L-CYSTEINE HYDROCHLORIDE AS A COMPLEXING AGENT FOR THE DETERMINATION OF COBALT(II) BY SPECTROPHOTOMETRIC METHOD

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ABSTRACT
In this study, a sensitive and selective spectrophotometric method has been developed for the estimation of cobalt(II) by using a new chromogenic reagent. The maximum absorbance was found to be at 356nm. Experimental conditions were optimized. Beer’s law was seen in 1.786-11.786 µg/mL of cobalt concentration range. Calculated molar absorptivity is 3.7535x10^3 L/mol/cm. The study of interference of common ions was carried out. The current process was enforced for the estimation of cobalt in water samples, in an alloy and also in the pharmaceutical sample.

Keywords: Spectrophotometry, L-Cysteine Hydrochloride, Cobalt(II), Job’s method, Mole ratio method

INTRODUCTION
Cobalt is found in chemically combined form in the earth’s crust. The free element produced by reductive smelting is a hard, lustrous, silver-grey metal. Cobalt metal shows ferromagnetic behavior. The Curie temperature is found to be 1,115°C.1 Cobalt shows weak reducing character, passivating oxide film protects it from oxidation.

Cobalt compounds have been utilized for centuries to transmit a rich blue color to glazes, ceramics and glass.2 Cobalt is essential to the metabolism of all animals. Cobalt is the key constituent of cobalamin, also called vitamin B12, the primary biological reservoir of cobalt as an ultra-trace element.3,4 Numerous reagents of high selectivity have been discovered, which includes heterocyclic azo dye5, porphyrin reagent6, fluorescent ketone reagent7, Schiff base8 and triazene reagent.9 Several spectrophotometric determinations of cobalt in trace amount were done, for example by using 4-(6-nitro-2-benzothiazolylazo) resorcinol10, bis(5-bromosalicylaldehyde)11, hydroxytriazene as selective chelating agents12 and quantitative determination of the cobalt-containing phthalocyanine fragments antitumor drugs13. The main class of chemical compounds receiving attention in scientific research are azo compounds, which exhibit high color and have been utilized as dyes and pigments for along times14, ethyl cyano (2-methyl carboxylate phenyl azo acetate) (ECA)15, 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]aniline16, [2-(4-methoxyphenyl) azo(4,5-diphenylimidazole)]17, 2,6-Dithiophenol and its derivatives in the presence of Hydrophobic Amines.18

Most of the methods which were reported earlier include heating, extraction and the many reagents that are not selective. The reagent used in the present work is found to be selective in nature. It does not require heating and extraction. This work develops a new spectrophotometric method which is a speedy and easy method and also to provide high-quality results for cobalt determination in trace amounts in samples of water, steel and pharmaceutical samples.

EXPERIMENTAL
Material and Methods
Spectrophotometric measurements were done using Agilent Cary win UV software-based spectrophotometer, the pH of the different buffer solutions was measured using Systronics µ 361 pH meter. High purity reagents were used. Stock solution of 0.02M Cobalt(II) chloride hexahydrate was
prepared by dissolving 1.18965g in 250mL standard flask using Millipore water. Reagent, L-Cysteine hydrochloride (0.02M) was prepared by dissolving it in a minimum quantity of Millipore water and then made up to the mark in 250mL standard flask. Different pH solutions from 1 to 12 were prepared using 0.2M KCl and 0.2M HCl (pH1), 0.1M potassium hydrogen phthalate and varying amounts of 0.1M HCl (pH2-5), 0.1M potassium dihydrogen phosphate and varying amounts of 0.1M NaOH (pH6-8), 0.025M borax and 0.1M HCl (pH9), 0.025M borax and 0.1M NaOH (pH10), 0.05M disodium hydrogen phosphate and varying amounts of 0.1M NaOH (pH11 and pH12).

General Procedure

Verification of Beer-Lambert’s law
To each set of different 10mL standard flask varying volumes of Co(II) chloride solution in microliters, were added. 2ml of L-Cysteine hydrochloride was added in equal quantity to each standard flask which is followed by the addition of 5ml of buffer solution (pH11) and then made up to the mark by adding Millipore water. Measurement of absorbance was done at $\lambda_{\text{max}}$ 356nm against the blank solution. A calibration plot was drawn.

Analysis of Water Samples
The sample of Co(II) in river water, tap water, well water, sewage water and rainwater (10 μg/ml) was mixed by taking a requisite amount of CoCl$_2$.6H$_2$O. Dissolving it in all types of water and transferred to a standard flask and diluted and absorbance of each sample was measured to find out the amount of Co(II) present.

Determination of Co(II) in a Pharmaceutical Sample
About 1mL Neurobion ampoule injection sample was added to 50mL standard flask, to this flask nitric acid and sulphuric acid were added in the ratio 10:1. The solution was warmed to dryness. The residue was treated with dilute H$_2$SO$_4$ and the residue is diluted, till it becomes colorless. The solution was neutralized by adding sodium hydroxide. Then this solution is transferred to a standard flask and this known amount of L-cysteine and buffer solution of pH 11 was added. Then Spectrophotometric analysis was carried out.

Determination of Co(II) in An Alloy Sample
About 0.1 to 0.5g of an alloy sample, JSS 607-6, was added to aquaregia (15mL of concentrated hydrochloric acid and 5.0mL of con.HNO$_3$) in a beaker. The solution was concentrated to three fourth of its volume. The addition of 10mL of concentrated hydrochloric acid to the solution was followed by filtration and dilution. Then this solution is mixed with a known quantity of L-cysteine and buffer solution of pH 11, so that the Co(II) of an alloy sample forms the complex with L-cysteine and further analysis can be done by using a spectrophotometer.

RESULTS AND DISCUSSION

Absorption Spectra of L-Cysteine and Co(II)-L-cysteine Complex
Absorption spectra of blank and Co(II)-L-Cysteine complex were measured using a uv-visible spectrophotometer. At 356nm, the reagent blank solution did not show maximum absorbance (Fig.-1). But the maximum absorbance of the complex was found at 356nm (Fig.-2). Therefore at this $\lambda_{\text{max}}$ (356nm), a detailed study of the complex was done.

Impact of pH on the Complex Absorbance
Measurement of complex absorbance at 356nm using different pH solutions showed that maximum color intensity was produced by the use of pH11 solution (Fig.-3). Therefore the further analytical study of the complex was done by maintaining the solution pH11.

Impact of Reagent Concentration
The amount of reagent required for the complete formation of the complex was studied by taking 2mL of 0.001M Co(II) and adding varying volumes of L-cysteine hydrochloride solution. It was found that the absorbance of the complex was almost constant from 6.5mL to 10mL (Fig.-4).
Beer’s Law Sensitivity and Calibration Graph

Estimation of Co (II) at the micro-level was done by taking a different amount of Co(II) and measuring the absorbance at 356nm under the optimum condition. And then the calibration plot was constructed (Fig.-5), which shows that from 1.1786μg/mL-11.786μg/mL of Co(II) can be estimated accurately.
Stoichiometry and Nature of Complex

The composition of the complex was found to be, 1:3 (M:L), which was determined by Job’s continuous variation method (Fig.-6) and the result is supported by the mole ratio method (Fig.-7). The stability constant of the complex was found to be $1.8 \times 10^4$ (Fig.-8) which was determined by the turner Anderson method.

![Fig. 6: Job's method of continuous variation](image)

![Fig. 7: Mole ratio method](image)

![Fig. 8: Stability Constant by Turner Anderson Method](image)

Effect of Diverse Ions

In the existence of diverse ions, the absorbance value of the complex Co(II)-L-Cysteine containing 40µg of Co(II) was examined. The outcomes of the study are displayed in Table-1.

| Ions added | Tolerance limit |
|------------|-----------------|
| Ag(I)      | 60              |
| Cd(II)     | 100             |
| Cu(II)*    | 20              |
| Cr(VI)     | 38              |
| Ni(II)     | 60              |
| Pb(II)     | 180             |
| Zn(II)     | 100             |
| V(IV)      | 80              |
| Zr(IV)     | 40              |
| W(VI)      | 80              |
| Tartrate   | 400             |

Table-1: Study of Interference of Diverse Ions
The above data indicates that many associated anions and cations when they are existing in large quantities do not interfere during the estimation of Co(II).

**Precision and Accuracy**
To evaluate the precision and accuracy of the method, the amount of Co(II) was determined in five different samples under the reliable experimental conditions. The outcome of the study is mentioned in Table-2. The relative error and relative standard deviation are not exceeding ±0.42% and ±0.3%. Therefore the method is found to be more precise and accurate. Table-3 provides the entire analytical data.

### Table-2: Determination of Co(II) in Cobaltous Chloride Solution

| Co(II) (µg/mL) | Standard Deviation | Relative Standard Deviation | Relative Error |
|---------------|--------------------|-----------------------------|----------------|
| Taken         | Found*             |                             |                |
| 2.36          | 2.35               | 0.007                       | 0.301          | 0.42           |
| 3.54          | 3.53               | 0.01                        | 0.282          | -0.28          |
| 4.71          | 4.70               | 0.009                       | 0.190          | 0.13           |
| 5.89          | 5.88               | 0.008                       | 0.142          | 0.20           |
| 7.07          | 7.05               | 0.01                        | 0.162          | 0.23           |

*Average of five determinations.

### Table-3: Physico-Chemical Properties of Co(II)-L-Cysteine Complex

| Characteristics                     | Results |
|-------------------------------------|---------|
| \( \lambda_{\text{max}} \)         | 356     |
| Optimum pH range                    | 11      |
| Beer’s law validity range           | 1.1786 µg/mL - 11.786 µg/mL |
| Composition of the complex          | 1:3     |
| Standard deviation in the determination of Co(II) from 2.36-7.07 µg/mL | 0.0088 |
| Relative standard deviation         | 0.215   |
| Molar absorptivity                  | 3.7535x10³ L/mol/cm |
| Sandell’s sensitivity               | 0.015 µg cm⁻² |

### Applications

#### Analysis of Water
The technique was effectively applied for the estimation of Co(II) in tap water, well water, sewage water and rainwater. The results are shown in Table-4.

### Table-4: Analysis Co(II) in Various Samples of Water

| Various Water Samples Containing Co(II) | Taken (µg) | Found (µg) | Relative Error |
|----------------------------------------|------------|------------|----------------|
| Tap water                              | 10         | 10.05      | -0.5           |
| Well water                             | 10         | 10.12      | -1.2           |
| Sewage water                           | 10         | 10.09      | -0.9           |
| Rainwater                              | 10         | 10.07      | -0.7           |

#### Analysis of An Alloy Sample
The current method was also applied for the estimation of Co(II) in an alloy sample. The result is presented in Table-5.
Table 5: Estimation of Co(II) in an Alloy Sample

| Alloy     | Quantity of Co(II) ion present(µg) | Amount of Co(II) found(µg) | % RSD | % Relative error | % Recovery |
|-----------|-----------------------------------|----------------------------|-------|------------------|------------|
| JSS 607-6 | 14.01                             | 13.97                      | 0.39  | 0.139            | 99.7       |

Analysis of the Pharmaceutical Sample

The current method also holds good for the estimation of Co(II) in a pharmaceutical sample. The result is shown in Table-6.

Table 6: Determination of Co(II) in a Pharmaceutical Sample

| Sample    | Amount of Co(II) ion present(µg/mL) | Amount of Co(II) found (µg/mL) | % RSD | AAS process (µg/mL) | % RSD | % Recovery |
|-----------|------------------------------------|--------------------------------|-------|---------------------|-------|------------|
| Neurobin  | 21.74                              | 21.68                          | 0.4   | 21.69               | 0.4   | 98.0       |

CONCLUSION

The proposed method is found to be simple, speedy and accurate. It does not require heating and extraction. And also the reagent is readily available. This method can be used for the determination of the minute quantity of Co(II) in sewage water and also other water samples. And this method also can be employed in an alloy and pharmaceutical sample.

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