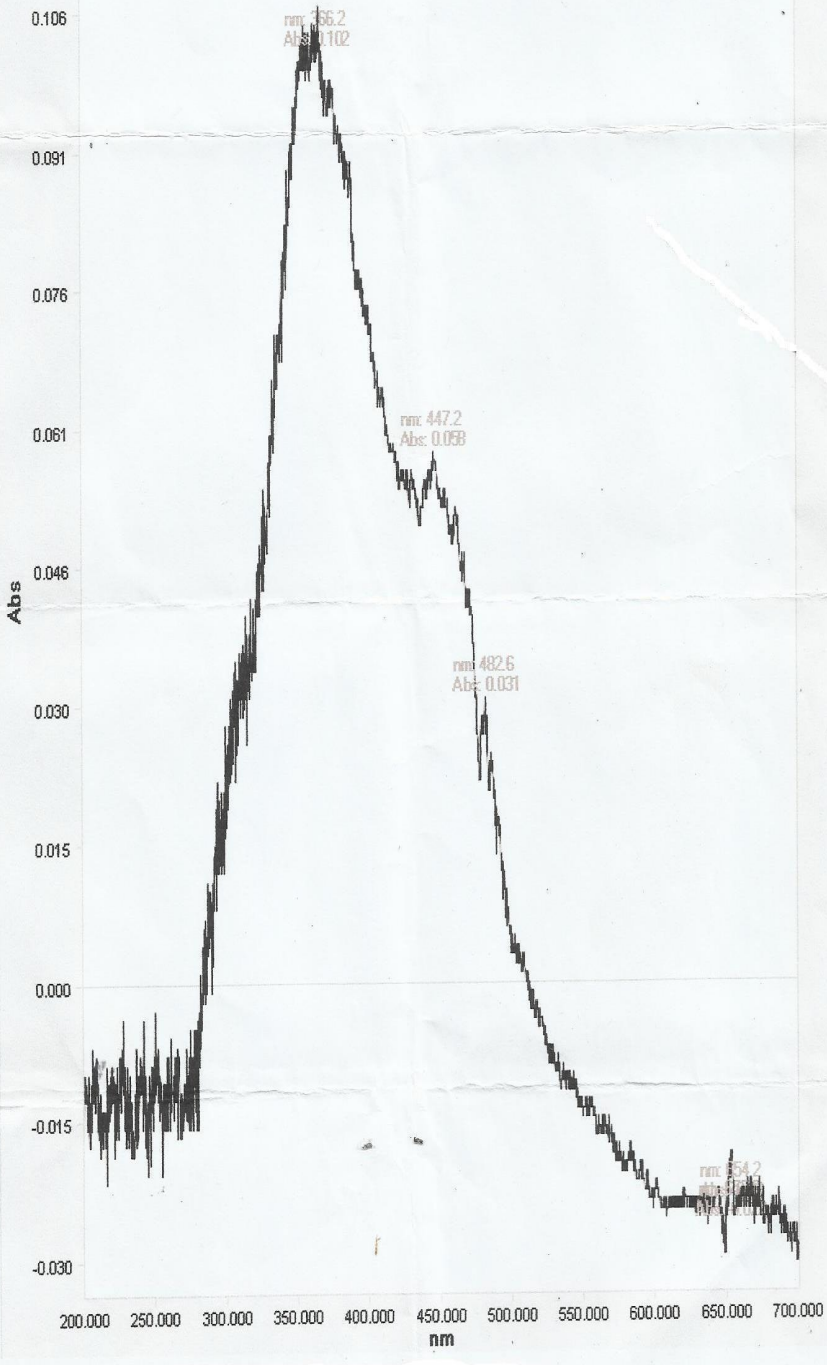


figure 4.27. The spectrum of the Cr(111) complex

APPENDIX B

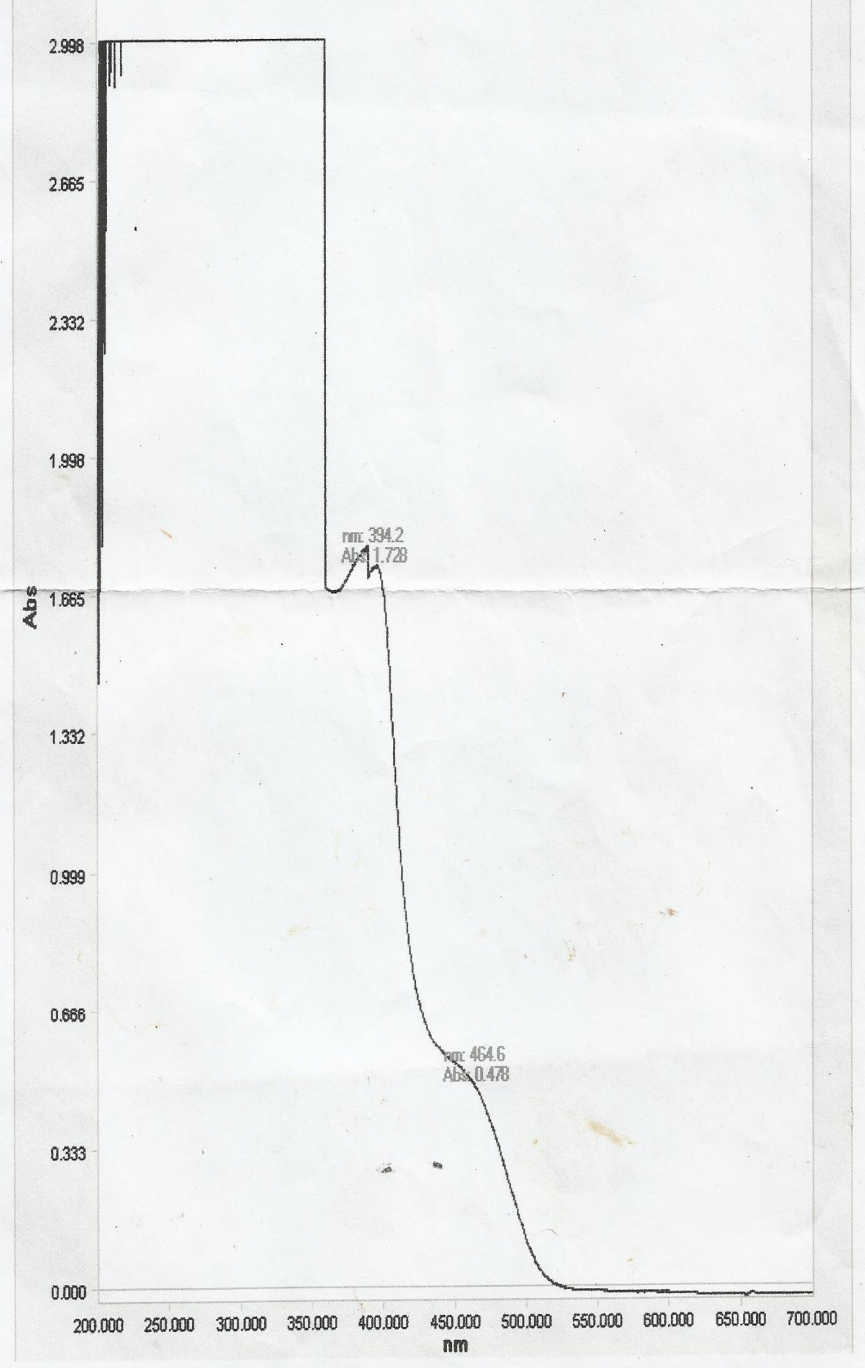


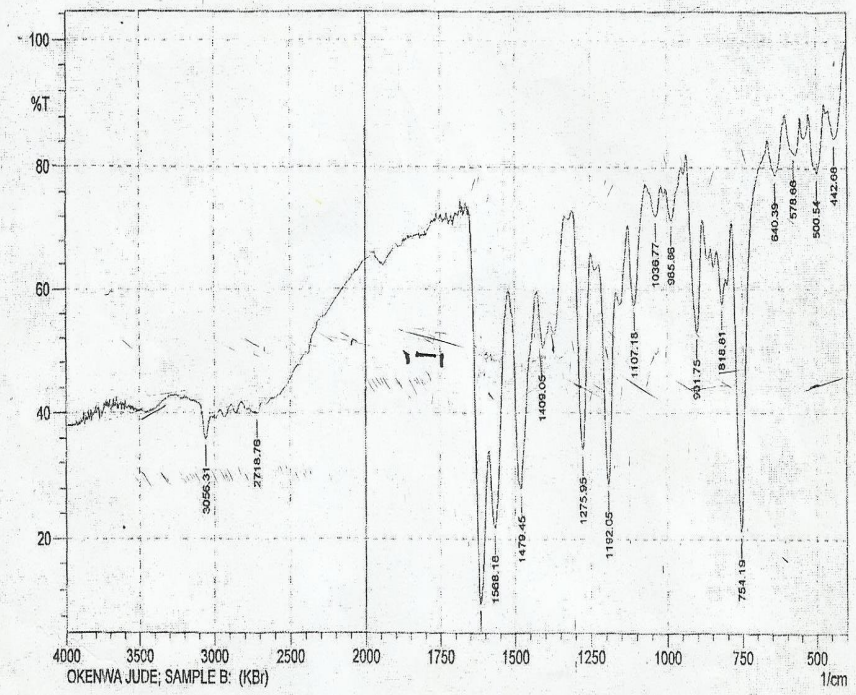
figure 4.28. The UV spectrum of the Cr(VI) complex

APPENDIX B

SHIMADZU

FTIR ANALYSIS RESULT NARICT,ZARIA

FTIR- 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	442.68	84.6545	0.2439	446.54	441.71	0.3426	0.008
2	500.54	79.1494	2.0584	505.37	475.47	2.4546	0.3596
3	578.66	82.4349	0.1193	585.42	577.7	0.638	0.003
4	640.39	78.7264	7.0687	665.46	614.35	4.5392	1.142
5	754.19	21.3026	52.8857	786.98	695.36	26.4768	15.2099
6	818.81	57.5582	6.0938	836.17	806.27	6.3917	0.594
7	901.75	52.8736	22.4223	936.47	882.46	10.5898	4.347
8	985.66	71.3785	6.4715	1003.98	953.83	6.3027	0.9685
9	1036.77	72.0862	4.485	1057.03	1019.41	4.9264	0.5571
10	1107.18	57.345	15.595	1127.43	1069.56	10.4284	2.8204
11	1192.05	28.7256	32.6953	1225.3	1166.01	20.4557	7.9032
12	1275.95	34.142	34.6885	1309.71	1249.91	17.6219	8.1324
13	1409.05	50.3457	0.9979	1426.41	1407.12	5.0466	0.0185
14	1479.45	28.0468	4.5784	1486.2	1431.23	20.82	-0.2645
15	1568.18	21.8442	0.9396	1586.5	1567.21	11.1041	0.282
16	1615.44	10	40.5627	1654.98	1586.5	36.9678	16.2901
17	2718.76	40.0598	0.6242	2733.22	2680.18	20.6674	0.2022
18	3056.31	35.7399	4.6142	3123.82	3017.73	43.2032	1.747

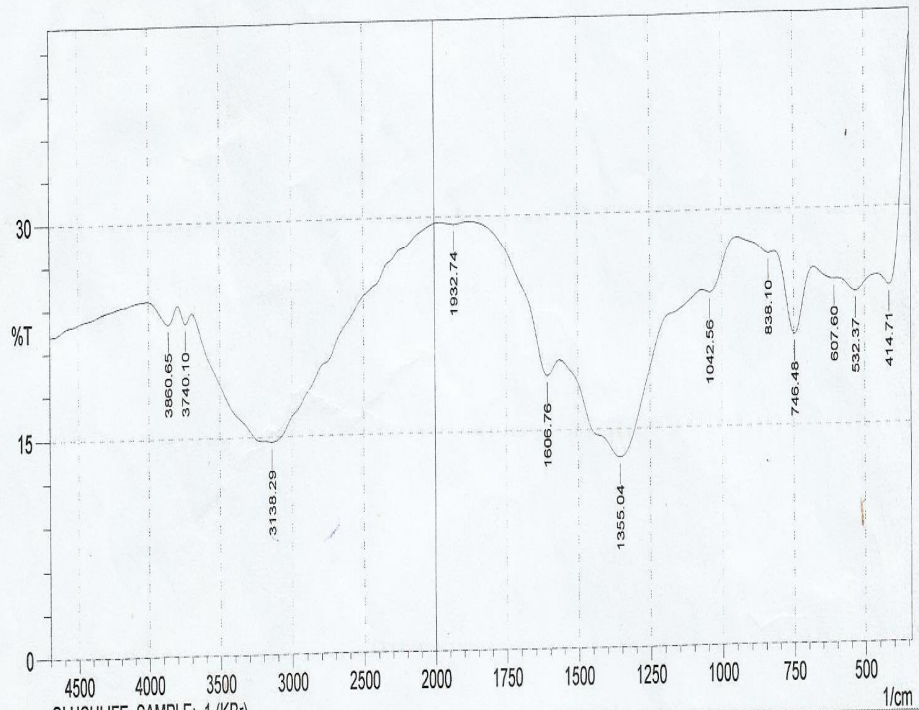
Figure 4.29. The IR spectrum of the ligand

APPENDIX B

SHIMADZU

FTIR ANALYSIS RESULT NARICT,ZARIA

FTIR- 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



OLUCHI IFE, SAMPLE: 1 (KBr)

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	414.71	24.503	6.855	457.14	339.48	63.748	6.641
2	532.37	24.152	0.957	596.99	458.11	84.355	1.022
3	607.6	25.011	0.102	678.97	597.95	48.367	0.18
4	746.48	21.237	5.158	817.85	679.93	85.375	5.618
5	838.1	26.899	0.251	947.08	818.81	71.977	0.143
6	1042.56	24.275	0.945	1068.6	948.04	70.856	0.906
7	1355.04	13.003	8.782	1563.36	1069.56	367.288	42.87
8	1606.76	18.781	2.401	1876.8	1564.32	188.845	2.416
9	1932.74	29.475	0.161	1983.85	1877.76	56.154	0.121
10	3138.29	14.648	10.955	3693.81	1984.82	1169.189	182.926
11	3740.1	22.971	0.952	3794.11	3694.77	62.542	0.871
12	3860.65	22.944	1.384	4009.18	3795.07	133.724	2.535

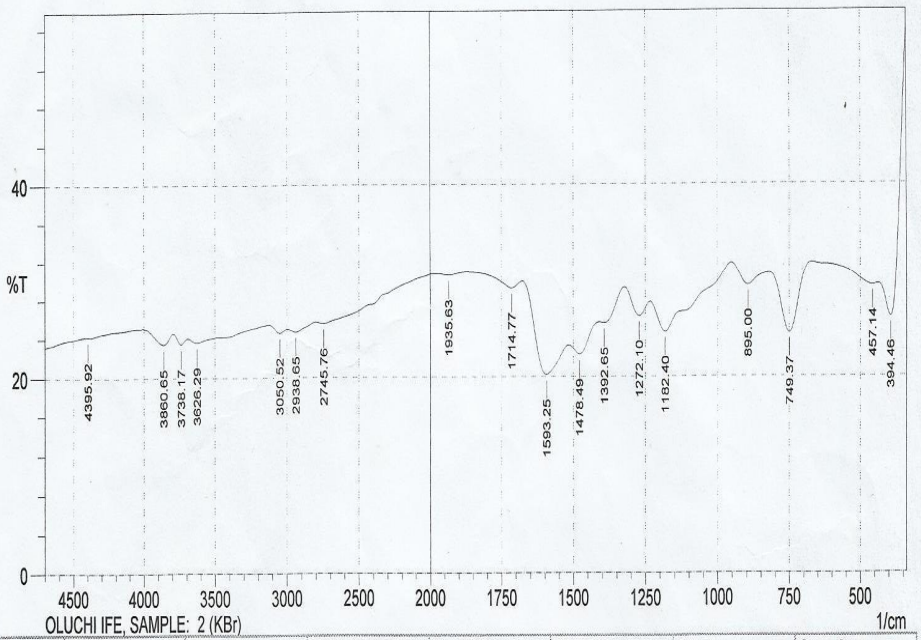
Figure 4.30. The IR Spectrum of the Cr(III) complex

APPENDIX B

SHIMADZU

FTIR ANALYSIS RESULT NARICT,ZARIA

FTIR- 8400S FOURIER TRANSFORM
INFRARED SPECTROPHOTOMETER



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	394.46	26.173	15.079	437.86	339.48	47.711	9.452
2	457.14	29.447	0.308	671.25	438.82	118.704	0.21
3	749.37	24.505	6.759	820.74	672.21	81.495	6.542
4	895	29.468	1.852	951.9	821.7	67.383	1.603
5	1182.4	24.643	3.849	1233.52	952.87	156.295	8.372
6	1272.1	26.283	2.119	1322.25	1234.48	49.369	1.511
7	1392.65	25.558	0.804	1410.01	1323.21	49.496	0.739
8	1478.49	22.322	1.799	1516.1	1410.98	65.882	1.585
9	1593.25	20.228	6.211	1677.16	1517.06	101.691	9.044
10	1714.77	29.212	0.896	1872.94	1678.13	101.337	0.717
11	1935.63	30.597	0.223	1980.96	1873.91	54.866	0.164
12	2745.76	25.612	0.486	2799.77	1981.92	452.898	3.413
13	2938.65	24.749	0.491	2994.59	2800.73	116.2	0.816
14	3050.52	24.656	0.561	3125.75	2995.55	78.402	0.579
15	3626.29	23.681	0.604	3690.91	3126.71	344.764	3.091
16	3738.17	23.524	0.849	3793.14	3691.88	62.827	0.775
17	3860.65	23.494	1.313	4007.25	3794.11	131.105	2.388
18	4395.92	24.249	0.036	4411.35	4008.21	244.522	0.051

Figure 4.31. The IR Spectrum of the Cr(VI) complex

APPENDIX B

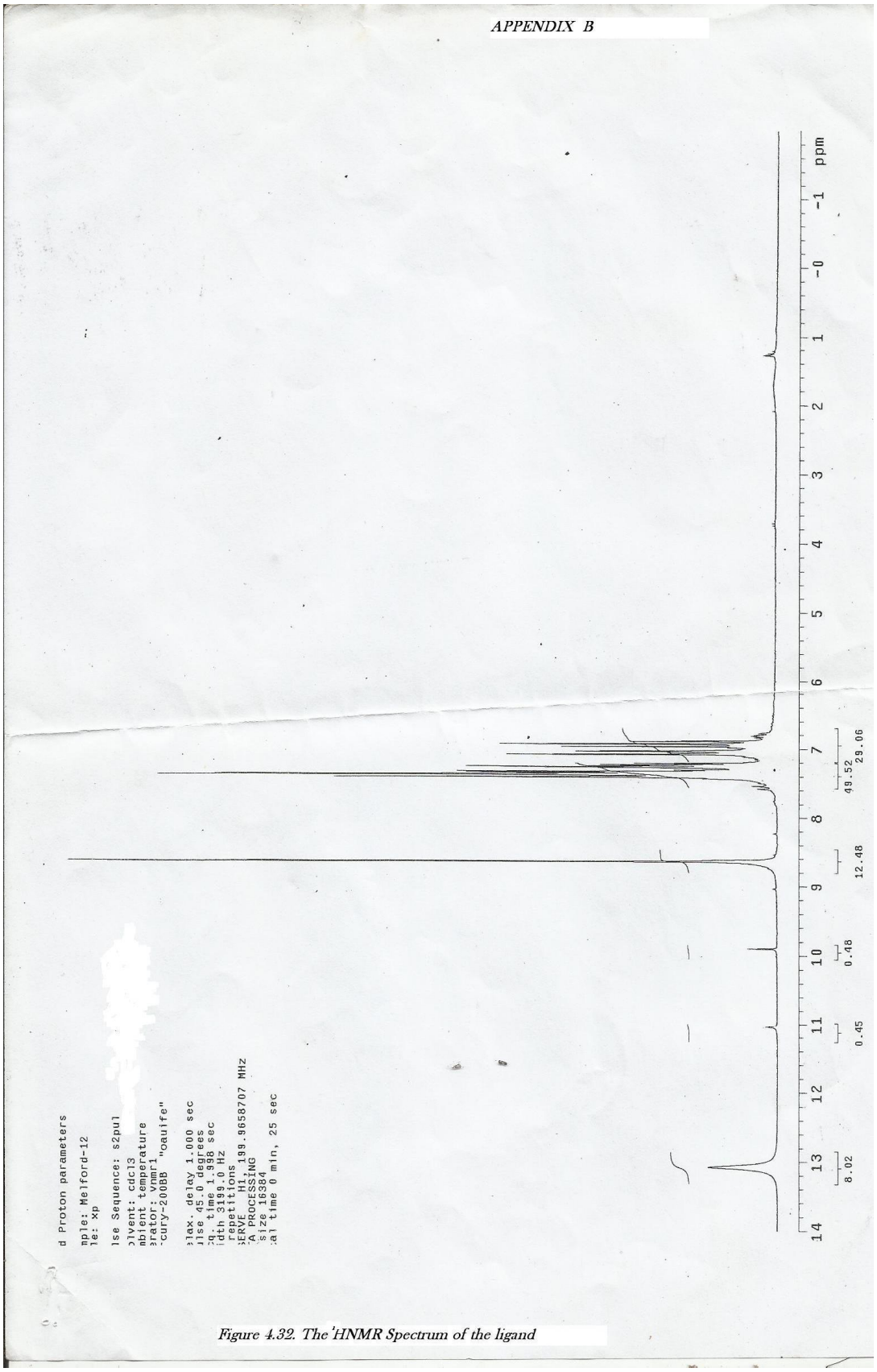


Figure 4.32. The ^{1}HNMR Spectrum of the ligand

APPENDIX B

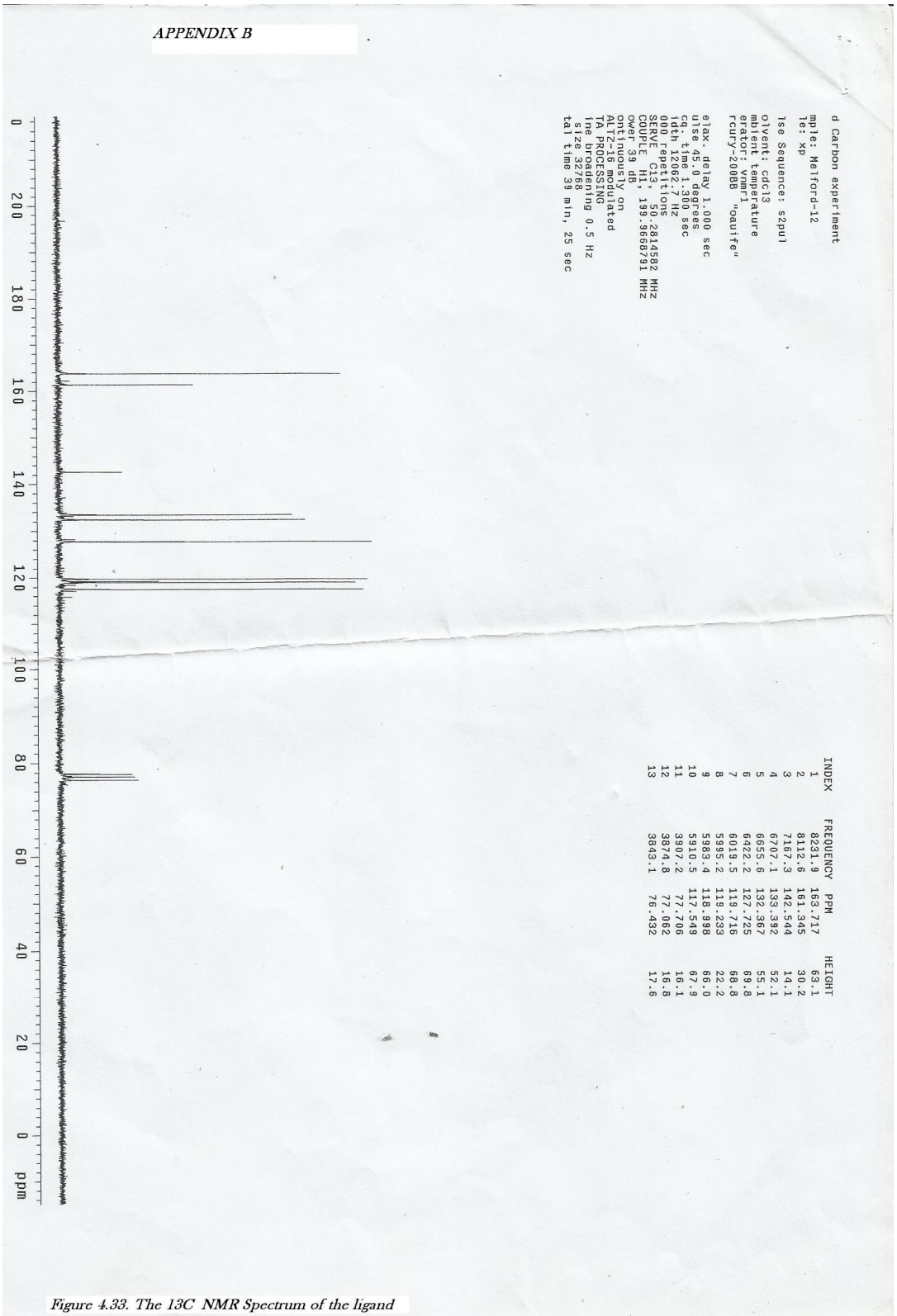


Figure 4.33. The 13C NMR Spectrum of the ligand

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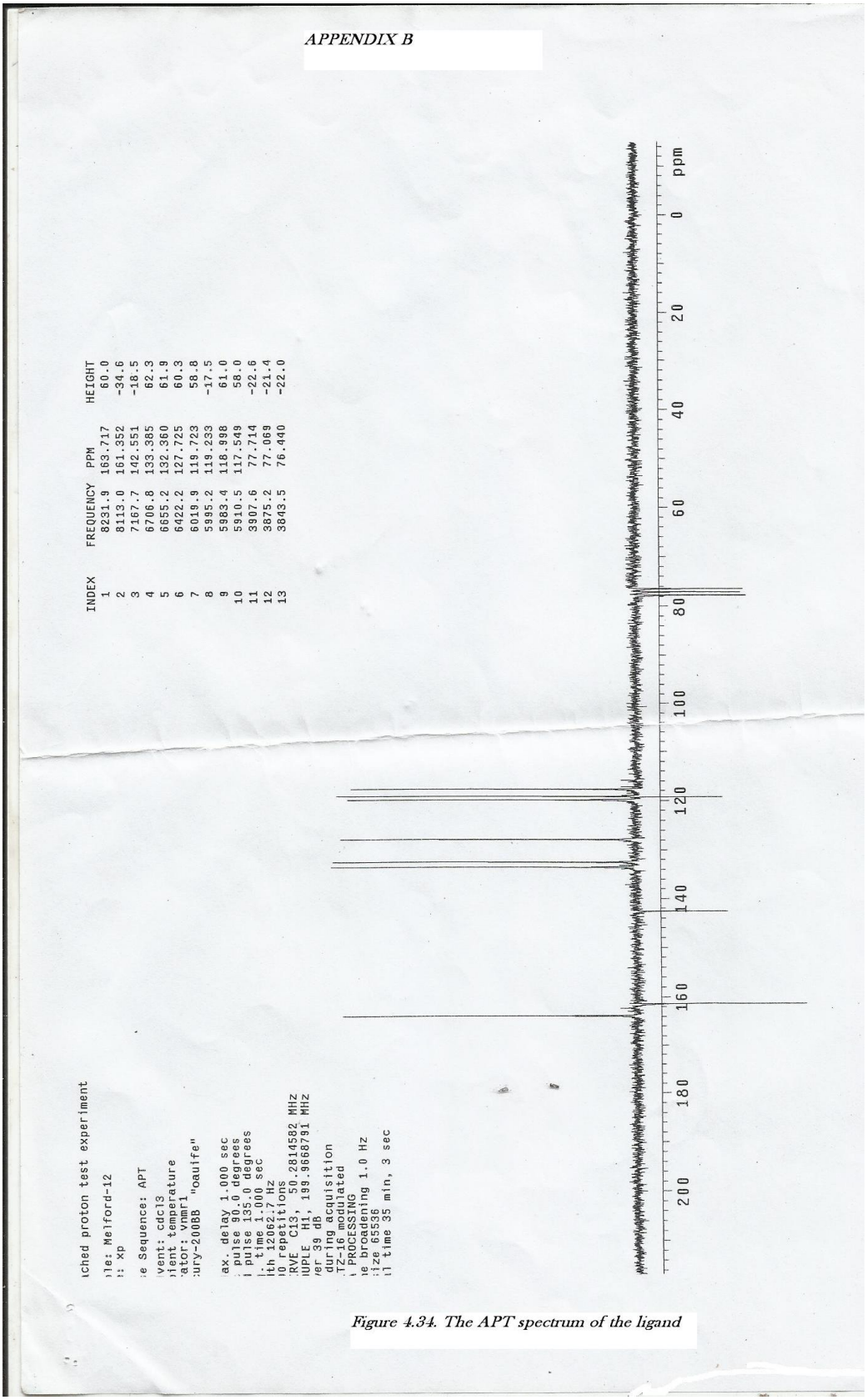

Figure 4.34. The APT spectrum of the ligand