

SYNTHESIS, CHARACTERIZATION AND SPECTROPHOTOMETRIC DETERMINATION OF NICKEL ION BY ISOCINCHOMERIC ACID**Chauhan Jayprakash S* and Pandya Ajit V**

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ABSTRACT

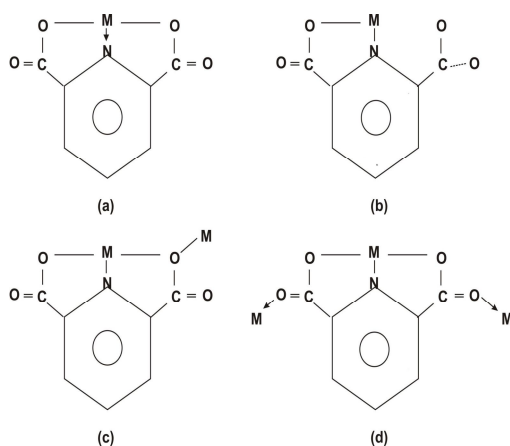
A new spectrophotometric method is developed for the determination of Ni (II) in an aqueous solution. The metal ion forms a blue colored complex with pyridine 2,5 dicarboxylic acid in the pH 6.0 to 8.5. The complex shows maximum absorbance at 620 nm. Job's method for continuous variation and mole ratio method shows metal ligand ratio in the complex to be 1:1. The complex is stable for days. The blue colored complex obeys the Beer's law in the concentration range of 250 to 600 μg s of nickel. The molar absorptivity (ξ) is found to be $2.1 \times 10^2 \text{ l mole}^{-1} \text{ cm}^{-1}$. The method has been used for the determination of Ni^{+2} in synthetic samples. The complex has been synthesized and FTIR studies has been carried out.

Key words: Pyridine 2,5 di carboxylic acid, Ni(II), spectrophotometry.

INTRODUCTION

Pyridine dicarboxylic acids are good complexing agents. Pyridine 2, 3-, 2, 4-, 2, 5-, 2, 6-, 3, 4-, 3, 5- dicarboxylic acids exhibit various co-ordination modes. Pyridine 2,3-dicarboxylic acid is known as quinolinic acid, Pyridine 2,5-dicarboxylic acid is known as isocinchomeric acid and Pyridine 2,6-dicarboxylic acid is known as dipicolinic acid. Pyridine 2, 6-dicarboxylic acid can act as partly or fully deprotonated and shows diverse coordination modes. 2, 6 pyridine dicarboxylic acid is found to be suitable ligand as it is well known versatile N, O chelator in coordination chemistry due to its diverse coordination modes¹⁻⁵. This ligand has attracted interest for a long time and progress has been made in understanding

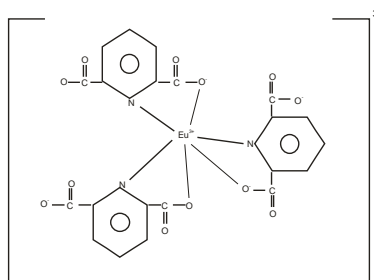
structure of its complexes in solution as well as in solid state^{48,49}. The coordination modes of pyridinedicarboxylate can be predicted as shown in fig.



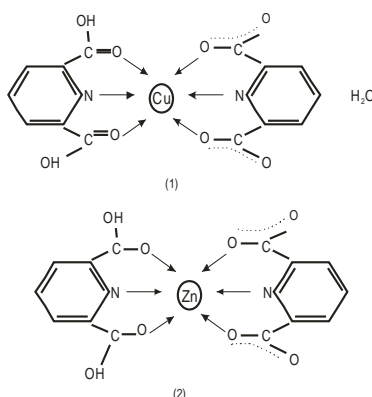
Most of the transition metals are reported to form fig (a) type of complexes^{50, 51}. A comparative study of the luminescent properties of europium and terbium coordinated with pyridine 2, 6 dicarboxylic acid in aqueous solutions has been described by Nadine Arnaud, Eric Vaquer and Joseph Georges⁵⁴.

It is also reported that this ligand is used to develop more effective anti HIV agents⁶⁻⁸. Pyridine dicarboxylic acids are found in the metabolic pathways of animals and they are used for the transport and scavenging of metal ions by the body. Pyridine 2, 6 dicarboxylic acid is reported to be present in bacillus spores, which is responsible for high thermal and UV stability of Bascillus spores⁴¹. Pyridine dicarboxylic acid has important biological function in the metabolism such as enzyme inhibitor⁴², plant preservative⁴³, and food sanitizer⁴⁴. These properties have attracted the interest of scientist not only in the field of coordination chemistry but also in inorganic and bioorganic chemistry.

Europium aquoion form chelate complexes with pyridine 2, 6 – dicarboxylic acid⁽⁸⁾. The structure of the complex is given as.



The 1:2 complexes of copper (II) and Zinc(II) with pyridine 2, 6 – dicarboxylic acid has been reported⁹. These complexes have distorted octahedral geometries.



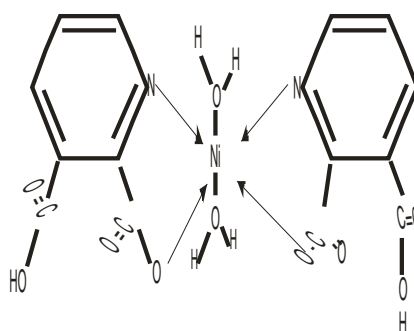
The complexes of Cobalt (II), nickel (II), rhodium (II) and rhodium (III) has been synthesized and their spectral and magnetic properties been studied¹⁰. Nickel is reported forming 1:2 complex i.e. $\text{Ni}(\text{dpCH})_2 \cdot 3\text{H}_2\text{O}$. Cobalt forms 1:1 complex i.e. $\text{Co}(\text{dpc}) \cdot 3\text{H}_2\text{O}$ which is six coordinate and contain co-ordinate water. Anhydrous polymeric $[\text{Co}(\text{dpc})]_n$ has also been reported¹⁰. Rhodium (II) and rhodium (III) forms $\text{Rh}(\text{dpc}) \cdot 3\text{H}_2\text{O}$ and $\text{Na} [\text{Rh}(\text{dpc})_2] \cdot 2\text{H}_2\text{O}$ respectively. Another study reports the dimeric complexes of Ni and Co with pyridine 2, 6 dicarboxylic acid. The structure of these complexes have been determined by single crystal x-ray crystallography¹¹. These dimeric complexes have been reported to have hexa coordinated environment with two different type of donor atoms i.e. nitrogen and oxygen¹¹. Manganese (II) has been reported to form a dinuclear complex i.e. hexaaquabis (Pyridine – 2, 6 – dicarboxylato) dimanganese (II) complex¹². Each Mn (II) ion is coordinated by three oxygen atoms and one Nitrogen atom from the pyridine 2, 6 dicarboxylate ligand and by three water oxygen atoms. Each manganese possess a distorted pentagonal bipyramidal coordination¹².

Chromatographic separation of transition metals by pyridine 2, 6 dicarboxylic acid (used as eluent) has been reported. The metals (Cu, Ni, Zn, Co, Cd, Mn) are separated as anionic chelates¹³.

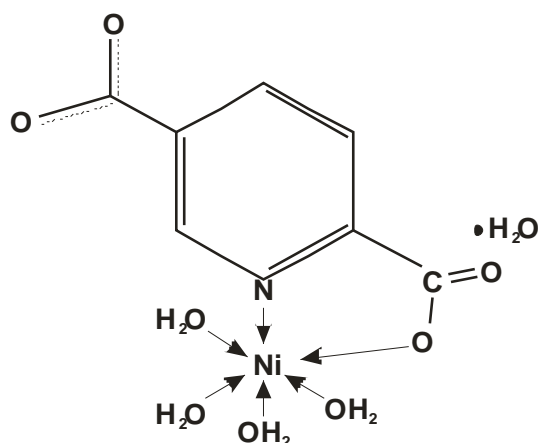
The complex formation studies of large number of cations is reported. Mixed ligand complexes of Nickel (II) and Cadmium (II) with Pyridine 2, 6 dicarboxylic acid have been studied potentiometrically¹⁴. Lanthanum, Dysprosium and Gadolinium (La, Dy, Gd) reacts with 2, 6 pyridine dicarboxylic acid in aqueous alkaline solution to give $\text{Ln}(\text{Pdc})(\text{HPdc}) \cdot m\text{H}_2\text{O}$. The thermal dehydration of these lanthanum compounds have been studied¹⁵. The

study of complex formation of Dysprosium (III) and pyridine 2, 6 dicarboxylic acid has been reported¹⁶. Electron Spin Resonance studies of complexes of silver (I) and copper (II) with pyridine 2, 6 dicarboxylic acid have been reported¹⁷. The complex of copper with pyridine 2, 3- dicarboxylic acid i.e. $[\text{Cu} (2, 3\text{- pydcH})_2]$ has been reported¹⁸. It is a chain polymer. Two ligands occupy the equatorial plane of each tetragonally elongated Cu^{+2} coordination sphere, chelating through the pyridine nitrogen and one oxygen of the deprotonated 2- carboxylic acid group, the axial positions are occupied by long bonds to a 3-carboxylic acid oxygen of adjacent $\text{Cu} (2, 3 \text{ PydcH})_2$ repeat unit. The coordination polymer of Mn with pyridine 2, 3 dicarboxylate has been synthesized and crystal structure has been proposed based on the experimental data¹⁹. According to this report Mn^{+2} ion is coordinated in a distorted octahedral environment by the O atoms of two water molecules, one N and one O atoms of the chelating pyridine 2, 3- dicarboxylate (PDC) dianion, and two axial bridging carboxylate O atoms from two adjacent PDC ligands¹⁹.

The complexes of the type $\text{M} (\text{H-Quin})_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ and Zn) where $\text{H}_2 - \text{Qin} =$ Quinolinic acid i.e. Pyridine 2, 3 dicarboxylic acid have been prepared and characterized²⁰. All these reported complexes have octahedral distorted structure. The nickel atom in $\text{Ni}(\text{H-Quin})_2 \cdot 2\text{H}_2\text{O}$ is octahedrally coordinated by two nitrogen atoms and two oxygen atoms belonging to the two H-Quin^- anions and two trans-aqua molecules²⁰. The structure of $\text{Ni}(\text{II})$ with quinolinic acid can be represented as.

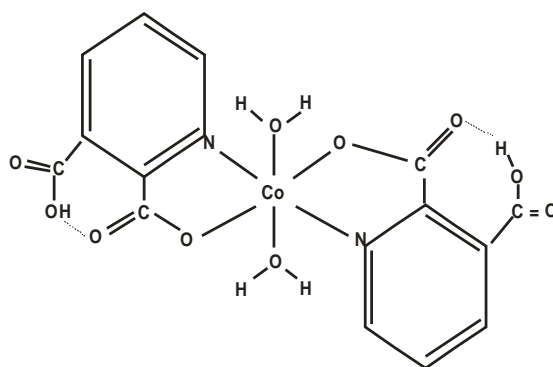


The crystal structure of $\text{Ni}(\text{II})$ with pyridine 2, 5 dicarboxylic acid has been reported⁴⁰. This compound i.e. $[\text{Ni}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ is synthesized by reaction of $\text{Ni}(\text{II})$ with pyridine-2, 5-dicarboxylic acid and piperazine in water. The compound contains a six coordinate $\text{Ni}(\text{II})$ ion which has a distorted octahedral structure. Following is the reported structure.

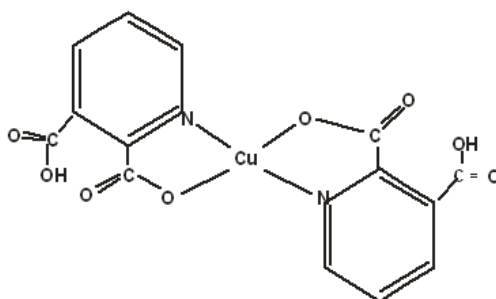


The complex $\text{Mn}(\text{H-Quin})_2 \cdot 2\text{H}_2\text{O}$ has been formulated as $[\text{Mn}(\text{H}_2\text{O})_6][\text{Mn}(\text{H-Quin})_3]_2$. The octahedral $[\text{Mn}(\text{H-Quin})_3]^-$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ units lie on different three fold axis.²⁰ Lanthanide (III) quinolinate complexes have been prepared and reported and evidence is presented which indicates that these complexes may be six-coordinated²¹. Calcium (II) complexes with pyridine 2, 3- dicarboxylate (Quinolinic acid) has been synthesized and crystal structure has been reported²². The complexes of uranium (IV) with quinolinic acid has been synthesized and reported²³. Two types of complexes of cadmium with quinolinic acid has been synthesized and reported²⁴. They are $[\text{Cd}(2, 3 \text{ pydcH})_3][\text{Cd}(\text{H}_2\text{O})_6]$ and $[\text{Cd}(2, 3 \text{ pydc})(\text{H}_2\text{O})_3]_n$. The chromium (III) – quinolinato complexes $[\text{Cr}(\text{quinH})_3]^{+3}$ $[\text{Cr}(\text{QuinH})_2(\text{H}_2\text{O})_2]^+$ and $[\text{Cr}(\text{quinH})(\text{H}_2\text{O})_4]^{2+}$ have been obtained and characterized in solution²⁵.

The structure of some Cu(I), Ag(II) and Cu(II) compounds with quinolinic acid have been established based on X-ray crystallographic studies²⁶⁻²⁸ in each case, quin is bonded as a monoanion through pyridine nitrogen and carboxylate oxygen atoms forming the 5-membered chelate ring. The same coordination mode is postulated for other quin-complexes with Cr(III), Cd(II), Fe(II)^{29, 32} though no structural studies were conducted. The spectrophotometric evaluation of iron (II) quinolinic acid complex (1:2) metal ligand system has been reported³³. Quinolinic acid i.e. pyridine 2, 3 dicarboxylic acid forms a 1:2 complex with Fe(II) at 5.9 pH which absorbs at 420 nm. The complex of cobalt with quinolinic acid has been synthesized and structure has been reported³⁴. The following structure of hydrated cobalt (II) complex of quinolinic acid has been reported³⁴.

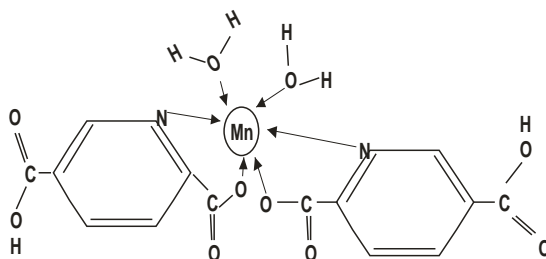


The crystal structure of copper with pyridine 2, 3 dicarboxylic acid has been investigated⁴⁷. Following structure has been reported.



A metal – organic polymer of Fe(II) with pyridine 2, 5 dycarboxylic acid has been hydrothermally synthesized and characterized by x-ray diffraction method⁵². It is reported that Zn(II) forms Zn (Hpydc)₂(H₂O) where pydc = pyridine 2, 5 dicarboxylate⁵³.

The complex formed by Mn(II) and pyridine 2, 5 dicarboxylic acid has been synthesized and characterized by elemental analysis, IR, electronic spectra, thermogravimetric analysis and x-ray diffraction techniques³⁵. The Mn(II) ion is coordinated by two water molecules and two chelated Pyridine 2, 5 dicarboxylic ligands. Water molecules coordinate with Mn(II) ion in cis mode.



Conductometric and potentiometric methods of quantitative determination of Aluminium (III), Indium (III), and Lanthanum (III) with pyridine 2, 6 dicarboxylic acid has been reported³⁶. Uranium (VI) and Vanadium (III) forms complexes with pyridine 2, 6

dicarboxylic acid which has been used for quantitative determination by conductometric and potentiometric methods³⁷. Nickel (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Ni (II) forms 1:2 coloured complex which is stable and independent of pH and its λ_{max} is at $1025 \text{ m}\mu$ ³⁸. Iron (II) has been determined spectrophotometrically with pyridine 2, 6 dicarboxylic acid. Fe (II) forms 1:2 complex at pH 5.2 and maximum absorption is at 510 nm ³⁹. Cr(III) forms 1: 2 complex with pyridine 2, 6 dicarboxylate in aq. Solution. The stability constants of the metals as Ba^{2+} , Ca^{2+} , Cd^{2+} , Ce^{3+} , Co^{2+} , Cu^{2+} , Dy^{3+} , Er^{3+} , Eu^{3+} , Fe^{2+} , Fe^{3+} , Gd^{3+} , Ho^{3+} , La^{3+} , Lu^{3+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Nd^{3+} , Ni^{2+} , Pb^{2+} , Pr^{2+} , Pr^{3+} , Sm^{3+} , Sr^{2+} , Tb^{3+} , Tm^{3+} , Y^{3+} , Yb^{3+} and Zn^{2+} with pyridine 2, 6 dicarboxylic acid have been reported.

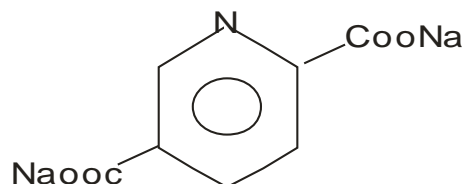
Spectrophotometric determination of Mn(II) by pyridine 2, 6 dicarboxylic acid has been reported by Chauhan J. S. and Pandya A. V.⁵⁵. A new method is developed for the determination of Mn(II) in solution by pyridine 2, 3 dicarboxylic acid⁵⁶. Ni(II) has been reported to form a 1:2 complex in aqueous solution and a method for its determination has been developed⁵⁷.

A further literature survey showed that the solution studies of Ni(II) with pdc 2,5 has not been reported. A study of complexation of Ni(II) with pyridine 2, 5 dicarboxylic acid and its application for quantitative determination have been carried out.

MATERIALS AND METHODS

An UV-VIS spectrophotometer-108 equipped with 1cm quartz cell was used for spectrophotometric measurements. The pH measurements were made with an Elico LI 120 pH meter.

The reagent used was pyridine 2,5dicarboxylic acid. The substance was dissolved in minimum amount of NaOH and its sodium salt solution was used.



A 0.01 M solution of the ligand was used.

Ni (II) solution :- A 0.01 M stock solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ prepared by dissolving in distilled water and was made acidic by adding HCl. The pH was maintained by using dilute NaOH and dilute HCl.

Procedure: In each set of different 50 ml standard flasks, various volumes of Ni (II) and reagent solution were taken, the pH was maintained (6.0 to 8.5) and made up to the mark with distilled water. The absorbance was measured at 620 nm against the reagent blank. The calibration curve was prepared by plotting absorbance against the amount of Ni. (II)

RESULTS AND DISCUSSION

(1) Determination of λ_{max} of the complex,

The absorption spectra of blue colored complex solution were recorded in the wavelength region 400-800nm as shown in the fig. It was observed that the complex showed the maximum absorbance at 620 nm where as the reagent blank is colorless solution and does not absorb in the visible region. The absorption spectra of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ has also been recorded. The λ_{max} of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ occurs at 690 nm which is an aquo complex of nickel. The λ_{max} of complex is shown in Fig 1.

(2) Effect of pH

Studies on the effect of variation in pH shows that the complex has maximum absorption in the pH range.6.0. to 8.5 pH. This is shown in Fig – 2.

(3) Effect of time

The Nickel (II) – Pyridine2,5dicarboxylic acid complex forms readily and there after it is stable.

(4) Effect of Temperature

The Ni (II) complex is stable in the temp. range of 30 – 70⁰ C Fig - 3.

(5) The effect of the reagent concentration (PDC) on the complex.

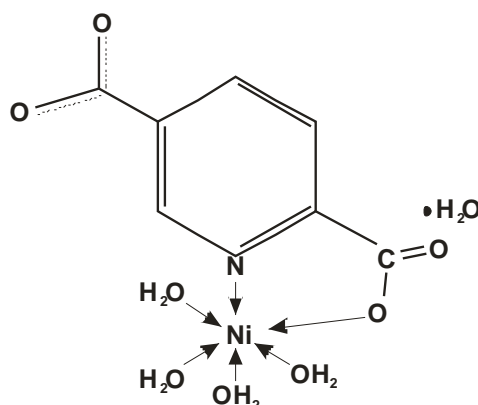
It seems that the complex formation requires the same concentration of the ligand This is shown in Fig – 4.

(6) Job's Method

Composition of the complex as determined by the job's method and the mole ratio method was found to be 1:1. This is shown in Fig – 5.

(7) The Beer's Law

The beer's law is obeyed in the concentration range 250 to 600 μ gms of Ni (II). The method that has been developed has moderate sensitivity. Calibration graph Fig – 6. Solution studies of Ni(II) shows that it forms blue coloured complex in the range of 6.0 to 8.5 pH with pyridine 2, 5 dicarboxylic acid. The reaction is pH sensitive. The complex formed is stable for few days. Pyridine 2, 5 dicarboxylic acid has proved to be interesting and versatile ligand and may exhibit various coordination modes. Pyridine 2, 5 dicarboxylic acid (2, 5 Pydc H₂), being a potential polydentate ligand, has aroused considerable interest of many groups and the literature cites numerous examples of different metal complexes. The Ligand can act as partly or fully deprotonated and shows diverse coordination modes such as monodentate or bridging. It may be due to this reason that contradictory reports for the crystal structure appears in the literature^{1, 3, 4, 19}. It is predicted that Pyridine 2, 5 dicarboxylic acid may be forming 1:1 complex with Ni(II) in solution. The following structure may be assigned in solution.



Synthesis and characterization of the complex

Five ml of 0.01 M Ni(II) solution was taken in a container. To this solution 10ml of 0.01 M isocinchomeric acid solution (Prepared by dissolving the acid in minimum amount of NaOH) was added. The acidic pH of 2.0 to 5.0 was maintained. In acidic pH the complex precipitates out from the solution leaving behind colorless solution. The bluish-green crystals obtained were separated and washed with distilled water and dried. We have also carried out F.T.I.R. studies.

The spectra was recorded in the range 4000 – 400 cm^{-1} . The IR spectra contained several indicative peaks such as an absorption band at 1400-1600 cm^{-1} which refers to the stretching vibrations of C=O bond. The stretching frequencies due to the aromatic rings are found at

3000-3100 cm^{-1} . The frequencies around 1600-1630 cm^{-1} regions are due to HOH bendings. The presence of COO^- group is revealed by IR spectrum which shows absorption bands at 1653 and 1400 cm^{-1} corresponding to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ vibrations.

Predominant vibrations of isocinchomeric acid associated with O – H are 2800 cm^{-1} { $\nu(\text{O-H})$ }, 1417 cm^{-1} { $\delta(\text{O-H})$ } and 927 cm^{-1} { $\gamma(\text{OH})$ }, which are absent indicating the deprotonation of $-\text{COOH}$ group and coordination with the Ni(II). The absorption bands in the region 657-750 cm^{-1} are attributed to the vibrations of the coordinated pyridine molecules. The presence of IR bands around 1700 cm^{-1} indicates that all the COOH – carboxylic groups are not deprotonated.

The frequency at 1663, and 1610 cm^{-1} indicates the carbonyl frequency of the carboxyl group which is attached with the metal as $\overset{\text{O}}{\parallel} \text{C}-\text{O} \rightarrow \text{M}$.

The metal – nitrogen (M – N) and metal – Oxygen (M – O) bonds were further confirmed by the presence of the band around 650 – 450 cm^{-1} and (570 – 400) cm^{-1} .⁴⁵⁻⁴⁶

Effect of foreign ions in the spectrophotometric studies

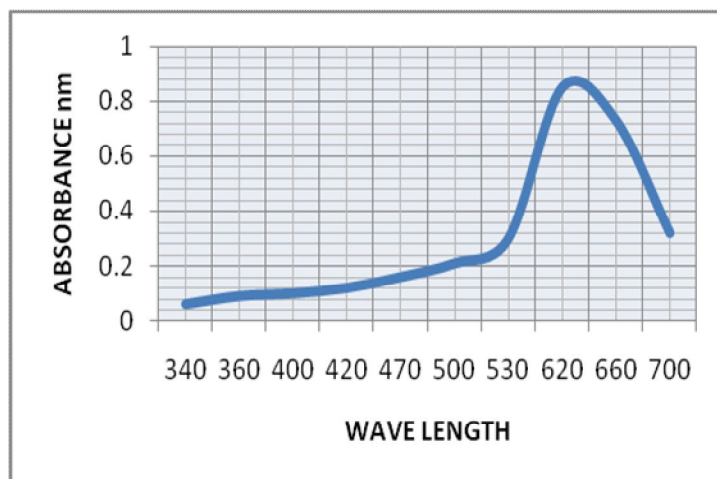
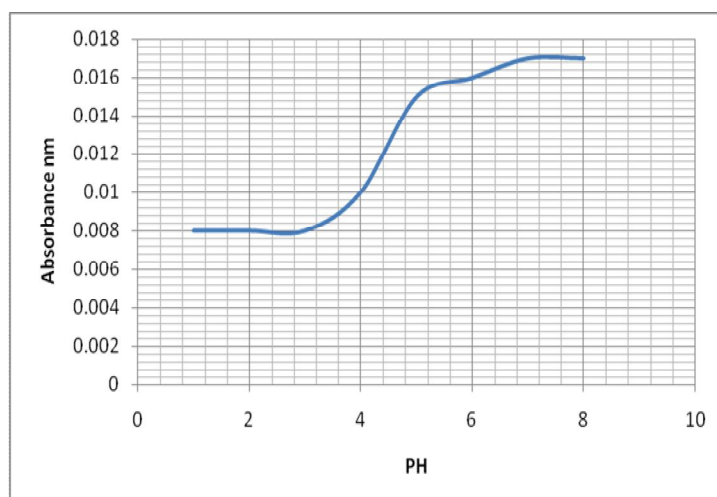
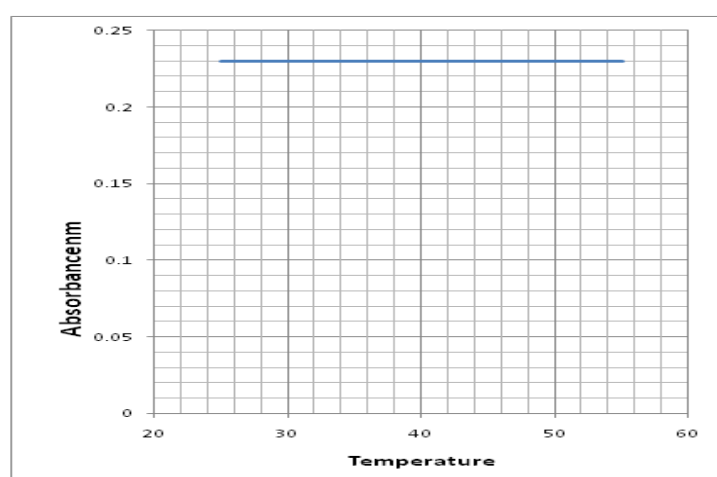
The effect of various anions and cations on the determination of Ni(II) under optimum conditions was studied. It was noticed that Cu^{+2} , Co^{+2} , Fe^{+2} , Mn^{+2} , Cr^{+3} and Ba^{+2} strongly interfere when present in the same concentration range. They do not interfere when present in ten fold less concentration than the analyte solution. Ions such as Fe^{+3} , V^{+3} , Sn^{+2} , K^+ , Na^+ , NH_4^+ , Zn^{+2} , I^- , Cl^- , Br^- , SO_4^{2-} , CO_3^{2-} , F^- does not interfere even when present in large excess. (i.e. ten fold excess)

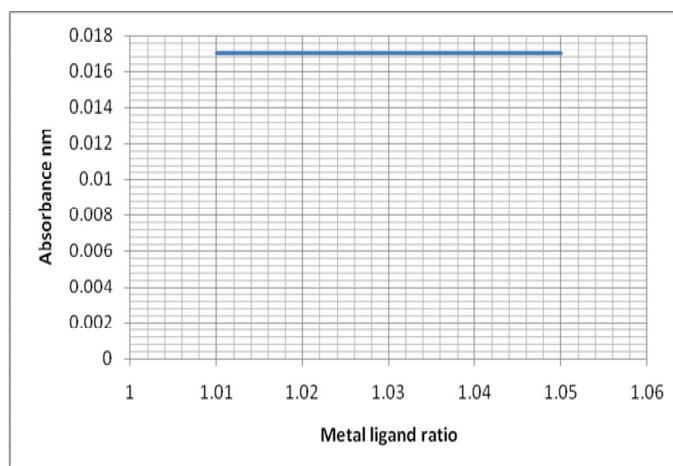
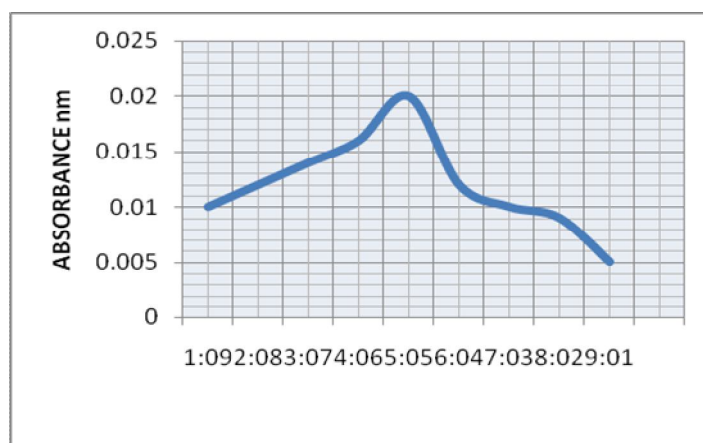
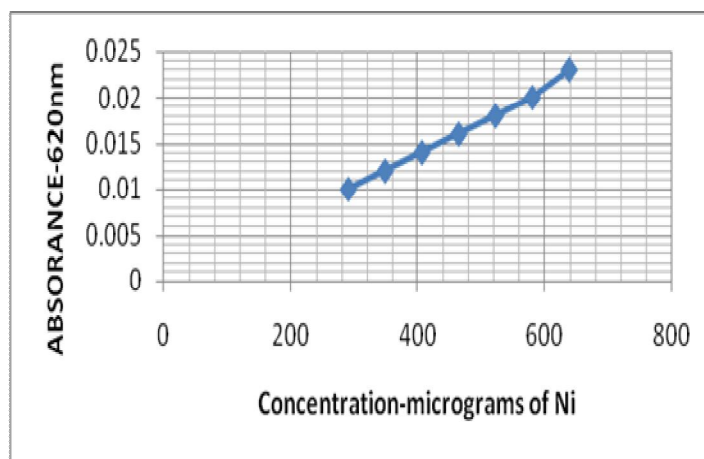
Validity of the method

A number of synthetic samples were prepared for the analysis. Spectrophotometric determination was carried out by the proposed method. The results are given in the table.

Table-1 Validity of the method

Sample	Ni(II) taken μgs	Abs Average	Ni(II) found μgs	Relative error %
Synthetic Sample – 1	580	0.021	600	3.4%
Synthetic Sample – 2	406	0.013	402	-1%
SyntheticS-3	464	0.017	471	3.4%

**Fig-1 Absorption Spectra****Fig-2 Effect of P^H****Fig-3 Effect Of Temp**

**Fig-4 Metal Ligand Ratio****Fig-5 Job's Method****Fig-6 Beer's Law Graph**

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