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 3.7535×10^3 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

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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 reagent ⁶, fluorescent ketone reagent ⁷, 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 exhibits 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-Dithiolphenol 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).¹⁹

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)²⁰ and then made up to the mark by adding Millipore water. Measurement of absorbance was done at λ_{max} 356nm against the blank solution. A calibration plot was drawn.²¹

Analysis of Water Samples

The sample of Co(II) in river water, tap water, well water, sewage water and rainwater (10 $\mu\text{g/ml}$) was mixed by taking a requisite amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. 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.^{22,23}

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^{11, 24}. The residue was treated with dilute H_2SO_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^{25, 26, 27}. Then this solution is mixed with a known quantity of L-cysteine and buffer solution of pH11, 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 λ_{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).

Fig 1: Absorption spectra of reagent blank

Fig 2: Absorption spectra of Co(II)-L-Cysteine Complex

Fig.-3: Impact of pH on Absorbance

Fig4: Effect L-Cysteine concentration

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 1.1786 $\mu\text{g/mL}$ -11.786 $\mu\text{g/mL}$ of Co(II) can be estimated accurately.

Fig.-5: Beer's Law Plot for Cobalt(II)-L-cysteine Complex

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 1.8×10^4 (Fig.-8) which was determined by the turner Anderson method.

Fig.-8: Stability Constant by Turner Anderson Method

Effect of Diverse Ions

In the existence of diverse ions, the absorbance value of the complex Co(II)-L-Cysteine containing $40 \mu\text{g}$ of Co(II) was examined. The outcomes of the study are displayed in Table-1.

Table-1: Study of Interference of Diverse Ions

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

Oxalate	130
Citrate	130
Nitrate	160
Chloride	140
Phosphate	170
Sulphate	200

*Interference of Cu(II) was observed, which can be nullified by the use of suitable masking agent-Thiosulphate.

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 $\pm 0.42\%$ and $\pm 0.3\%$. 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
$\lambda_{\max}$	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	3.7535×10^3 L/mol/cm
Sandell's sensitivity	$0.015 \mu\text{gcm}^{-2}$

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 Pharmaceurticle 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($\mu\text{g/mL}$)	Amount of Co(II) found ($\mu\text{g/mL}$)	% RSD	AAS process ($\mu\text{g/mL}$)	% RSD	% Recovery
Neurobion	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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