Chapter-IV
ZERO, FIRST AND SECOND ORDER DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) METAL ION
Section-1 Color reactions of some metal ions with 2,4-Dihydroxyacetyl,4-hydroxybenzoic hydrazone (2,4-DHAHB):

The color reactions of 2,4-Dihydroxyacetyl,4-hydroxy benzoic hydrazone (2,4-DHAHB) with various metal ions are studied in acidic and basic media. The results are presented in table 4.1.

Table 4.1

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Colour reaction with 2,4-DHAHB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acidic Medium</td>
</tr>
<tr>
<td>Ferrous (II)</td>
<td>Dark brown</td>
</tr>
<tr>
<td>Molybdenum(VI)</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>Titanium (IV)</td>
<td>Brown</td>
</tr>
<tr>
<td>Thorium (IV)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Zirconium (IV)</td>
<td>Light yellow</td>
</tr>
<tr>
<td>Platinum (IV)</td>
<td>yellow</td>
</tr>
<tr>
<td>Gold(III)</td>
<td>violet</td>
</tr>
<tr>
<td>Manganese (II)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>Light blue</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>Light yellow</td>
</tr>
<tr>
<td>Tungsten (VI)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Cerium(IV)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Ruthenium(IV)</td>
<td>Very light brown</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>Greenish yellow</td>
</tr>
<tr>
<td>Uranium (VI)</td>
<td>No reaction</td>
</tr>
<tr>
<td>Iron (III)</td>
<td>Reddish brown</td>
</tr>
</tbody>
</table>
The observations recorded clearly indicate that 2,4-DHAHB is a potential analytical spectrophotometric reagent. It is seen from the table that the reagent forms coloured complexes with several transition metal ions. Hence, a comprehensive study of zero and first order derivative spectrophotometric determination of some important transition metal ions was undertaken with a view to develop new, simple and rapid procedures for individual and simultaneous determination in mixtures of some transition metal ions of industrial, agricultural and biological importance.

Direct spectrophotometric studies relating to the colour reactions between 2,4-DHAHB and cobalt(II) and nickel(II) are presented in this chapter.

**Section-2 Spectrophotometric determination of Cobalt(II) system:**

Cobalt is a ferromagnetic, silver-white, hard, lustrous and brittle element. It is a member of group VIII of the periodic table. The compounds containing cobalt in +2 oxidation state are known to exist. Like iron, it can be magnetized. It is similar to iron and nickel in its physical properties. The element is active chemically, forming many compounds. Cobalt is stable in air and unaffected by water, but is slowly attacked by dilute acids. Cobalt is used in many alloys (super alloys for parts in gas turbine, aircraft engines, corrosion resistant alloys, high-speed steels, cemented carbides), in magnets and magnetic recording media, as catalyst for the petroleum and chemical industries, as drying agent for paints and inks. Cobalt blue is an important part of artists’ palette and is used by craft workers in porcelain, pottery, stained glass, and enamel jewellery. The radioactive isotope, cobalt-60, is used in medical treatment and also to irradiate food, so as to preserve it.

**Cobalt in the environment:**

Cobalt is of relatively low abundance in the Earth’s crust and in natural waters, from which it is precipitated as the highly insoluble cobalt sulfide CoS. Although the average level of cobalt in soils is 8ppm, there are soils with as little as 0.1 ppm and others with as high as 70 ppm. In the marine environment cobalt is needed by blue-green algae (cyanobacteria) and other nitrogen-fixing organisms. Cobalt is not found as a free metal and is generally found in the form of ores. Cobalt is usually not mined alone, and tends to be produced as by-product of nickel and
copper mining activities. The main ores of cobalt are cobaltite, earthrise, glaucodot, and skutterudite. The world's major producers of cobalt are the Democratic Republic of the Congo, mainland China, Zambia, Russia and Australia. It is also found in Finland, Azerbaijan, and Kazakhstan. The overall World production is 17,000 tonnes per year.

**Health effects of cobalt:**

As cobalt is widely dispersed in the environment, humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure.

Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, the uptake by plants and animals is higher and accumulation in plants and animals may occur.

Cobalt is beneficial for humans because it is a part of vitamin B$_{12}$, which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. The total daily intake of cobalt is variable and may be as much as 1 mg, but almost all will pass through the body unabsorbed, except that in vitamin B$_{12}$.

However, too high concentrations of cobalt may damage human health. When we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia. This mainly occurs with people that work with cobalt.

When plants grow on contaminated soils they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Soils near mining and melting facilities may contain very high amounts of cobalt, so that the uptake by humans through eating plants can cause health effects.

Health effects that are a result of the uptake of high concentrations of cobalt are:

- Vomiting and nausea
- Vision problems
- Heart problems
- Thyroid damage
Health effects may also be caused by radiation of radioactive cobalt isotopes. This can cause steril hair loss, vomiting, bleeding, diarrhoea, coma and even death. This radiation is sometimes used with cancer-patients to destroy tumors. These patients also suffer from hair loss, diarrhea and vomiting.

Analytical chemistry of cobalt:

A large number of organic compounds were reported as analytical reagents for the determination of cobalt. These include oximes, phenyl hydrazones, azo compounds etc. 1-Nitroso-2-napthol, proposed by Ilinsky et al [1] was one of the first organic analytical reagents employed for the determination of cobalt. This reagent along with its isomer, 2-Nitroso-1-napthal was used for the spectrophotometric determination of cobalt in several real samples [2-4]. Many reports are available for the spectrophotometric determination of cobalt. Some of the recent references are listed here.

Syama Sundar and his coworkers [5] employed 1-(benzimidazole-2-y1) ethanone thiosemicarbazonc for the extractive spectrophotometric determination of Co(II). A sensitive spectrophotometric method for the determination of Co(II) using 1-methyl,2-acetyl benzimidazole thiosemicarbazonc was reported [6]. Chiranjeevi et al [7] developed a facile, rapid and economical flow injection method for the spectrophotometric determination of Co(II) using 3,5-dibromosalicylaldehyde thiosemicarbazonc and applied the method for its determination in various environmental samples.

Tejam and Thakkar [8] employed 1-phenyl 1,2-butane dione dioxime as a new reagent for the extractive spectrophotometric determination of Co(II) at trace levels. Reddy [9] proposed cyanex 923 for the extractive spectrophotometric determination of Co(II) in synthetic and pharmaceutical samples. A selective method for the FIA spectrophotometric determination of Co(II) based on the use of pyridoxal 4-phenylthiosemicarbazonc as reagent was developed by Enrique Cristofol de Alcaraz et al [10]. Gonez Ariza [11] and his coworkers used picolinaldehyde 4-phenyl-3-thiosemicarbazonc for the spectrophotometric determination of small amounts of cobalt in the presence of iron.

No spectrophotometric determination of Co(II) using 2,4-dihydroxyacetyl4-hydroxybenzoichydrazone(2,4-DHAHB) is reported. Hence the author as undertaken a detailed spectrophotometric and first and second derivative spectrophotometric determination of Co(II) using 2,4-DHAHB.

Present Investigations:

2,4-DHAHB forms lightpink coloured water soluble complex with cobalt(II) in the pH range of 7.0 to 11.0. The lightpink coloured solution is therefore, investigated spectrophotometrically for the possible determination of cobalt(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 9.0) and that of the complex solution against the reagent blank are recorded in the wavelength range 350 nm to 500 nm.

The spectra show that the complex has an absorption maximum at 405 nm. The reagent has negligible absorbance at 450 nm. Hence, further analytical studies are made at 405 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 7.0 to 11.0. Hence, pH 9.0 is selected for further studies.

![Graph showing absorbance vs wavelength with pH range 3.0 to 11.0]

**Fig. 4.1.** (a) Absorption spectra of (a) 2,4-DHAHB vs buffer blank; (b) Co (II) – 2,4-DHAHB vs reagent blank

\[
\begin{align*}
[\text{Co (II)}] &= 2 \times 10^{-3} \text{ M} \\
[\text{2,4-DHAHB}] &= 3 \times 10^{-4} \text{ M} \\
\text{pH} &= 9.0
\end{align*}
\]
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 4.2

<table>
<thead>
<tr>
<th>[Co(II)] : [2,4-DHAHB]</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 02</td>
<td>0.363</td>
</tr>
<tr>
<td>1 : 05</td>
<td>0.450</td>
</tr>
<tr>
<td>1 : 10</td>
<td>0.478</td>
</tr>
<tr>
<td>1 : 15</td>
<td>0.486</td>
</tr>
<tr>
<td>1 : 20</td>
<td>0.498</td>
</tr>
<tr>
<td>1 : 25</td>
<td>0.500</td>
</tr>
</tbody>
</table>

The results indicate that a 15 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, Co(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.

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.
Fig. 4.2. Effect of pH on the absorbance of Co (II) – 2,4-DHAHB system

\[
\begin{align*}
[\text{Co (II)}] & = 2 \times 10^{-5} \text{ M} \\
[\text{2,4-DHAHB}] & = 3 \times 10^{-4} \text{ M} \\
\text{Wavelength} & = 405 \text{ nm} \\
\text{pH} & = 9.0
\end{align*}
\]
Fig. 4.3. Applicability of Beer’s law

\[ A_{405} = 0.3574C + 0.0054 \]

- [2,4-DHAHB] = 3 x 10^{-4} M
- Wavelength = 405 nm
- pH = 9.0
f) Adherence of the system to Beer's law:

To explore the possibility of employing the colour reaction for the determination of cobalt(II) keeping the reagent concentration constant, the absorbance of experimental solutions is measured at 405 nm.

The results are presented in the form of a plot of absorbance vs amount of Co (II). The straight line plot obtained obeys the equation $A_{405} = 0.3574c + 0.0054$. The linear plot between the absorbance and the amount of Co(II) indicates that Beer's law is obeyed in the range of 0.2950-2.59 µg/ml of Co (II).

The molar absorptivity and Sandell's sensitivity are $0.14 \pm 0.002 \times 10^4$ 1 mol$^{-1}$ cm$^{-1}$ and 0.0102 µg/cm$^2$ respectively. The standard deviation of the method for ten determinations of 2.59 µg/ml of Co (II) is 0.008. The correlation coefficient ($\gamma$) of the calibration equation for the experimental data is 0.9985.

g) 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.

h) Job's method:

Equimolar solutions ($1 \times 10^{-3}$M) of cobalt(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 $1.76 \times 10^5$. 87
i) Mole ratio method:

Mole ratio method carried out from a series of solutions containing 0.6 ml of cobalt(II) \((1\times10^{-3} \text{M})\) solution and different volumes of 2,4-DHAHB solution. The mole ratio plot confirms the composition as 1:1 [Co(II) : 2,4-DHAHB].

![Job's curve](image)

**Fig 4.4. Job's curve**

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

- Wavelength = 405 nm
- pH = 9.0
Fig. 4.5. Molar ratio method

\[ [\text{Co (II)}] = [\text{2,4-DHAHB}] \]

- Wavelength = 405 nm
- pH = 9.0
- Volume of Co (II) taken = 0.4 ml
- Concentration of Co (II) = $1 \times 10^{-3}$ M
Section-3 Firstorder derivative spectrophotometric determination of cobalt(II):

Cobalt (II) forms lightpink coloured water soluable 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 405 nm. The optimal conditions for the determination of Co(II) are pH 9.0 and 15 fold molar excess of 2,4-DHAHB. The absorbance measurements are made at 405 nm.

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

First derivative spectrum of Co(II) complex solution:

The first derivative spectrum of Co(II) - 2,4-DHAHB system at pH 9.0 is recorded. The derivative spectrum shows a peak at 445 nm and a zero cross at 400 nm. To ascertain the possibility of determining Co(II) in trace quantities at 445 nm, the first derivative spectra of three solutions containing different amounts of Co(II) at pH 9.0.

The graph indicates that the amplitude at 445 nm is proportional to the amount of Co(II) and that the zero cross at 400 nm is independent of the amount of Co(II) and this indicates a first derivative spectrophotometric determination of Co(II) in microgram levels is possible.
Fig. 4.6. First order derivative spectra of Co (II) – 2,4-DHAHB

Amount of Co (II) (μg mL⁻¹): a. 0.279; b. 0.558; c. 0.836; d. 1.115; e. 1.394
Fig. 4.7. Beer's law plot for first order derivative data

\[ A_{465} = 0.1253C - 0.0008 \]

\[
\begin{align*}
[2,4\text{-DHAHB}] & = 3 \times 10^{-4} \text{ M} \\
pH & = 9.0
\end{align*}
\]
Determination of Co(II):

To determine Co(II), the procedure is followed and the first derivative spectra for various amounts of Co(II) are recorded. The amplitude at 445 nm is measured in each case. A plot is made between the amount of Co (II) and the first derivative amplitude and shown the plot obeys the equation $A_{445} = 0.1253C - 0.0008$ and Co(II) can be determined in amounts as low as 1.00 µg/ml. The correlation coefficient of the experimental data is 0.9989. The standard deviation of the method for the determinations of 1.530 µg/ml of Co (II) is 0.183.

Section-4 Second order derivative spectrophotometric determination of Cobalt(II):

The second order amplitude at 415 nm is proportional to the concentration of Co(II) solution and Co(II) is determined by measuring the derivative amplitude for different concentration of Co(II). The plot drawn between the amount of Co(II) and derivative amplitude is found to be linear and conform to the relation $A_{415} = 0.219C + 0.0004$. It enables the determination of Co(II) in amount as low as 0.131 mg/ml.

At 460 nm the plot drawn between the amount of Co(II) and derivative amplitude is found to be linear and conform to the relation $A_{460} = 0.126C + 0.0011$. It enables the determination of Co(II) in amount as low as 0.142 mg/ml.
Fig. 4.8. Second derivative spectra of Co (II) – 2,4-DHAHB

Amount of Co (II) (μg mL⁻¹): a. 0.279; b. 0.558; c. 0.836; d. 1.115; e. 1.394
Fig. 4.9. Beer’s law plots for second order derivative data

\[
A_{415} = 0.219C + 0.0004 \\
A_{460} = 0.126C + 0.0011
\]

[2,4-DHAHB] = 3 x 10^{-4} M
pH = 9.0
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 0.943μg/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 ±2% 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 Co(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 4.3.
**Table-4.3**

**Tolerance limit of foreign ions**

Tolerance limit of foreign ions in the determination of 0.943 μg/ml of Co(II)

pH = 9.0; \( \lambda_{\text{max}} = 364.5 \text{ nm} \)

<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>16.52</td>
<td>Mo (VI)</td>
<td>15.35</td>
</tr>
<tr>
<td>Chloride</td>
<td>24.70</td>
<td>Mg (II)</td>
<td>6.27</td>
</tr>
<tr>
<td>Iodide</td>
<td>483.40</td>
<td>W (VI)</td>
<td>35.87</td>
</tr>
<tr>
<td>Nitrate</td>
<td>37.86</td>
<td>Zr (III)</td>
<td>36.49</td>
</tr>
<tr>
<td>Acetate</td>
<td>41.40</td>
<td>Se (IV)</td>
<td>7.35</td>
</tr>
<tr>
<td>Oxalate</td>
<td>30.61</td>
<td>Mn (II)</td>
<td>19.98</td>
</tr>
<tr>
<td>EDTA</td>
<td>326.50</td>
<td>Y (III)</td>
<td>35.56</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>128.30</td>
<td>Cu (II)</td>
<td>0.781</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe (II)</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni (II)</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg (II)</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd (II)</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd (II)</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn (II)</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U (VI)</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru (III)</td>
<td>4.68</td>
</tr>
</tbody>
</table>
Applications:

The amount of cobalt present in some alloy steel samples was determined by the present method and the results obtained were compared with certified values.

Determination of cobalt in alloy steel sample:

In order to demonstrate the usefulness of proposed method, it was applied to the determination of cobalt in standard alloy steel samples for which the cobalt content was known. The results obtained were found to be in good agreement with certified values.

Preparation of alloy steel samples solution:

A 0.1-0.5 g of the sample is dissolved in a mixture of 2 ml HCl and 10 ml HNO₃. The resulting solution is evaporated to a small volume. To this 5 ml of 1:1 H₂O:H₂SO₄ mixture is added and evaporated to dryness. The residue is dissolved in 15 ml of distilled water and filtered through whatman filter paper No.41. The filtrate is collected in a 100 ml volumetric flask and made upto the mark with distilled water.

Procedure:

A known aliquot of the sample solution is taken in a 25 ml volumetric flask containing 10ml of buffer solution of pH 9, 0.5ml of 0.5M citrate solution (to mask iron) and 1 ml of 5 x 10⁻³ M reagent solution. The contents were made up to the mark with distilled water and the absorbance was measured at 364.5 nm. The cobalt was calculated from a predetermined calibration plot and the values are shown in table.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Cobalt (II) (%)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Certified</td>
<td>Found</td>
</tr>
<tr>
<td>Eligiloy M-1712a</td>
<td>40.00</td>
<td>39.58</td>
</tr>
</tbody>
</table>
References