Synthesis and Characterization of N-Benzylidene Aniline Ligand for Spectrophotometric Determination of Nickel

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Abstract

Schiff bases are compounds containing azomethine group (-HC=N-). They are condensation products of ketones or aldehydes (aldehydes and ketones) with primary amines. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The spectrophotometric determination of metals using Schiff base metal complex is very important in analytical chemistry. This study has helped to establish a novel, simple and cheap analytical method for the determination of nickel in an environmental sample especially in developing countries where the cost and maintenance of sophisticated instruments are extremely high. In this study, Schiff base ligand was synthesized using benzaldehyde and aniline to form a metal complex with the target analyte (Ni^{2+}). The melting point and electrical conductivity of the synthesized nickel complex were 175.6^{o}C and 84x10^{-6}Ω^{-1}cm^{-1}respectively and the maximum absorbance at 360nm was 0.60. The complex was characterized using different spectroscopic techniques. The peak in FT-IR spectra at 1625.2 cm^{-1} confirmed the (C=N) stretching vibration. The ^{13}C and ^{1}H NMR spectra showed 193.8 and 10.0 ppm respectively of (CH=N) which was assigned to the azomethine carbon atom and the GC-MS analysis revealed a plausible structure of the complex. The stoichiometry of the Schiff base nickel (SB-Ni) complex was established as NiSB$_2$by Job's method of continuous variation, mole-ratio and slope-ratio methods. The three procedures are in agreement over the stoichiometry of the SB-Ni complex.

Keywords: Complex, Stoichiometry, N-benzylideneaniline, Spectrophotometric, Ligand

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1. INTRODUCTION

The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids (Amit *et al*. 2014). Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures and it is also formed typically by the condensation of a primary amine and an aldehyde/ketone (Annapoorani and Krishnan 2013). The resultant compound, $R_1R_2C=NR_3$ is called a Schiff base, where R_1 is an aryl group, R_2 is a hydrogen atom and R_3 is either an alkyl or aryl group. However, compounds where R_3 is an alkyl or aromatic group are also regarded as Schiff bases (Archana 2013). Schiff bases that contain aryl substituent are substantially more stable and readily synthesized, while those which contain alkyl substituent are relatively unstable (Chaundhary 2013). Schiff bases generally are bi, tri, or tetra-dentate chelate ligands and form very stable complexes with metal ions. Their chemical and physical properties in various fields such as preparative uses, identification, or protection and determination of aldehyde or ketones, purification of carbonyl and amino compounds or production of these compounds in complex or sensitive reactions have been studied by various researchers (Garima and Jyoti 2015; Consiglio *et al*. 2012; Badekar *et al*. 2016). Schiff bases are also known as anils, imines or azomethines and several studies showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance (Katwal *et al*. 2013; Chandraleka *et al*. 2011; Anita and Manish 2013). Due to the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with a metal ion. Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable (Anand *et al*. 2012; Al-Resayes *et al*. 2011; Okolo and Okuo 2003; Skoog *et al*. 2007). Nickel is one of the ubiquitous elements and ranks 23 in order of abundance. Its average concentration in the earth's crust is 75 mg/kg. Nickel is relatively toxic and widespread in the environment. Nickel enters the environment through two main pathways: natural- such as weathering of minerals, rocks and geochemical emission, and anthropogenic such as industrial and vehicular emissions (Manno *et al*. 2006). Nickel particles in the air settle to the ground or are taken out of the air in rain. Much of the nickel in the environment is found in soil and sediments because nickel attaches to particles that contain iron or manganese, which are often present in soil and sediments (Mtunzi *et al*. 2015). It is considered as a borderline element between hard and soft acid acceptors in chemical interactions towards donor atoms. Nickel salts are soluble and can occur as a leachate from nickel bearing rocks. The effects of nickel exposure vary from skin irritation to damage to

lungs, the nervous system, and mucous membranes. It is also a known carcinogen (Singh *et al*. 2012).

The objectives of this study are: 1. Synthesis of Schiff base ligand from benzaldehyde and aniline followed by synthesis of nickel (Ni) complex using the ligand as a complexing agent. 2. Characterization of the synthesized ligand and its Ni complex using nuclear magnetic resonance (NMR), melting point determination, electrical conductivity, IR, AAS, GC-MS and UV-VIS spectroscopic techniques. 3. Establishing the stoichiometry of the SB–Ni complex using mole-ratio, slope-ratio and job's method of continuous variation. 4. Determination of the accuracy and precision of the proposed method. 5. Applying and comparing the new method with a known method of Ni determination such as atomic absorption spectroscopy (AAS).

2. MATHERIALS AND METHODS
2.1 Materials
Brucker Advance Neo III (400 Hz) Nuclear Magnetic Resonance (NMR) Spectrophotometer Schimadzu AAS Analyst 7000, Agilent Technology FT-IR Spectrophotometer, Jenway 3020 pH meter, Gynesis 90 thermoscientificUV/Vis-spectrophotometer, AR 2130OhausCoporation analytical balance; Brucker FT-IR Spec, Magnetic stirrer: Stuart heat-stir hot plate SD162, Agilent Technology 7890 GC-MS, Volumetric (calibrated) flasks, beakers and conical flasks. All reagents used were of analytical grade: HCl, $NiCl_2.6H_2O$, HNO_3, NaOH, DMSO, aniline, methylamine, benzaldehyde, 95% ethanol, petroleum ether, methanol and distilled water.

2.2 Methods
2.2.1 Preparation of N-benzilideneaniline Ligand
Equimolar quantity of benzaldehyde 10.143 ml (1.025 mmol) and aniline 9.099 ml (1.010 mmol) were mixed with rapid stirring in a 250 ml round bottom flask provided with a stirring bar, thermometer and reflux condenser for 2 minutes. The reaction began after five seconds followed by evolution of heat and separation of water. The mixture was allowed to reflux at 80^0C for four hours and then poured with fast stirring into a 600 ml beaker containing 16.5 ml absolute ethanol. Crystallization of the product was achieved by allowing the mixture to further stand in an ice bath for 30 minutes. Solid mass of the product, N-benzilideneaniline was quantitatively transferred to a filter paper and allowed to dry in a desiccator using activated silica gel for 48 hours. 83.986% product yield was obtained and the melting point was found to be 56.2^0C.

2.2.2 Synthesis of Metal Complex
The nickel metal complex of N-benzilideneaniline ligand was prepared by dissolving 2.377 g of 0.01 mole of $NiCl_2.6H_2O$ in 5 ml dry methanol in a 100 ml round bottom flask. 3.625 g of 0.02 mole of the synthesized N-benzilideneaniline ligand was dissolved in 10 ml of methanol in a separate 100 ml round bottom flask. The methanolic solution of the metal chloride and the ligand were mixed and refluxed in a 250 ml round bottom flask provided with a magnetic stirrer, thermometer and reflux condenser. Refluxing was continued for six hours at 80^0C under constant stirring. Finally, the solution was allowed to cool for 24 hours and 10 ml of ethanol was added. A colored complex was separated out, filtered, washed with petroleum ether and dried under desiccator using activated silica gel. The purity of the complex was checked by thin layer chromatography (TLC).

2.2.3 Determination of Optimum pH of SB-Ni Complex
The optimum pH of SB-Ni complex was determined using the method of Okoye et al. (2013). Reaction mixtures each containing 4.0 ppm Ni^{2+} and 0.72% (m/v) which is the optimum concentration of SB-Ni complex obtained from the maximum absorbance of the SB along with 3ml 0.5 M NaOH and 3 ml methylamine were prepared in twenty-one separate 25-ml calibrated flasks. Each was adjusted to a given pH ranging from 3 to 13, using 1.0 M NaOH. The absorbance of each solution was taken at 360nm. A plot of absorbance vs pH was made.

2.2.4 Determination of Wavelength of Maximum Absorption (λmax) of Schiff Base Nickel (SB-Ni) Complex
The absorption spectra of the SB-Ni complex at pH 12.50 were investigated using the methods of Okolo and Okuo. (2003). At 4.0ppm Ni^{2+} ion concentration, the solution was treated with the reaction mixture (Rm)[5ml 3% SB, 3ml 0.50M NaOH and 3ml methylamine] and made up to 25ml final solution with distilled water in a standard flask [reaction mixture (Rm)]. A reagent blank (Rb), which was the reaction mixture without the analyte (Ni^{2+}) was also prepared.

The wavelength of maximum absorption (λmax) of the Rm and Rb was established by scanning from 190 to 570 nm in 1 cm matched silica cells using Gynesis 90 thermoscientific UV/Vis- spectrophotometer.

2.2.5 Determination of Schiff Base Concentration on the Absorbance of the SB-Ni Complex
Investigation of the variation of absorbance of SB-Ni complex with SB concentration was carried out by measuring the absorbance of the usual reaction mixture solutions containing 4.0ppm of Ni^{2+} with varying amounts of SB at 360nm and pH 12.50. The absorbance was plotted against SB concentrations (%m/v) (Okolo and Okuo 2003).

2.2.6 Effect of Reaction Time
This determines the maximum time required for maximum colour development in the SB-Ni system. The absorbance of the Rm vs Rb was taken at 5-minute interval at 360nm and pH 12.50 in matched 1-cm silica cells (Garima and Jyoti 2015).

2.2.7 Determination of the stability of Rm and Rb)

To determine the stability of the Rm and Rb after maximum colour had been developed at optimum pH 12.50. The Rm and Rb were prepared and allowed to stand for 20 minutes for maximum colour development, The pH was adjusted to 12.50 and the absorbance readings were taken at 30-minute interval at 360nm in matched 1-cm silica cells (Gononka et al. 2015).

2.2.8 Order of Addition of Reagent

0.72% (m/v) SB, Ni^{2+} concentration of 4.0 ppm, 3.0 ml of 0.5 M NaOH, and 3.0ml of methylamine were mixed in a 25 ml volumetric flask in the order of a+b+c+d and made up to mark with distilled water. This was allowed to stand for 20 minutes for max colour development, and then adjusted to pH 12.50. Absorbance reading of the solution was taken at 360 nm in a matched 1 cm silica cells. The order of addition of reagents was varied Twenty four times to obtain the optimum order, using permutation principles ($^4P_4$) (Ekoko, 2014).

2.2.9 Adherence to Beer's Law

Ni^{2+} concentration range of 0.5-6.0 ppm and the Rm, were placed in a 25 ml volumetric flasks, and made up to mark with distilled water. The reaction mixture (Rm) was allowed to stand for 20 minutes. The pH was adjusted to 12.50 with 1.0 M NaOH. The absorbance reading of each Rm was taken at 360 nm, at ambient temperature, 25-30° C (Okolo and Okuo 2003). A plot of absorbance vsanalyte concentration was made.

2.2.10 Stoichiometric Determination

Several methods can be used to determine the ratio of the ligand to the metal in a complex (Manno et al. 2006). In this study, Job's method of continuous variation, mole ratio and slope ratio methods were used to complement one another.

2.2.11 Interference Studies

The possible interfering effects of foreign ions on the analytical signal of 4.0 ppm Ni^{2+}were studied using a similar procedure of Okolo and Okuo (2003). Some of the ions chosen are constituents of major components of natural waters while others are those that form ion-associated complexes with Ni^{2+} e.g. $Ag+$, NO_3^-, Ca^{2+}, Zn^{2+}, SO_4^{2-} etc. The criterion for the interference was fixed at ± 5.0 % thus concentration of foreign ions which caused relative deviation in absorbance equal to or lower than 5.0 % were tolerated.

Three samples were prepared: reference sample (Rs), test sample (Ts) and reagent blank (Rb). The reference sample (Rs) was the reaction mixture (Rm) containing 4.0 ppm Ni^{2+}, the test sample (Ts) was the reaction mixture plus the interference, while the reagent blank was the reaction mixture without the analyle. The Rs, Ts and Rb were allowed to stand for 20 minutes and pH adjusted to 12.5. The absorbance (A) readings were taken at 360 nm. The relative deviation due to the interference was calculated using the relation:

$$\text{Relative deviation} = \frac{\text{Absorbance without interference - Absorbance with interference}}{\text{Absorbance without interference}} \times 100$$

(2.1)

2.2.12 Recovery Tests on SB-Ni Complex

This test estimates the fraction of the analyte (Ni) obtained after a standard solution of the analyte has been analysed using the proposed method. It established the effectiveness (precision and accuracy) of the method. Distilled – deionized water samples were spiked with known amounts of nickel [0 to 6.0 ppm ($\mu g/ml$)] each contained 0.72% (m/v) SB, 3 ml of 0.5 M NaOH and 3.0 ml of methylamine (Rm) and all made up to final volume of 25.0 ml with distilled-deionized water. The solution was allowed to stand for 20 minutes for maximum colour development before adjusting their pH to 12.5 with 1.0 M NaOH. The absorbance was taken at 360 nm in 1-cm matched silica cells against the reagent blank.

Following the procedure of Okolo and Okuo (2003), a calibration curve was prepared to cover Ni^{2+} concentration range 0-6.00 ppm. From the calibration curve, the Ni^{2+} concentration in each 25.0 ml final volume was determined in five replicates. The standard deviation (SD), relative standard deviation (RSD), and 95 % confidence limit were calculated using the method of Okolo and Okuo (2003).

2.2.13 Limit of detection (LOD), limit of quantitation (LOQ), and method sensitivity (MS)

The LOD and LOQ were estimated from 10 replicate reaction mixtures, each containing 0.05 $\mu g/ml$ Ni^{2+}, while the MS was determined from figure 3.12. These were the minimum concentration of the analyte that gave an analytical signal based on this method (Raman et al. 2009).

3. RESULTS AND DISCUSSION

3.1 Physico-chemicacharacterization of N-benzylideneaniline Ligand and Metal Complex

The complex was air-stable with high melting point and was soluble in methanol, chloroform, diethylether, ethanol and dimethylsulphoxide (DMSO). Table 3.1 summarizes the physical characteristics of the ligand and its metal complex.

Table3.1Physico-chemical Characterization of N-benzylideneaniline and its Metal Complex

Variables	Colour	Melting point	IR (C=N)	[1]CNMR(CH=N)	[1]H(CH=N)	
Literature Value	Olive green	176.1^0C	1627.0	194.0	9.9	
Experimental Value	Olive green	175.6^0C	1625.2	193.8	10.0	

3.1.1 Measurement of Electrical Conductivity

The electrical conductance measurement was done to ascertain the anions of the metal complex remain inside or outside the coordination sphere of the central metal atom.

The specific conductance of the synthesized Ni^{2+} complex (Ni^{2+}=26.87 Ω^{-1}) was $84 \times 10^{-6} \Omega^{-1} cm^{-1}$. The conductance of 0.2 M KCl used was $849 \Omega^{-1}$. This was used to calculate the cell constant which gave 2.9×10^{-6} cm^{-1}. The high value of the molar conductance suggests that the complex behaves like an electrolyte.

3.1.2 UV-Visible Spectra

The UV-visible spectra of the Schiff base complex recorded in DMSO solvent with the wavelength range of 900-200nm at room temperature showed two absorption bands of 375.909 and 386.434 nm. These two absorption bands in the electronic spectrum of the ligand could be assigned to n- π^* and π-π^* transition. These transitions are also found in the spectra of complexes, but they appeared to be shifted towards lower and higher frequencies, confirming the coordination of ligands to metal ion.

3.1.3 FT-IR Spectra

The infra-red (IR) spectra of the N-benzylidene aniline (Schiff base) ligand shown in Figure 3.1 shows stretching and out-of-plane bending vibration for (sp^2=C-H) at 3059.50 and 689.92cm^{-1} respectively. This indicates the presence of aromatic ring in the Schiff base ligand. This extremely intense absorption of out-of-plane C-H bending vibration resulting from strong coupling with adjacent hydrogen atom, explains the presence of monosubstituted alkyl-(methyl group) attached to the aromatic ring (Ar-CH). The methyl hydrogen furnishes only one weak C-H stretching at 2889.4cm^{-1}. The N-benzylidene free ligand also shows stretching vibration of the azomethine nitrogen with the aromatic ring at 1191.22cm^{-1}(Ar-N) in the spectrum. The IR spectra of the complex show the coordination sites that may be involved in the chelation (Figure 3.2). There were some guide peaks in the spectra of the ligand which were helpful in achieving the result. The position and/or the intensities of the peaks were expected to change upon chelation.
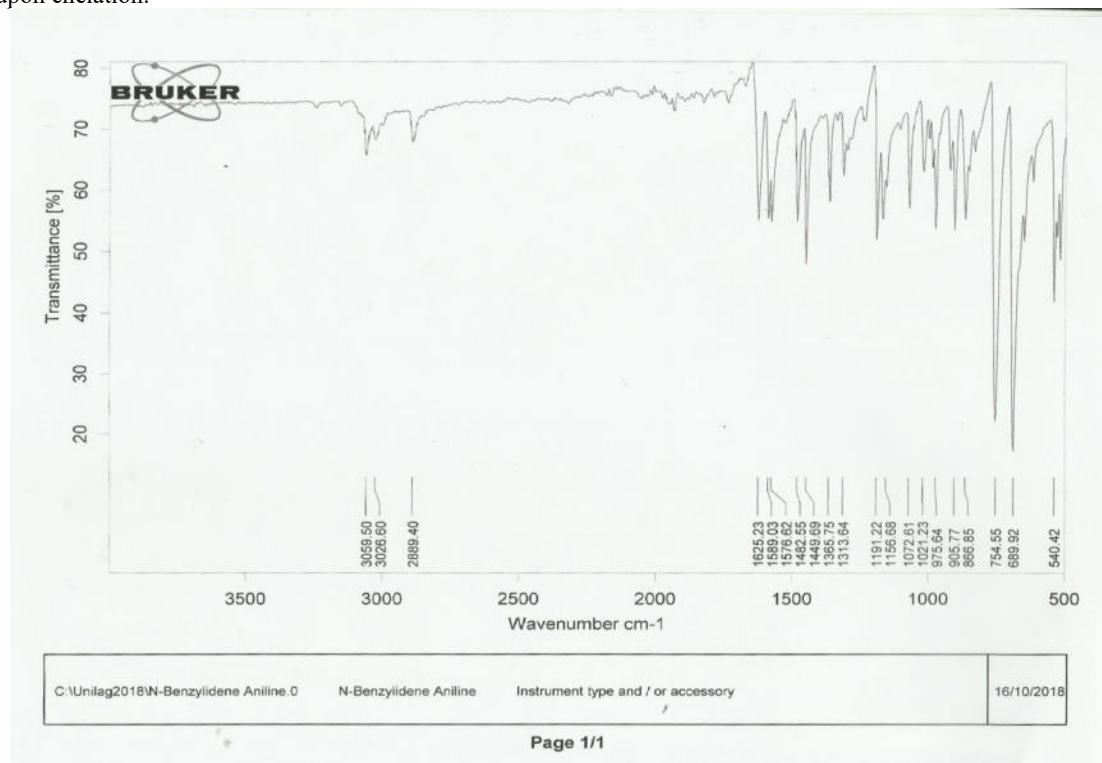

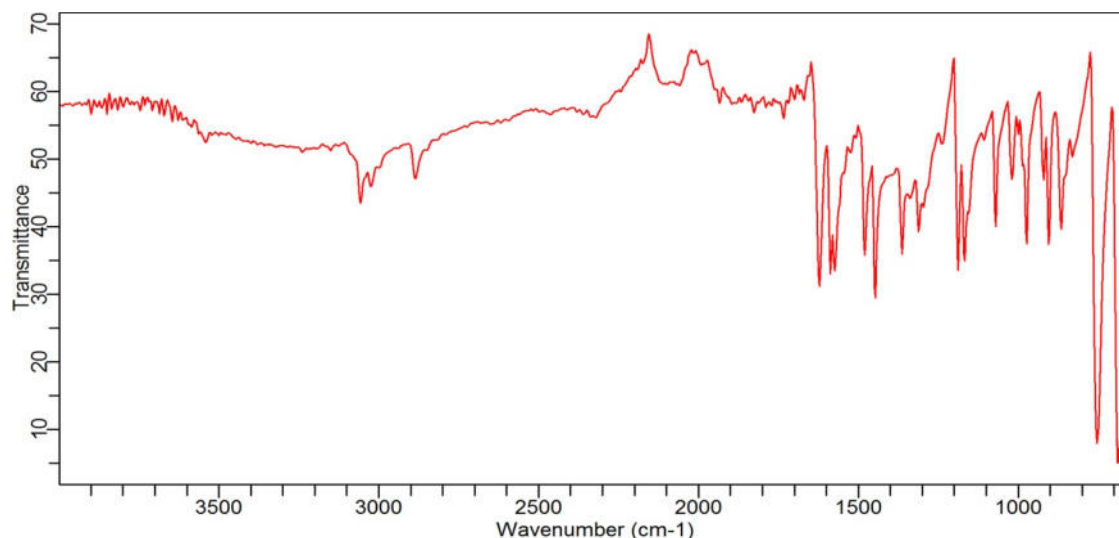**Figure 3.1 FT-IR Spectra and Mode of Vibrational Frequencies of Schiff Base Ligand**

Figure3.2 FT-IR Spectra and Mode of Vibrational Frequencies of Schiff Base-Nickel Complex

3.1.4 Nuclear Magnetic Resonance (NMR) Spectroscopy of Schiff Base-Nickel Complex

Nuclear magnetic resonance spectroscopy was conducted to determine the plausible structure of N-benzylideneaniline nickel complex.

3.1.4.1 Carbon 13 (^{13}C) NMR

The ^{13}C spectra recorded on dimethyl sulphoxide (DMSO) in Figure 3.3 showed a signal which appeared at ð 193.670ppm and was assigned to the azomethine carbon atom (CH=N). The chemically nonequivalent aromatic ring carbon atom of the ligand furnished resonance peaks at chemical shift of 116.2032, 126.4297, 129.1367, 129.2748, 129.6608, 129.9444, 131.9332, 135.0332, 136.4846, 136.6676, 151.9367, 161.1494 ppm and quaternary carbon atoms which were parts of the rings and adjacent to the azomethine carbon and nitrogen as well, provided low intensity signals at ð of 136.4846 and 151.9367 ppm. Trace of phenylamine droplets which were found in the ligand shows peaks at 114.4172, 121.4172, 121.4309 and 129.6170 ppm.
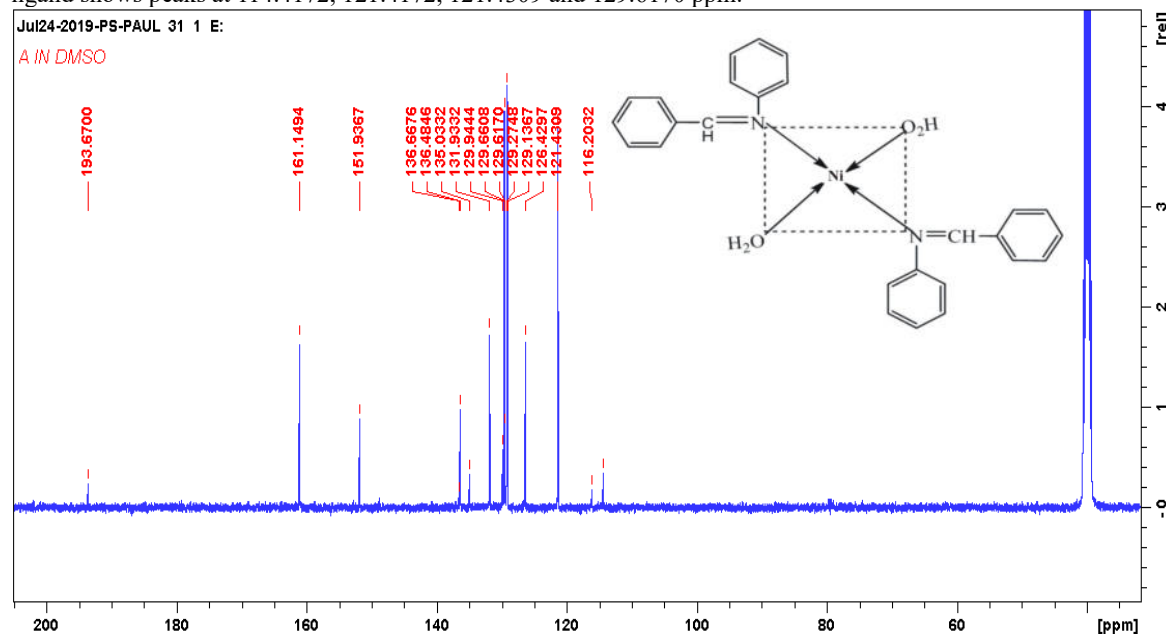

Figure 3.3 ^{13}C NMR Spectra of Schiff Base-Nickel Complex

3.1.4.2 Proton (^{1}H) NMR

The Schiff base (SB) proton NMR in Figure 3.4 shows highly de-shielded singlet absorption at ð (10.0183 ppm 1H) which can be attributed to the azomethine proton (HC=N-). The region of ð (6.4941–8.6123 ppm, 10 H) with multiple signal absorption were assigned to chemically nonequivalent aromatic protons (Ar-H). The strong signal which appeared at ð 3.3389 ppm can be attributed to unreacted or excess droplets of phenyl amine protons during ligand synthesis. Dimethyl sulphoxide (DMSO) used as solvent was not 100% isotopically pure and contains some

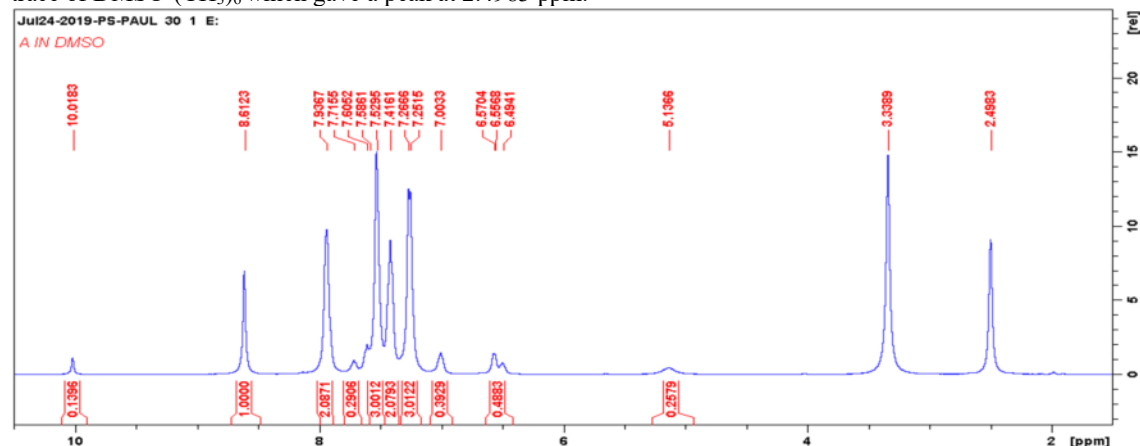trace of DMSO-$(CH_3)_6$ which gave a peak at 2.4983 ppm.

Figure 3.4 ^{1}H NMR Spectra of Schiff Base-Nickel Complex

3.1.5 GC-MS Scan

The GC-MS scan shown in Figure 3.5 explains the analysis of N-benzylideneaniline nickel complex in chloroform using helium as the carrier gas. The oven temperature program was 80^0C to hold for two minutes at ten degrees per minute to a final temperature of 240^0C to hold for ten minutes. The volume of sample injected was 1 μL, the scan range is from 50 to 550 amu. The mass spectrum of the component identified was compared with the spectrum of the known component stored in the National Institute of Standard and Technology (NIST) library and the name, molecular weight and the structure of the test sample was ascertained as represented on the chromatogram.
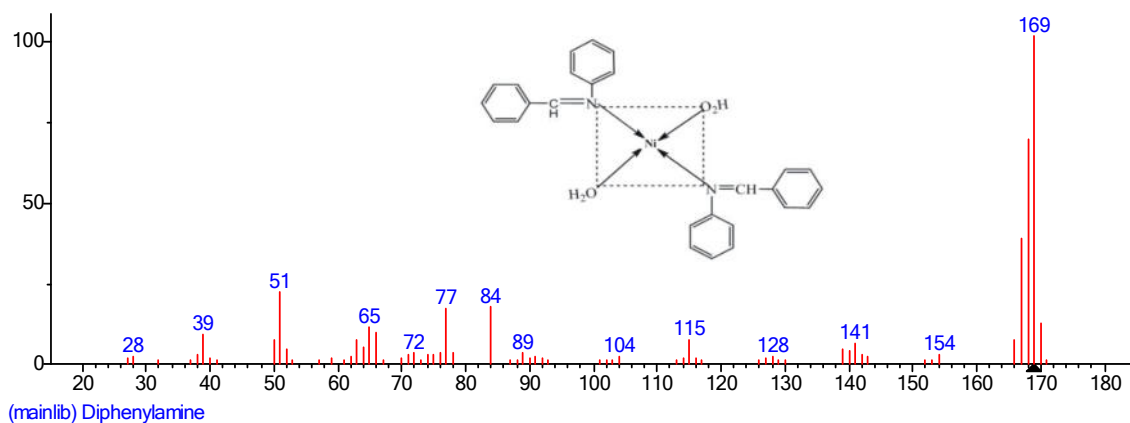

(mainlib) Diphenylamine

Figure 3.5 GC-MS Scan of Schiff Base-Nickel Complex

3.1.6 Determination of Optimum pH of the SB-Ni Method

Considering the Ni^{2+} and SB concentrations of 4.0 ppm and 0.72% (m/v) respectively, and at λmax of 360 nm, the variation of absorbance with pH is shown in Figure 3.8. These absorbance values showed prominent peaks at 0.391, 0.586 and 0.989, corresponding to the pH of 6.5, 8.5 and 12.5, respectively. Further investigations revealed that at both pH 6.5 and 8.5, the Rm and Rb were unstable, while the Rm and Rb at pH value of 12.5 were far more stable. Therefore, pH value of 12.5 was chosen as the optimum pH for this method.
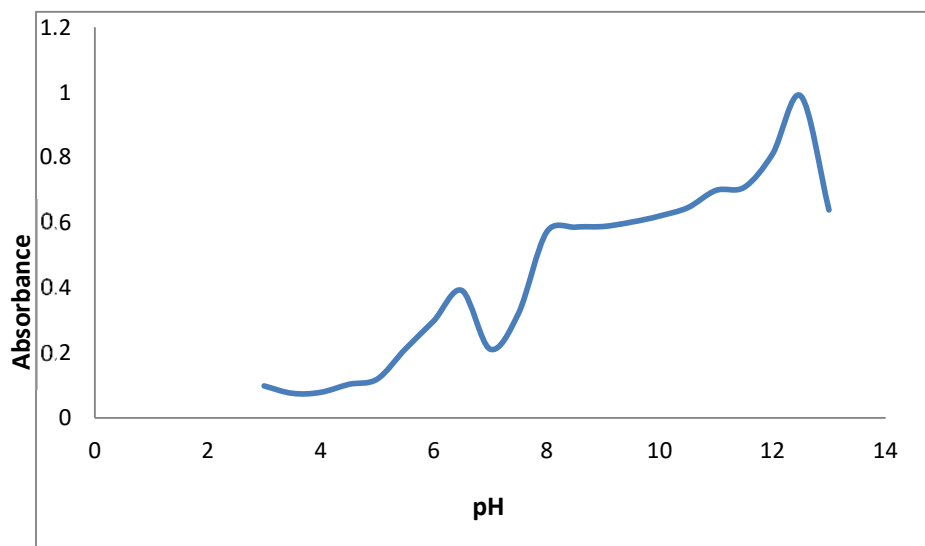
Figure 3.6 Effect of pH and Absorbance

3.1.7 Determination of Wavelength of Maximum Absorption (λmax) for SB-Ni Complex

Figure 3.6 shows the maximum absorbance for the SB-Ni complex and the reagent blank (Rb) at 0.60 and the corresponding wavelength (λ max) is at 360 nm. For the (Rb) and water, the maximum absorbance is at about 0.01 which is far below the 0.60 for SB-Ni complex. This indicates that the Rb does not interfere with the absorbance due to the analyte.
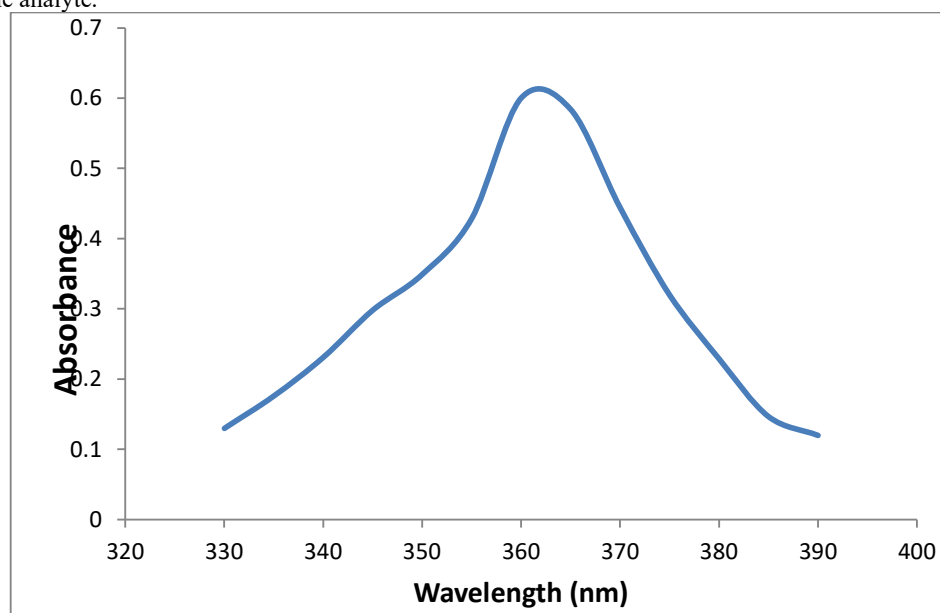

Figure 3.7 Determination of the wavelength of maximum absorption (λmax)

3.1.8 Effect of SB Concentration on the Absorbance of SB-Ni Complex

The effect of the SB concentration on the absorbance of SB-Ni complex is shown in Figure 3.7At 4.0 ppm Ni^{2+} concentration and varied concentrations of SB from 0.022 to 1.060 % (m/v), the absorbance increased from 0.110 to a peak of 0.231 and then decreased steadily to 0.051. The SB concentration of 0.720 % (m/v) [6.0 ml of 3 % (m/v) SB solution in 25 ml final volume] was therefore chosen as the optimum concentration for the SB-Ni method.
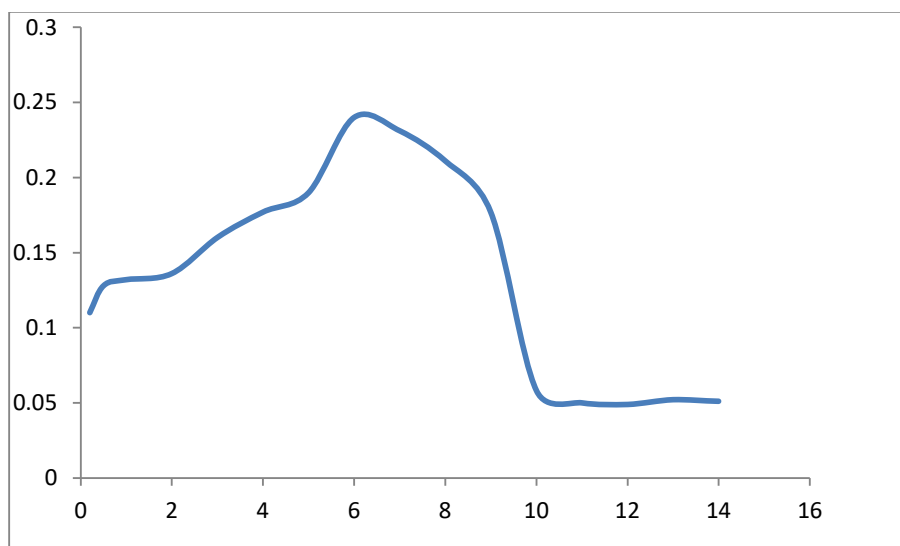
Figure 3.8: Effect of the SB Concentration on the SB-Ni system

3.1.9 Effect of Reaction Time on Absorbance of SB-Ni System

Figure 3.10 indicates that colour developed instantaneously on addition of methylamine to the reaction mixture. The absorbance reached a maximum after 20 minutes. Therefore 20 minutes was chosen for the maximum colour development of the reaction mixture (Rm).
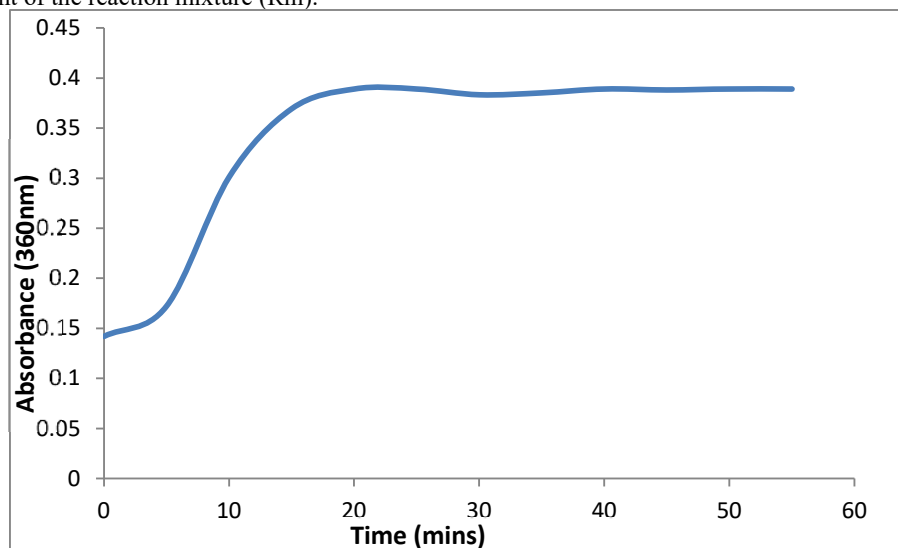

Figure 3.9 Effect of Reaction Time

3.1.10 Stability of the Reaction Mixture (Rm) and Reagent Blank (Rb)

Figure 3.10 above showed that colour developed instantaneously after addition of methylamine during the formation of the SB-Ni complex and reached a maximum after 20 minutes. Figure 3.11 reveals that after attainment of maximum colour development followed by pH adjustment to 12.5, the absorbance of Rm and Rb remained constant for 80 minutes. After 80 minutes, absorbance decreased gradually. From the foregoing, therefore, it is recommended that once the maximum colour is attained and pH adjusted to 12.5, the Rm and Rb were used within the next 1hr 20 minutes (80 minutes). Thereafter the Rb and Rm were discarded.
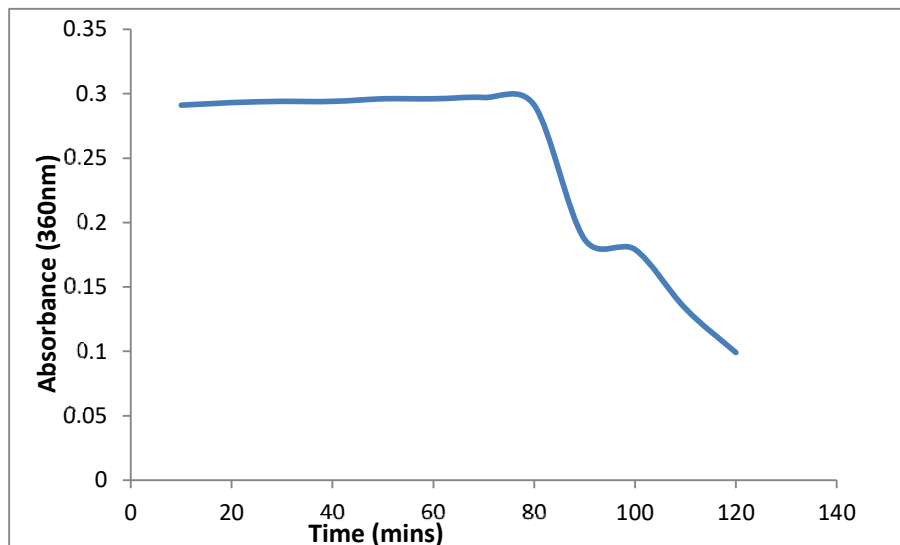
Figure 3.10: Stability of Rm and Rb

3.1.11 Order of Addition of Reagents

The effect of order of addition of reagents was studied. From the results obtained, the optimum order of addition of reagents is as follows: a + b + c + d (where a= Ni^{2+}, b= SB, c= NaOH, d= methylamine) (Figure 3.12)**.**

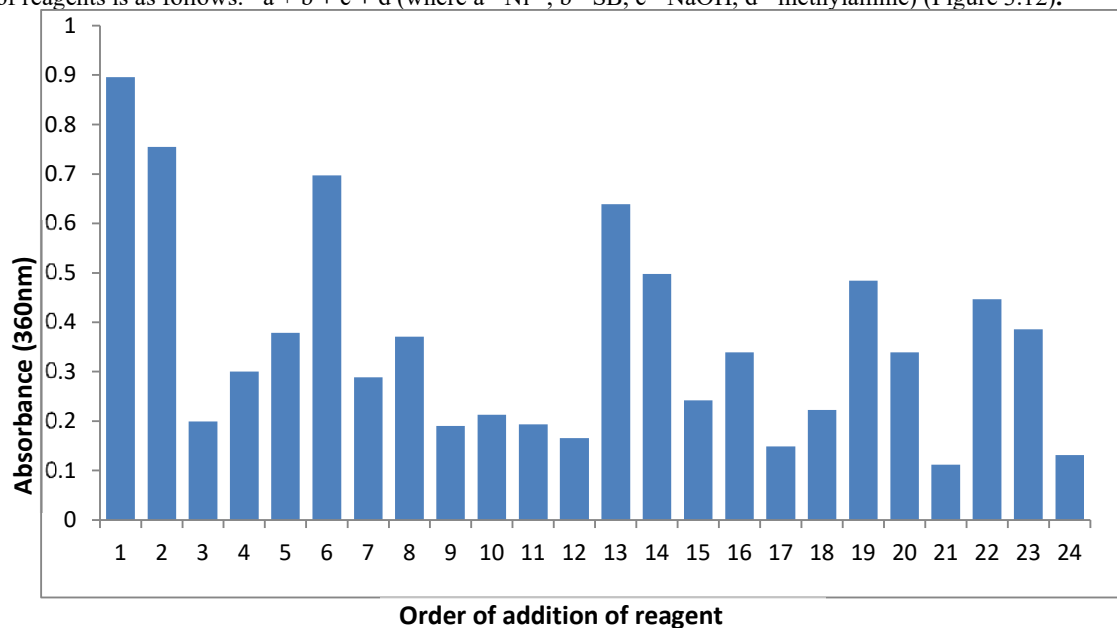**Order of addition of reagent**

Figure 3.11 Order of Addition of Reagent

3.1.12 Adherence to Beer's Law

Figure 3.13 reveals that when the recommended procedure is followed, Beer's law is obeyed up   to 6.0 ppm Ni^{2+}. Beyond 6.0 ppm, positive deviation is observed.
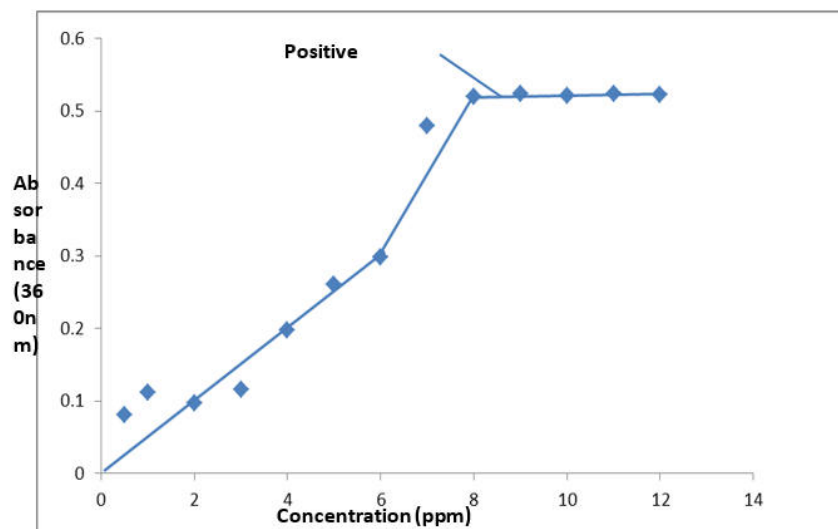
Figure 3.12 Adherence to Beer's Law

3.1.13 Stoichiometry of the SB-Ni Complex

Several methods can be used to determine the ratio of the ligand to the metal in a complex. In this study, Job's method of continuous variation, mole ratio and slope ratio methods were used to complement each other.

3.1.13.1 *Job's Method Of Continuous Variation*

The molar Absorptivity (ε) of the 2×10^{-3} M Ni^{2+} solution was calculated using the Beer-Lambert law:

$$A_{(Ni^{2+})} = \varepsilon_{(Ni^{2+})}. \, b.c \tag{3.1}$$

Where $A_{(Ni^{2+})}$ is the measured absorbance of the 2×10^{-3} M Ni^{2+}, $\varepsilon_{(Ni^{2+})}$ is the molar absorptivity of the solution, b is the path length of the cell in cm and c is the concentration of the Ni^{2+} ion in $molL^{-1}$.

The corrected absorbances Ac, for each of the nine reaction mixtures were calculated using the relation:

$$Ac = A - [\varepsilon_{(Ni^{2+})}(1-X). \, b \,.c] \tag{3.2}$$

Where; A is the uncorrected absorbance for each of the reaction mixtures and X is the mole fraction of the SB. A graph of Ac against X was plotted and the value of X was located where the extrapolated straight-line portions of the graph intersected, Figure 3.13.
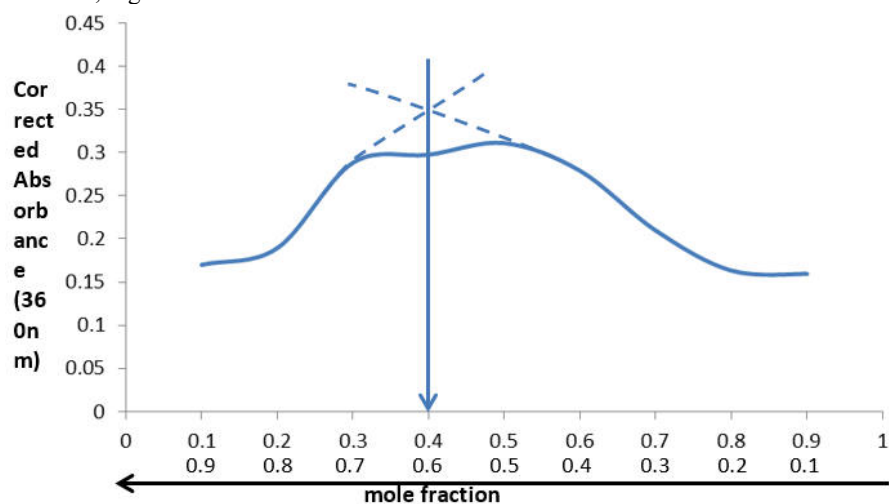

Figure 3.13 Job's plot for SB-Ni^{2+} complex

SB-Ni complex was established by being evaluated as follows:

From Figure 3.13, the value of X (mole ratio of SB) at the point of inflection is 0.41 and that of Ni^{2+} is 0.61. Therefore,

$$X_{Ni} = \frac{V_{Ni}}{V_{Ni} + V_{SB}} = 0.41 \tag{3.3}$$

$$X_{SB} = \frac{V_{SB}}{V_{SB} + V_{Ni}} = 0.61 \qquad (3.4)$$

Dividing equation (3.3) by equation (3.4)

$$\frac{V_{Ni}}{V_{SB}} = \frac{0.41}{0.61} \approx \frac{1}{2} \qquad (3.5)$$

The stoichiometry of the SB-Ni complex may therfore be established as $NiSB_2$

3.1.13.2 Mole-Ratio Method

A plot of absorbance against mole ratio , [SB]/[Ni^{2+}], was made (Figure3.14) and the value of the mole ratio where the extrapolated straight line portions of the graph intersected was located. From Figure 3.14, the value of mole ratio at the point of inflection is 1.5.

That is, [SB]/[Ni^{2+}] = 1.5/1 $\approx$ 2/1

The stoichiometry of the SB-Ni complex may therefore be established as $NiSB_2$
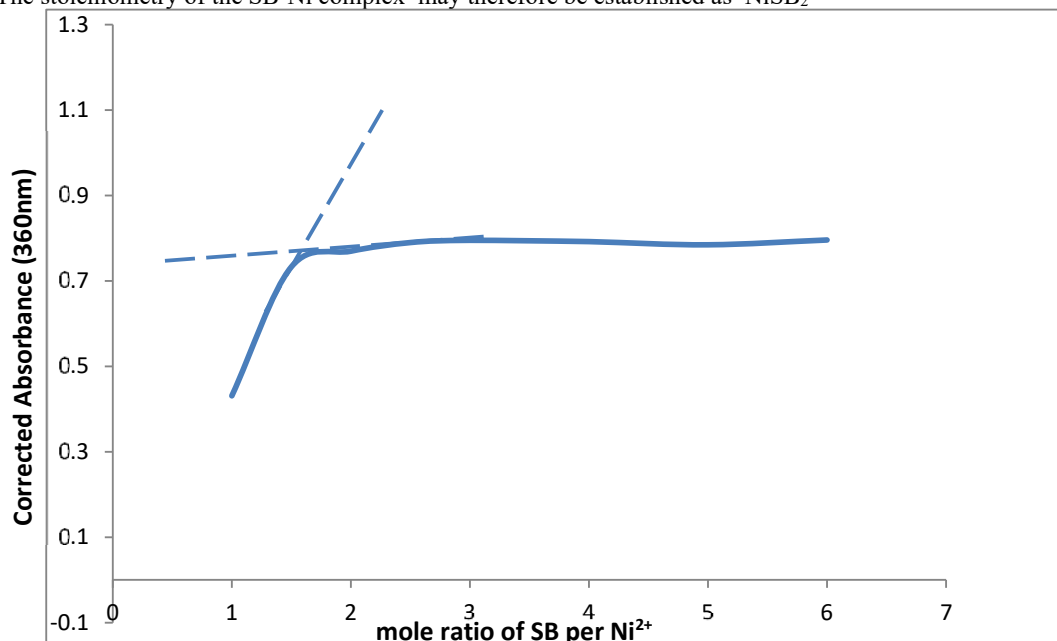
Figure 3.12: Mole-ratio plot for SB-Ni complex

3.1.13.3 Slope-ratio Method

Two sets of solution were prepared in this method; sets A and B. In set A, the concentration of the ligand was kept constant, while that of the metal ion in solution is varied, In set B, the concentration of the metal was kept constant while that of the ligand is varied.

In series A, a plot is prepared of the absorbance against concentration of metal, and in series B, a plot was prepared of absorbance against concentration of ligand.

$\frac{Slope\ A}{Slope\ B}$ gives the metal to ligand ratio

Figure 3.13: Slope Ratio Plot of Absorbance against Ni^{2+}for Set A

Slope of set A = 0.0125
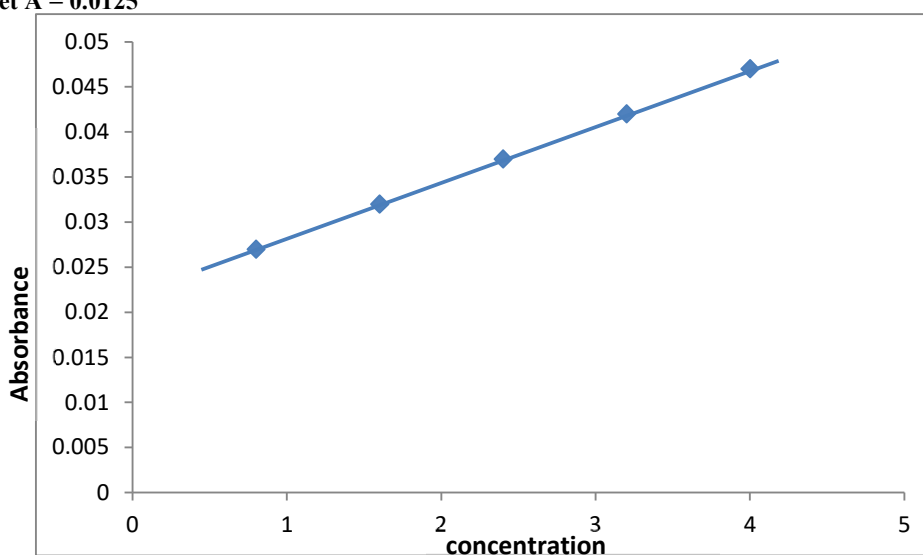
Figure 3.14: Slope Ratio Plot of Absorbance against Ligand Concentration
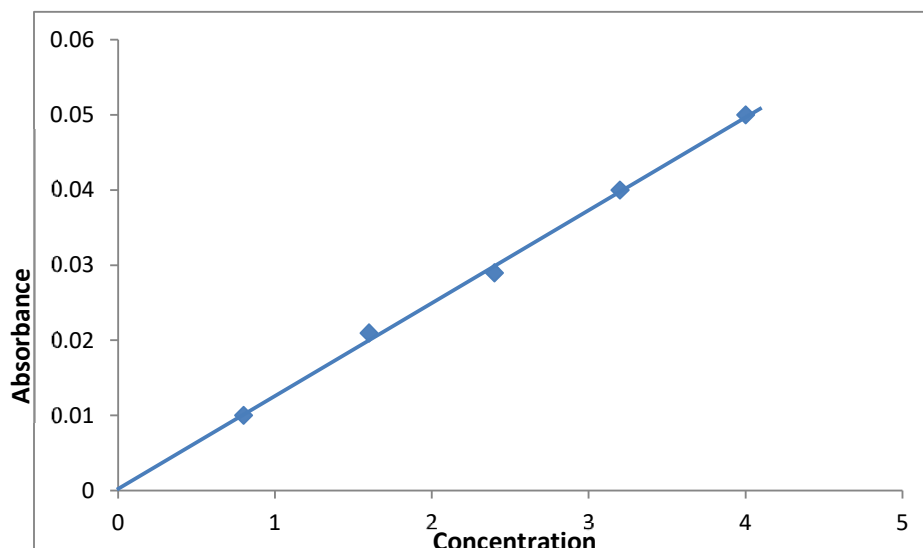
Slope of set B = 0.00625

Metal to ligand ratio $= \dfrac{slope\ A}{Slope\ B} = \dfrac{0.0125}{0.00625} = \dfrac{1}{2}$ (3.6)

The three procedures, continuous variation (Job's), mole-ratio and slope-ratio methods are in agreement over the stoichiometry of the SB-Ni complex.

3.1.14 Interference Studies

The effect of foreign ions on the absorbance of 4.0 ppm nickel ion concentration is shown in Table 3.2.

The criterion for interference was fixed at $\pm 0.5\%$. That is, concentrations of foreign ions which cause relative deviations equal to, or lower than 5.0 % were tolerated. Most of the ions tested were tolerated in a wide range of concentrations.

Some of the most tolerated ions are Ag$^+$,SO$_4^{2-}$,Cd^{2+}, (1.00x10^{-1} molL^{-1}max.) and least tolerated ions areCa, $^+$, Zn^{2+}, NO$^-_3$,Cl$^-$, CO$_3^{2-}$(5.00 X 10^{-4} molL^{-1} max).

Table 3.2: Effect of foreign ions on the absorbance of 4 ppm Ni^{2+}

Species	Added as	Tolerated conc.(molL^{-1})	Relative deviation (%)
Ca^{2+}	CaSO$_4$	5×10^{-4}	2.9
Zn^{2+}	ZnCl$_2$	4.0×10^{-2}	2.5
Cd^{2+},SO$_4^{2-}$	CdSO$_4$.6H$_2$O	1.4×10^{-4}	-2.63
Cu^{2+},Cl$^-$	CuCl$_2$	3.0×10^{-2}	-2.91
Ag$^+$,NO$_3^{2-}$	AgNO$_3$	1.0×10^{-1}	-3.61
K$^+$,CO$_3^{2-}$	K$_2$CO$_3$	5×10^{-4}	3.7

3.1.15. Recovery tests

The accuracy and precision of the proposed method was studied by spiking water samples (deionized, distilled water) with nickel and analyzing five replicates of each. The results are shown below. Recovery range of 90-120 % is acceptable (Manno *et al*. 2006).

3.1.16 Recovery of 0.2 µg/ml Ni^{2+} Spiked into 20 ml Deionized, Distilled Water

The recovery of 0.2 µg/ml Ni^{2+} added to 20 ml deionized, distilled water, and Tables 3.3 and 3.4, show details used for the recovery calculation.

Table 3.3 Recovery of 0.2 µg/ml Ni^{2+}Absorbance Measurements

Replicate spiked water sample (0.2µg/ml Ni^{2+} added)	Absorbance (360nm)	Conc. (ppm)w.r.t 25ml final solution as read from calibr. Curve	Corresponding conc. (ppm) w.r.t 20ml spiked water sample
s$_1$	0.082	0.170	0.2125
s$_2$	0.084	0.172	0.2150
s$_3$	0.084	0.172	0.2150
s$_4$	0.082	0.170	0.2125
s$_5$	0.082	0.170	0.2125

Table 3.4 Recovery of 0.2 µg/ml Ni^{2+}Calculations of Standard Deviation (SD), Relative Standard Deviation(RSD), 95% Confidence Limit, and % Recovery

S/N	s_i	$\bar{s}$	$s_i^1 - \bar{s}$	$\left(s_i - \bar{s}\right)^2$	$\sum\left(s_i - \bar{s}\right)^2$
1	0.2125		-0.010	0.000100	
2	0.2150		0.015	0.000225	
3	0.2150	0.2135	0.015	0.00225	0.00075
4	0.2125		-0.010	0.0001	
5	0.2125		-0.010	0.0001	

$$SD = \sqrt{\frac{\sum\left(s_i - \bar{s}\right)^2}{N-1}} = \sqrt{\frac{0.00075}{4}} = 0.014 \qquad (3.7)$$

$$RSD = \frac{SD}{\bar{\bar{S}}} = \frac{0.014}{0.2135} = 0.066 \qquad (3.8)$$

95% confidence limit = $\bar{s} \pm t\dfrac{SD}{\sqrt{N}}$ $\qquad (3.9)$

where t = 2.78, from statistical table.

$\therefore$ 95% conf. limit = 0.2 135$\pm$ $\dfrac{2.78 X 0.014}{\sqrt{5}}$

$= 0.2135 \pm 0.017\mu g / ml$

$\%$ Recovery = $\dfrac{\text{amount found x 100\%}}{\text{amount added}}$ $= \dfrac{0.2135}{0.2}\times100\%$ $\qquad (3.10)$

= 106.75%

3.1.17 Application of the SB-Ni Method

The proposed method (SB-Ni system) was applied to the determination of Ni^{2+} in digested soil sample, tap water, well water and waste water. In order to further test the accuracy, results were compared with those obtained by one of the standard methods: the Atomic Absorption Spectroscopy, AAS. Table 3.5 shows that the two methods

are in agreement.

Table 3.5: Application of SB-Ni System and AAS in the Determination of Ni^{2+} in Environmental Sample.

Sample	AAS		SB-Ni method
	25ml soln (µg/ml)	Absorbance (360nm)	Corresponding Conc. µg/ml in 25ml Rm
Digested soil sample	2.104	0.202	1.971
tap water	0.000	0.004	ND
ground water	0.000	0.012	ND
Waste water	0.393	0.031	0.401

From Table 3.2, the AAS quantified the Ni^{2+} ion in the soil sample as 2.104 µg/ml with respect to 25ml final sample solution while the proposed SB-Ni system registered 1.971 µg/ml. For the wastewater sample, the AAS indicated Ni^{2+} ion concentration in 25ml sample solution as 0.393µg/ml, while the proposed method gave 0.401µg/ml. In the other water samples; tap water and ground water, both AAS and the proposed method showed no detectable Ni^{2+} ion in the samples. The two methods are thus in agreement.

3.1.18 Limit of Detection (LOD), Limit of Quantitation (LOQ) and Method Sensitivity (MS).

The LOD and LOQ are estimated as 0.0554 µg/ml, 0.0764 µg/ml respectively, as calculated from Tables 3.6 and 3.7, while MS was given as 0.0503 obtained from figure 3.12

Table 3.6: Data for the Calculation of LOD, LOQ

S/N	Absorbance (360nm)	Corresponding conc.(µg/ml) w.r.t the original 100ml	Conc(µg/ml)w.r.t the final 25ml
1	0.021	0.250	0.050
2	0.022	0.250	0.050
3	0.022	0.250	0.050
4	0.022	0.250	0.050
5	0.019	0.220	0.044
6	0.019	0.220	0.044
7	0.019	0.220	0.044
8	0.019	0.220	0.044
9	0.019	0.220	0.044
10	0.019	0.220	0.044

Table 3.7: Derived Data for the Calculation of LOD, LOQ and MS

s_i	$\bar{s}$	$s_i - \bar{s}$	$(s_i - \bar{s})^2$	$\sum (s_i - \bar{s})^2$
0.050		0.0036	1.296×10^{-5}	
0.050		0.0036	1.296×10^{-5}	
0.050		0.0036	1.296×10^{-5}	
0.050		0.0036	1.296×10^{-5}	
0.044	0.0464	0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	8.64×10^{-5}
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	
0.044		0.0024	5.76×10^{-6}	

$$\delta = \sqrt{\frac{\sum (s_i - \bar{s})^2}{N-1}} = \sqrt{\frac{8.64 x 10^{-5}}{9}} = \sqrt{9.6 x 10^{-6}} = 0.003 \tag{3.11}$$

$$\text{LOD} = \bar{s} + 3\delta = \tag{3.12}$$
$$= 0.0464 + 3(0.003)$$
$$= 0.0554 \mu g / ml$$

$$\text{LOQ} = \bar{s} + 10\delta \tag{3.13}$$
$$= 0.0464 + 10(0.003)$$
$$= 0.0764 \mu g / ml$$

Calculation of MS

$$MS = \text{slope of Figure 3.12} = \frac{\Delta A}{\Delta conc.} = \frac{0.201}{4} = 0.0503$$

(3.14)

4. CONCLUSION

Schiff bases are among the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common solvents. Thus, they have played an important role in the development of coordination chemistry, as they readily form stable complexes with most of the metals. The spectroscopic determination of metals using Schiff base metal complex is very important in analytical chemistry. This would be a veritable contribution to solving environmental problems associated with toxic metals (Ni).This study helped to establish a novel, simple and cheap analytical method for the determination of nickel in an environmental media especially in developing countries where the cost and maintenance of sophisticated instruments are extremely high. In this study, Schiff base ligand was synthesized using benzaldehyde and aniline to form a metal complex with the target analyte (Ni^{2+}). The synthesized ligand and its Ni complex were characterized using nuclear magnetic resonance (NMR),GC-MS, melting point determination, electrical conductivity, IR, and UV-VIS spectroscopic techniques. The stoichiometry of the Schiff base–Ni complex was established using Job's method of continuous variation, mole- ratio and slope-ratio methods.

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