Chapter-V

ZERO, FIRST AND SECOND ORDER DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) METAL ION
Nickel is a silvery-white, hard, malleable, and ductile metal. It is of the iron group and it takes on a high polish. The compounds containing nickel in +2 oxidation state are known to exist. It is a fairly good conductor of heat and electricity. In its familiar compounds, nickel is bivalent although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.

The major use of nickel is in the preparation of alloys. Nickel alloys are characterized by strength, ductility, and resistance to corrosion and heat. About 65% of the nickel consumed in the western world is used to make stainless steel, whose composition can vary but is typically iron with around 18% chromium and 8% nickel. 12% of all the nickel consumed goes into super alloys. The remaining 23% of consumption is divided between alloy steels, rechargeable batteries, catalysts and other chemicals, coinage, foundry products, and plating.

Nickel is easy to work and can be drawn into wire. It resist to corrosion even at high temperatures and for this reason it is used in gas turbines and rocked engines. Monel is an alloy of nickel and copper (e.g. 80% nickel, 30% copper with traces of iron, manganese and silicon), which is not only hard but can resist corrosion by sea water, so that it is ideal for propeller shaft in boats and desalination plants.

Nickel in the environment:

Most nickel on earth is inaccessible because it is locked away in the planet’s iron-nickel molten core, which is 10% nickel. The total amount of nickel dissolved in the sea has been calculated which is around 8 tonnes. Organic matter has a strong ability to absorb the metal that is why coal and oil contain considerable amounts of nickel. The nickel content in soil can be as low as 0.2 ppm or as high as 450 ppm in some clay and loamy soils. The average is around 20 ppm. Nickel occurs in some beans where it is an essential, component of some enzymes. Another relatively rich source of nickel is tea which has 7.6mg/kg of dried leaves.
Nickel occurs combined with sulphur in millerite, with arsenic in the mineral niccolite, and with arsenic and sulphur in nickel glance. Most ores from which nickel is extracted are iron-nickel sulphides, such as pentlandite. The metal is mined in Russia, Australia, New Caledonia, Cuba, Canada and South Africa. Annual production exceeds 500,000 tonnes and easily workable reserves will last at least 150 years.

Several spectrophotometric methods for determining Ni(II) based on organic reagents containing sulphur as a ligand atom are known. Among them thiosemicarbazones are the most important. Though a good number of thiosemicarbazones were prepared, their potentiality for the photometric determination of Ni(II) has not been explored much.

Bendito et al [1] reported the use of biacetylmonoxime thiosemicarbazone (BAMOT) for the spectrophotometric determination of nickel. Cano Pavon et al [2] found that in comparison with BAMOT, biacetylmonoxime-4-phenyl-3-thiosemicarbazone (BAMOPT) has enhanced sensitivity in the photometric determination of nickel. Khasnis et al [3] observed that quinoline-2-aldehyde thiosemicarbazone was more selective than the corresponding reagent, picolin aldehyde thiosemicarbazone in the extraction photometric determination of Ni(II). Sanke Gowda et al [4] studied the colour reaction between Ni(II) and p-anisaldehyde thiosemicarbazone spectrophotometrically. They also analysed alloys and minerals by applying the reaction. Subbarami Reddy et al [5] employed salicylaldehyde thiosemicarbazone for the direct and extraction spectrophotometric determination of Ni(II).

Gomez Ariza et al [6] developed a method for the direct and extraction spectrophotometric determination of nickel using picolin aldehyde-4-phenyl-3-thiosemicarbazone. They also applied the method to determine nickel and cobalt in mixtures. Hussain Reddy et al [7] studied 1,3-cyclohexanenedione bithiosemicarbazone for the photometric determination of nickel in the pH range 8.5 to 10.0. This procedure was applied to determine nickel in alloy steels. Bhahamande et al [8] employed dipyridyl glyoxal thiosemicarbazone for the extraction photometric determination of nickel. Phenanthroquinone monothiosemicarbazone was used as analytical reagent for the
photometric determination of nickel by Sinha et al [9]. They determined nickel in bright way ‘G’ wire. Salim et al [10] studied 5,5-dimethyl-1,2,3-cyclohexane trione 1,2-dioxime 3-thiosemicarbazone as a reagent for the spectrophotometric determination of nickel.

Youngwen Liu et al [11] developed a method for solid-phase spectrophotometric determination of nickel in water and vegetable samples at sub-μg/l level with O-carboxylphenyldiazoaminoazobenzene loaded XAD-4. adsorbed resin phase spectrophotometric determination of nickel was developed by LI R et al [12]. Surfactant extraction-spectrophotometric determination of nickel(II) in the samples of a high salinity was developed by Tagashira shoji et al. [13]. Tagashira shoji et al [14] developed a method for micellar extraction and spectrophotometric determination of Ni(II) as the dodecylxanthato complex in a solution of the anionic surfactant sodium dodecylsulfate.

Spectrophotometric determination of nickel using a new chromogenic reagent in plant leaves was developed by Suresh Kumar et al [15]. Studies on solid phase extraction and spectrophotometric determination of nickel in waters and biological samples was reported by Qiufin Hu et al[16].

**Present Investigations:**

2,4-DHAHB forms light brown coloured water soluble complex with nickel(II) in the pH range of 8.0 to 11.0. The light brown coloured solution is therefore, investigated spectrophotometrically for the possible determination of nickel(II) in micro amounts.

**a) Absorption spectra of the reagent and the experimental solution:**

The absorption spectra of the reagent solution against corresponding buffer (pH 10.0) and that of the complex solution against the reagent blank are recorded in the wavelength range 340 nm to 550 nm. The spectra show that the complex has an absorption maximum at 390
The reagent has negligible absorbance at 390 nm. Hence, further analytical studies are made at 390 nm.

**b) Effect of pH on the absorbance of experimental solution:**

The optimum pH required for the maximum colour development is established from the results obtained in the experiment. The plot drawn between absorbance and pH indicates that the absorbance is maximum and constant in the pH range of 9.0 to 11.0. Hence, pH 10.0 is selected for further studies.
Fig. 5.1. Absorption spectra of (a) 2,4-DHAHB vs buffer blank (b) Ni (II) – 2,4-DHAHB vs reagent blank

\[
\begin{align*}
[Ni \text{ (II)}] &= 2 \times 10^{-5} \text{ M} \\
[2,4\text{-DHAHB}] &= 6 \times 10^{-4} \text{ M} \\
pH &= 10
\end{align*}
\]
c) Effect of 2,4-DHAHB concentration on the absorbance of the experimental solution:

The optimum concentration of 2,4-DHAHB required to obtain maximum absorbance and the results are presented in table-5.1.

<table>
<thead>
<tr>
<th>[Ni(II)] : [2,4-DHAHB]</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 2</td>
<td>0.284</td>
</tr>
<tr>
<td>1 : 4</td>
<td>0.550</td>
</tr>
<tr>
<td>1 : 6</td>
<td>0.678</td>
</tr>
<tr>
<td>1 : 8</td>
<td>0.783</td>
</tr>
<tr>
<td>1 : 10</td>
<td>0.776</td>
</tr>
<tr>
<td>1 : 15</td>
<td>0.772</td>
</tr>
</tbody>
</table>

The results indicate that a 10 molar excess of the reagent is necessary for achieving maximum absorbance. Hence, the same ratio is maintained throughout the studies.

d) Order of addition of constituent solutions on the absorbance of the experimental Solution:

The order of addition of the constituent solutions (buffer solution, Ni (II) solution and the reagent solution) has no effect on the absorbance of the experimental solutions. Hence, it is not necessary to scrupulously follow a particular order of addition of various components of the experimental solution.
Fig. 5.2. Effect of pH on the absorbance of Ni (II) – 2,4-DHAHB system

\[
\begin{align*}
[Ni \text{ (II)}] &= 2 \times 10^{-5} \text{ M} \\
[2,4-DHAHB] &= 6 \times 10^{-4} \text{ M} \\
\text{Wavelength} &= 390 \text{ nm} \\
\text{pH} &= 10.0
\end{align*}
\]
Fig. 5.3. Applicability of Beer's law

\[
A_{390} = 0.1908C - 0.0019
\]

| [2,4-DHAHB] | \(6 \times 10^{-4}\) M |
| pH          | 10.0 |
| Wavelength  | 390 nm |
e) **Effect of time on colour development and time stability of the colour:**

To study the effect of time on the absorbance, it is noticed that the colour development is instantaneous and remains constant for 24 hours.

f) **Adherence of the system to Beer's law:**

To explore the possibility of employing the colour reaction for the determination of nickel(II) keeping the reagent concentration constant, the absorbance of experimental solutions is measured at 390 nm. The results are presented in the form of a plot of absorbance vs amount of nickel (II). The straight line plot obtained obeys the equation $A_{390} = 0.1908 - 0.0019$. The linear plot between the absorbance and the amount of nickel(II) indicates that Beer's law is obeyed in the range of 0.520-5.09 $\mu$g/ml of nickel (II).

The molar absorptivity and Sandell's sensitivity are $1.34 \pm 0.002 \times 10^5$ l mol$^{-1}$ cm$^{-1}$ and 0.0012 $\mu$g/cm$^2$ respectively. The standard deviation of the method for ten determinations of 1.86 $\mu$g/ml of Ni (II) is 0.009. The correlation coefficient ($\gamma$) of the calibration equation for the experimental data is 0.9995.

h) **Composition and stability constant of the complex:**

The composition of the complex is determined by Job's continuous variation method and mole ratio method and stability constant by Job's method.

i) **Job's method:**

Equimolar solutions ($1 \times 10^{-3}$M) of nickel(II) and 2,4-DHAHB are prepared and mixed in different volume proportions keeping the total volume of the mixture constant. The results are presented in the given graph. From the plot it is seen that the composition of the complex is 1:1 and the stability constant $\beta$ as calculated from the job's method is $3.40 \times 10^4$. 
ii) **Mole ratio method:**

Mole ratio method carried out from a series of solutions containing 0.5 ml of nickel(II)\((1\times10^{-3} M)\) solution and different volumes of 2,4-DHAHB solution. The mole ratio plot confirms the composition as 1:1 \([\text{Ni (II)}: 2,4\text{-DHAHB}]\).

---

**Fig.5.4. Job's curve**

\[
\begin{align*}
\text{[Ni (II)]: [2,4-DHAHB]} &\quad = \quad 1 \times 10^{-3} \text{ M} \\
\text{pH} &\quad = \quad 10.0 \\
\text{Wavelength} &\quad = \quad 390 \text{ nm}
\end{align*}
\]
Fig. 5.5. Molar ratio method

\[
\text{[Ni (II)} : [2,4-DHAHB] = 1 \times 10^{-3} \text{ M}
\]

Wavelength = 390 nm

pH = 10.0

Volume of Ni (II) taken = 0.5 ml
**First order derivative spectrophotometric determination of Nickel(II):**

Nickel (II) forms light brown coloured water soluble complex with 2,4-DHAHB. The colour is stable for more than 24 hours. The zero order spectrum of the complex shows a $\lambda_{\text{max}}$ at 390 nm. The optimal conditions for the determination of nickel(II) are pH 10.0 and 15 fold molar excess of 2,4-DHAHB. The absorbance measurements are made at 390 nm.

Derivative spectrophotometric methods for the determination of nickel(II) are very few. Hence an attempt is made to develop a first derivative spectrophotometric method for the determination of nickel(II) in micro quantities and the results are presented in this section.

**First derivative spectrum of Ni(II) complex solution:**

The first derivative spectrum of Ni(II)- 2,4-DHAHB system at pH 10.0 is recorded. The derivative spectrum shows a peak at 425 nm and a zero cross at 410 nm. To ascertain the possibility of determining Ni(II) in trace quantities at 445 nm, the first derivative spectra of three solutions containing different amounts of Ni (II) at pH 10.0.

The graph indicates that the amplitude at 425 nm is proportional to the amount of Ni(II) and that the zero cross at 410 nm is independent of the amount of Ni(II) and this indicates a first derivative spectrophotometric determination of Ni(II) in microgram levels is possible.
Fig. 5.6. First order derivative spectra of Ni (II) – 2,4-DHAHB

Amount of Ni (II) (µg mL⁻¹): a. 0.836; b. 1.672; c. 2.507; d. 3.343; e. 4.179
Fig. 5.7. Beer's law plot for first order derivative data

\[ [2,4-DHAHB] = 6 \times 10^{-4} \text{ M} \]

\[ \text{pH} = 10.0 \]
Determination of Ni (II):

To determine Ni(II), the procedure is followed and the first derivative spectra for various amounts of Ni(II) are recorded. The amplitude at 425 nm is measured in each case. A plot is made between the amount of Ni (II) and the first derivative amplitude and shown the plot obeys the equation $A_{425} = 0.053C - 0.0004$ and Ni(II) can be determined in amounts as low as 1.00 μg/ml. The standard deviation of the method for the determinations of 1.710 μg/ml of Ni (II) is 0.160.

Section-3 Second order derivative spectrophotometric determination of Nickel(II):

The second order amplitude at 455 nm is proportional to the concentration of Ni(II) solution and Ni(II) is determined by measuring the derivative amplitude for different concentration of Ni(II). The plot drawn between the amount of Ni(II) and derivative amplitude is found to be linear and conform to the relation $A_{455} = 0.015C + 0.009$. It enables the determination of Ni(II) in amount as low as 0.125 mg/ml.

At 495 nm plot drawn between the amount of Ni(II) and derivative amplitude is found to be linear and conform to the relation $A_{495} = 0.013C - 0.002$. It enables the determination of Ni(II) in amount as low as 0.101 mg/ml.
Fig. 5.8. Second order derivative spectra of Ni (II) – 2,4-DHAHB

Amount of Ni (II) (µg mL⁻¹): a. 0.836; b. 1.672; c. 2.507; d. 3.343; e. 4.179
Fig. 5.9. Beer's law plots for second order derivative data

\[ [2,4\text{-DHAHB}] = 6 \times 10^{-4} \text{ M} \]

\[ \text{pH} = 10.0 \]
Effect of foreign ions:

In order to assess the possible analytical applications of this colour reaction, the effect of some foreign ions was examined by carrying out determination of 2.348 µg/ml of Co(II) with a known amount of foreign ion by using above procedure. The criterion for interference is the absorbance value, varying more than ±3% from the expected value for Co(II) alone. The tolerance limits for various cations and anions are listed in the given table.

Thus, from the results presented in the above paragraphs, it can be concluded that the present method can be used for the analytical determination of Ni(II) in microgram quantities as well as the reagent 2,4-DHAHB in milligram quantities.

Statistical analysis of the data:

Statistical analysis of the data obtained in the experiment on cobalt with 2,4-DHAHB system is carried out. The standard deviation and relative standard deviation are calculated and the data is presented in the given table 5.2.
Table-5.2

**Tolerance limit of foreign ions**

Tolerance limit of foreign ions in the determination of 2.348 µg/ml of Ni(II)

pH = 10.0, \( \lambda_{\text{max}} = 363 \text{ nm} \)

<table>
<thead>
<tr>
<th>Foreign ion</th>
<th>Tolerance limit (µg/ml)</th>
<th>Foreign ion</th>
<th>Tolerance limit (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>16.70</td>
<td>Mo (VI)</td>
<td>65.20</td>
</tr>
<tr>
<td>Chloride</td>
<td>48.07</td>
<td>Pb (II)</td>
<td>2.63</td>
</tr>
<tr>
<td>iodide</td>
<td>62.67</td>
<td>W (VI)</td>
<td>735.4</td>
</tr>
<tr>
<td>nitrate</td>
<td>112.73</td>
<td>Co (II)</td>
<td>1.54</td>
</tr>
<tr>
<td>acetate</td>
<td>152.26</td>
<td>Se (IV)</td>
<td>110.53</td>
</tr>
<tr>
<td>oxalate</td>
<td>16.22</td>
<td>Mn (II)</td>
<td>3.23</td>
</tr>
<tr>
<td>EDTA</td>
<td>320.5</td>
<td>U (VI)</td>
<td>86.56</td>
</tr>
<tr>
<td>thiosulphate</td>
<td>55.65</td>
<td>Cu (II)</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti (IV)</td>
<td>127.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y (III)</td>
<td>33.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V (V)</td>
<td>22.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg (II)</td>
<td>11.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd (II)</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn (II)</td>
<td>2.272</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg (II)</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Th (IV)</td>
<td>9.055</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru (III)</td>
<td>11.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V (IV)</td>
<td>21.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn (II)</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd (II)</td>
<td>3.512</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr (IV)</td>
<td>3.72</td>
</tr>
</tbody>
</table>
Applications:

The present method is applied for the determination of Ni(II) in groundnut seeds and sesame seeds. The data shows that the results obtained by proposed method for groundnut seeds and sesame seeds are in good agreement with those obtained by the AAS method. The groundnut seeds and sesame seeds brought into solution by the procedure given below. The amount of nickel present in groundnut seeds and sesame seeds was determined by the following procedure.

Procedure:

50 g of biological material was heated in a 500 ml conical flask with 40 ml of conc. HNO₃ on a steam bath and shaken vigorously until a fine emulsion was formed. The heating was continued with the gradual addition of 6 per cent H₂O₂ (40 ml). The aqueous phase was then transferred to the beaker. The extraction was repeated twice with further addition of 20 ml of concentrated nitric acid and 20 ml of 6 percent H₂O₂. The combined extracts were evaporated to dryness. The residue was dissolved in minimum amount of dil. HCL and it is transferred into a 50-ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

Present method:

A known aliquot of the sample solution was taken in a 25 ml standard flask containing 10 ml of buffer solution. Then 2 ml of 1x10⁻⁵ M of the reagent solution was added. The contents were made up to the mark with distilled water. The absorption of the complex was measured at 363 nm against respective reagent blank solution. The absorbance values were referred to the predetermined calibration plot to compute the unknown amount of the metal ion.
Table 5.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of Ni(II) (μg/ml)</th>
<th>Error(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present method</td>
<td>AAS method</td>
</tr>
<tr>
<td>Groundnut seeds</td>
<td>1.189</td>
<td>1.205</td>
</tr>
<tr>
<td>Sesame seeds</td>
<td>1.261</td>
<td>1.273</td>
</tr>
</tbody>
</table>

* Average of five determinations
REFERENCES