Direct and Derivative Spectrophotometric Determination of Cobalt (II) using 3,4-DihydroxyBenzaldehyde-1-(3-Chloro-2-Quinoxalinyl)Hydrazone(DHBCQH) in Presence of Micelle Medium

M.Mogalali Raju, V.Tejeswara Rao, K.Ramakrishna

Department of Chemistry, GITAM Institute of science, GITAM University, Visakhapatnam-530045, A.P. India.

Abstract- A rapid and sensitive method has been developed for the determination of Cobalt(II) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehyde-1-(3-Chloro-2-Quinoxalinyl)Hydrazone (DHBCQH) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at 450 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24hs. The method obeys Beer's law in the range 29.46 to 132.59ng/ml. The apparent molar absorptivity of 4.45×105 L mol-1 cm-1 and Sandell's sensitivity 0.13ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of ≥ 100 folds in excess of foreign ions. The method was successfully used in the determination of Cobalt(II) in Biological samples. Second order derivative spectrophotometric method were developed at λmax = 482nm for the determination of Cobalt(II), which was more sensitive than the zero order method.

Index Terms- Spectrophotometric Determination, Cobalt (II), 3,4-DHBCQH, Surfactant Tween-80, Biological sample, Alloy sample..

I. INTRODUCTION

Dissolved cobalt occurs in the environment at concentrations ranging from 0.5 to 12µg/L in the sea water up to 100 µg/L in wastewater [1,2] . Calculation of the inorganic complexation of cobalt using an ion-paring model and stability constants [3] shows that it is weakly complexed by inorganic ligands, the predominate inorganic species being Co(II) and its chloride complexes. On the other hand, there is evidence that cobalt is strongly complexed by organic ligands especially in burdened waters and solids [4, 5].

A literary survey reveals that there are several techniques and methods for the determination of cobalt in different samples including atomic fluorescence [6], atomic absorption [7, 8], Chromato graphy [9, 10], x-rays fluorescence [11], inductively coupled plasma –atomic emission spectrometry [12] and spectrometry [13, 14]. Among the most widely used analytical methods are those based on the Uv-visable spectrophotometric techniques due to the resulting experimental rapidity, simplicity and wide application. 3,4-Dihydroxybenzaldehyde-1-(3-chloro-

2-quinoxalinyl) hydrazone (DHBCQH) is a new chromogenic regent recently synthesized and has been applied to the spectrometric determination of trace Cobalt(II) . it is shown that DHBCQH reacts with Cobalt(II) to form a stable , water-soluble ,positively charged, 1:2 binary complex. Water –miscible organic solvents such as N,N-dimethyl formamide (DMF),aceton , dioxide and their aqueous solution (higherthan 20%) may be used for solubilizing the chromogenic reagent and increasing the sensitivity of the chromogenic reaction. The recent literature on the analytical Applications of the entitled reagent 3,4–dihydroxybenzadehyde-1-(3-Chloro-2-Quinoaxalinyl)Hydrazone abbreviated as (3,4 –DHBCQH) has revealed no study on the use of reagent for Cobalt(II) determination. Therefore, the goals of the present manuscript are focused on the synthesis and spectroscopic characterization(Uv-Vis IR and H NMR, Mass) of the DHBCQH reagent. Moreover the stiochiometry of the formed cobalt (II)-DHBCQH chelate was elucidated in an attempt to develop and accurate method for the analysis of cobalt(II) in Biological samples.

Recently enhanced sensitivity in spectrophotometer was achieved by utilizing the ability of certain surfactants to sensitize the binary complexes of the metal ion with chromogenic ligands[15,16] sensitization are result of the replacement of acidic protons of the liganded dye molecule by surfactant[17] (or) adsorption of the metal reagent complex on the micelles of the surfactant [18] cationic, anionic and nonionic surfactants are often used to sensitize the metallochromic indicators . In this context, updated surfactant – sensitized reaction has recently been developed in spectrophotometer [19-23].

The present study was hence planned to suggest a very simple and reasonably good method for determination cobalt (II) ions at low concentration, using the DHBCQH reagent. DHBCQH as binary complex and sensitizing the reagent with Tween- 80 as ternary complex using spectrophotometer which is still frequently used because of its low cost and simplicity.

II. EXPERIMENTAL

2.1. Apparatus

The Absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV -160A) fitted with 1cm Quartz cells and Philips digital pH meter (model L1 613 respectively.)

2.2. Reagents and solution

All chemicals used were of analytical reagents grade or the highest purity available. Double distilled deionized water, which is non-absorbent under ultraviolet radiation, was used throughout. Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated HNO_3 and rinsed several times with deionized water.

2.2.1 Tween-80 solution 1%. . A 100 mL of Tween-80 solution was prepared by dissolving 1 mL of pure tween-80 in 100 mL if doubly distilled deionized water, sonicated for 15 min and diluted with deionized water when it became transparent.

2.2.2.   3,4-Dihydroxybenzaldehyde-1-(3-chloro-2-quinoxalinyl)hydrazone (DHBCQH) (1 X 10^{-2}mol/dm^3): A 25 mL solution was prepared by dissolving 0.0783 g of recrystalised sample in   dimethylformamide and it was suitably diluted to get the required concentration.

2.2.3. Cobalt(II) standard solution (1 X 10^{-2}mol/dm^3): A 100 mL stock solution (1 mg/mL) of divalent mercury was prepared by dissolving 0.291 g of cobalt nitrate (Merck, Darmstadt) in deionized water containing 1 – 2 mL of nitric acid (1 + 1). More dilute standard solution was prepared from this stock solution, as and when required.   .

2.3. Procedure
2.3.1. Direct spectrophotometry

In each of set of different 10 mL volumetric flasks, 5 ml of buffer solution (pH 5.0),1 mL of DHBCQH(1 x 10^{-3}mol/dm^3) and various volumes of 1x 10^{-6}mol/dm^3 cobalt(II)finally added 1 mL of 1% Tween-80 and f solution were taken and made up to the mark with double distilled water. The absorbance was measured at 450nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of cobalt(II).

2.3.2. Second order derivative spectrophotometry

For the above solutions, second order derivative spectra was recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees freedom, in the wavelength range 390-510 nm. The derivative amplitude measured at wavelength 482 nm and plotted against amount of cobalt (II) to obtain the calibration.

The calibration graph follows the straight line equation   Y = aC +b [24]; where C is the concentration of the solution, Y is measured absorbance or peak or valley height and a and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as $A_{450} = 0.065C + 0.051$ for zero order method ,$A_{482} = 0.0013C + 0.002$ for second order derivative method.

III.   RESULTS AND DISCUSSION

3.1. Factors affecting the absorbance
3.1.1. Absorption spectra

The absorption spectra of the cobalt (II)-3,4-DHBCQH system in a micellar medium is recorded using a spectrophotometer. The absorption spectra of the Co(II)-3,4-DHBCQH is a symmetric curve with the maximum absorbance at 450mm and an average molar absorption coefficient of 4.45 x 10^5L mol^{-1} cm^{-1} (Fig. 1). The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 450 nm against a reagent blank.

3.1.2. Effect of surfactant: Of the various surfactants [nonionic{poly   oxyethylenedodecylether(Brij   -35), Polyoxyethylenesorbitanmonoplamitate   (Tween-40), Polyoxyethylenesorbitanmoni-oleate(Tween-80),   Triton-X-100} ; cationinc[cetyltrimethylamoniumbromite(CTAB) } : and anionic { cetlylpridinium chloride (CPC) , sodium dodecyl sulfate SDS } studied Tween-80 was found to be the best surfactant for the system. In a 1%(V/L) Tween-80 medium however, the maximum absorbance was observed hence, a 1%(V/L) Tween-80 solution was used in the determination procedure.

Different volumes of 1%(V/L)Ttween-80 were added to a fixed metal ion concentration, and the absorbance was measured according to the standard procedure. It was observed that at 58.93 ng/ml Co(II)-chelate metal. 0.25-1.75 mL of 1%(V/V) Tween-80 produced a contestant absorbance of the Co(II)-chelate(Fig. 2). A greater Excess of Tween-80 was not studied. For all subsequent measurements, 1mL 1%(V/V) Tween-80 was added.

3.1.3. Effect of Acidity

The absorbance of the complex reaches a maximum over a pH range of 4.0 to 6.0 The higher pH values may lead to hydrolysis of Co(II) -3,4-DHBCQH system. The absorbance was at a maximum and constant when a 10 ml of solution (1mgL^{-1}; path length ,1) contained 1-7 mL (pH5.0) of acidic buffer at room temperature (25±5 ℃) . Outside this range of acidity , the absorbance decreased (Fig. 3) .   For all subsequent measurements 5.0 ml (pH 5.0)acidic buffer was added.

3.1.4. Effect of time

The reaction is very fast. Constant maximum absorbance was obtained just after dilution to volume, and remained strictly unaltered 24hs.

3.1.5. Effect of reagent concentration:

Different molar excess of 3,4 –DHBCQH were added to a fixed metal ion concentration, and the absorbances were measured according to the standard procedure. It was observed that at 58.93 ng/ml Co(II) metal(optical path   lenth , 1 cm) reagent molar   ratios 1:10 and 1:100 produced a   constant absorbance of the Co(II)-Chelate(Fig. 4) . A greater excess of the reagent was not studied. For all subsequent measurement 1mL of 1 x 10^{-3}mol/dm^3 3, 4 –DHBCQH reagent was added.

3.1.6. Calibration graph (Beers Law and sensitivity)

The Calibration curve for the determination of Cobalt has been constructed (Fig. 5) using the optimum experimental conditions. The straight line calibration curve indicates that Beers’ law is obeyed at least over a range of 29.46 to132.59 ng of Cobalt (II) per10 mL. Linear regression analysis of the calibration curve gives a correlation coefficient of 0.9968. The apparent molar absorptivity(€_{450}) calculated from the slop of regression line is 4.45 X 10^5L mol^{-1} cm^{-1} The Sandell’s

sensitivity(concentration for 0.001 absorbance unit) was found to be 0.132 ng cm^{-2}.

3.1.7. Effect of foreign ions:

The effect of various foreign ions that are generally associated with cobalt (II) on the determination under optimum conditions developed was studied and the results are presented in Table 1. Cations like Ba(II), Sr(II) and U(VI) do not have any effect on the complex of Co(II)-DHBCQH, when present up to 4,900 µg, Zinc (II) and Tin (II) do not interfere in the determination of Cobalt(II), even present up to 4,700µg. Pb(II) and Mn(II) can be tolerated up to 3,600µg. Fe(III), Cu(II) and Hg(II) interference in the determination of Cobalt(II), even when present in trace amounts.

3.1.8. Composition of the Metal –Reagent complex

Jobs method of continuous variation (Fig.6) and the molar – ratio method were applied to ascertain the stoichiometeric composition of the complex. A Co (II) -3, 4-DHBCQH(1:2) complex was indicated by both methods. The stability constant was determined by Jobs method as 9.67×10^{6}.

IV.   APPLICATIONS

The Present method was successfully applied to the determination of cobalt (II) in biological samples and alloy steels.

4.1. Determination of Cobalt (II) in biological samples (Tea leaf and vehicle exhaust)

The tea leaf samples were supplied by Andhrapradesh Agricultural research institute (APARI), Hyderabad (A.P.) India. The vehicle exhaust sample was collected from Environment protection training and research institute (EPTRI), Hyderabad (A.P.) India. A 0.1 g of tea leaf sample was taken in a beaker and dissolved in conc. nitric acid (5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 100 mL water in a calibrated flask. Vehicle exhaust particles (1g) were dissolved in a mixture of 18 mL of conc. nitric acid, 18 mL of conc. perchloric acid and 2 mL of conc. hydrofluoric acid in a 100 mL Teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100 mL with distilled water. and the absorbance was measured at 450nm. The amount of cobalt was calculated from a predetermined calibration plot and the results are presented in Table 2.

4.2. Determination of Cobalt (II) in Alloy steel

A known aliquots of the sample solutions were taken in different 10ml volumetric flasks, 5 ml of buffer solution (pH 5.0). 1270µg of iodine (to mask Fe(II)) and 1860 µg ETDA (to mask Ni(II)) and 1ml of DHBCQH (8 x 10^{-3} M) were added to each flask. The contents were made up to the mark with distilled water and the absorbance was measured at 450nm. The amount of cobalt was calculated from a predetermined calibration plot and is given in Table 3.

4.3. Second order derivative method

The second order derivative curve recorded (Fig. 7) for experimental solution showed the derivative amplitude were measured at 482 nm (peak) for different concentrations of Cobalt(II) and plots were made between the amount of Co(II) and the derivative amplitude. The plots were linear and obeyed Beer`s law in the range 11.78-70.71 ng/mL at 482 nm respectively.

4.4. Effect of foreign ions

The effect of various cations and anions on the derivative amplitude was studied and it was noticed that all the ions that did not interfere in the zero order determinations of Co(II) also did not interfere in second order derivative method. The metal ions Cu(II),Hg(II) and Fe(II) were interfered in 3200 µg excess, in zero order method. But in second order derivative method. Cu(II) and Fe(II) were tolerate up to 3700µg excess.

V.   APPLICATION

5.1. Analysis of alloys and steels

A known aliquot of the sample solution was taken in a 10ml volumetric flask containing 5ml buffer solution (pH 5.0) and 1270 µg ml^{-1} of iodide (to mask Fe(II)) and 1ml of DHBCQH (8×10^{-3}M) solution. The contents of the flask were made up to the mark with distilled water. The second derivative spectrum of the solution was recorded. The derivative amplitude at 482 nm was measured and the amount of cobalt (II) was computed from the predetermined calibration plot and presented in Table 4.

5.2. Comparison of results

The analytical characteristics of the zero and second order derivative methods in the present investigations for Cobalt(II) were compared and presented in Table 5. The results in this table reveal that second order derivative method is more sensitive and selective than the zero order method.

The sensitivity of the zero method in the present investigations was compared with those of some reported methods and presented in Table 6.

VI.   CONCLUSION

This method offers several interesting features such as simplicity, rapidity, and low cost besides sensitivity. The number of associated elements does not interfere in the determination. The selectivity of the reagent is also improved by the use of suitable masking agents to suppress the interference of metal ions like Fe(III), Cu(II), and Hg(II). Hence the proposed method is recommended for the determination of Cobalt(II) with DHBCQH in the presence of micells by spectrophotometric method, at minor and trace levels, besides its use for analysis of real samples such as biological samples .

REFERENCES

[1] G.A .knauer , J.H .Martin, R.M. Gordon, *Nature* 297 (1982) 49-51..

[2] K. W.Bruland, Trace elements in sea-water ,in: j.p.Riley, R.Chester (Eds.), *chemical Oceanography* , Academic press ,vol. 8, London, 1993 (chapter 45).

[3] D.R.Turner , M.Whitfield, A.G.Dickison, Geochim. *Cosmochim. Acta* , 45 (1981) 855-881.

[4] H. Zhang, C.M.G. Vanden Berg, R. Wollast, Mar. Chem. 28 (1990) 285-300.

[5] J.R. Donat, K.W. Bruland, *Anal. Chem.* 60 (1988) 240-244.

[6] V. Rigin, *Anal. Chim. Acta* 283 (1993) 895.

[7] J. Jaganathan, I. Aggarwal, *Microchem. J.* 50 (1994) 44.

[8] S.L. Sachdev, J.W. Robinson, P.W. West, *Anal. Chim. Acta*, 38 (1967) 499.

[9] M.Y. Khuhawar, S.N. Lanjwani, *J. Chromatogr*, 695, (1995) 132.

[10] A. Galik, A. Vincourrova, *Anal. Chim. Acta*, 46 (1969) 113.

[11] A.W. Morris, *Anal. Chim. Acta*, 42 (1968) 397.

[12] K.S. Rao,T. Balaji, T.P. Rao, Y.Babu, G.R. Naidu, *Spectrochim. Acta*, 57 (2002) 1333.

[13] M.R. Ditusa, A.A. Schilt, *Microchem. J.* 32 (1985) 44.

[14] A.M.G. Rodriguez, A.G. Torres, J.M.C. Pavon, B. Ojeda, *Talanta*, 47 (1998) 463.

[15] M.D.Bezerra, M.A.Z. Arruda, S.L.C.Ferreira, Appl. Spectrosc. Rev, *40(*2005), 269-299

[16] T.PrasadRao, M.L.P.Reddy, A. RamalingomPillai, *Talanta, 46*,(1998), 765-813.

[17] T.PrasadRao, T.V.Ramakrishna, *Bull. Chem. Soc. Jpn, 53*,(1980), 2380.

[18] M.T.MZaki, A.Y. Elsayed, *Anal.Lett. 28,* (1995), 1525.

[19] S.Kundu, S.K.Ghosh, M.Mandal,T.pal, A.Pal, *Talanta, 58*,(2002), 935-942.

[20] M.Ghaedi,E.Asadpour,A.Vafaie,*Spectrochim. Acta A Mol. BiomolSpectrosc, 63*,(2006), 182-188.

[21] M.Ghaedi, Spectrochim. Acta A Mol. BiomolSpectrosc, 66,(2007), 295-301.

[22] M.Ghaedi, A.Daneshfar, A.Shokrollahi, H.Ghaedi, F.ArvinPili, *Ann Chim(Roma), 97,(* 2007), 971-982.

[23] A.Shokrollahi, M.Ghaedi, M.S.Niband, H.R.Rajabi, *J. Hazard. Mater,151,(* 2008), 642-648.

[24] A.Praveenkumar, P.Ravindrareddy, V.Krishnareddy, *Journal of Korean Chemical Society*,51(4), (2007),331- 337.

[25] J.M.C Pavon,;A. Levado, .; F.Pino,. *Mikrochim. Acta*,(1976), 11,233.

[26] M.R..Rueda, J.M.M.Leyva, Antonoi. *Quim. anal*. 29.(1975),122.

[27] N.S.Reddy, Ph.D. thesis, Sri Krishna Devaraya University, India,(1982).

[28] J.M.C. Pavon, D.P.Bendito, F. Pino ,*Quim .anal*. 65,(1969),667.

[29] S.K.Singh, Kamani ,Sindhawani, *J.Chtu.Chem.Soc.*(Taipei) 29,(1982),31.

[30] D.P.Bendito, F.Pino,*Inform Quim.Anal*, 21,(1967), 31.(anal. Abstr 1968, 15, 3342).

AUTHORS

First Author – M.Mogalali Raju, Department of Chemistry, GITAM Institute of science, GITAM University, Visakhapatnam-530045, A.P. India.
Second Author – V.Tejeswara Rao, Department of Chemistry, GITAM Institute of science, GITAM University, Visakhapatnam-530045, A.P. India.
Third Author – K.Ramakrishna, Department of Chemistry, GITAM Institute of science, GITAM University, Visakhapatnam-530045, A.P. India.

Table 1. Effect of Foreign ions in (58.93 ng/mL) amount of Cobalt(II)

Ions	Tolerance limit(μg)
Ba^{+2}, Sr^{+2}, U^{+6}	4900
Zn^{+2}, Sn^{+2}	4700
Pb^{+2}, Mn^{+2}	3600
$Fe^{+3}, Cu^{+2}, Hg^{+2}$	3200
F^-, Cl^-, CH_3COO^-,	5600
$I^-, So_4^{-2}, Br^-, HCO_3^-, SCN^-$	5100

Table 2.   Determination of Co(II) in biological samples

Sample	Amount of cobalt (mg/g)	
	Certified value	Present method[*]
Tea leaves	0.12	0.10
Vehicle exhaust	3.3	3.25

[*]Average of five determinations

Table 3.   Determination of Co(II) in Alloy steel samples

Sample	Amount of Co(II) (%)		Error (%)
	Certified	Found[*]	
Eligiloy M-1712 (40% Co, 20% Cr, 15% Ni, 15% Fe, 2% Mn, 0.05% C, 0.05%Be)	40.00	39.48	-1.3
BCS-483 (1.94% Co,10.8% W,3.21% Cr, 0.5%V,0.29% Mn,0.17% Mo,rest Fe)	1.94	1.93	-0.5

[*]Average of five determinations

Table 4.   Determination of Co(II) in Alloy steel samples

Sample	Amount of Co(II) (%)		Error (%)
	Certified	Found[*]	
High speed steel (6-18% W, 5.5% Mo, 4.15% Cr, 0.4% Mn, 0.35% Si, 0.05% S, Rest Fe)	9.26	9.29	+0.32
Udimet-700 (15% Cr, 4.3%Al,5.21% Mo,0.08% C,0.003% B)	18.00	18.10	+0.55

[*]Average of five determinations

Table 5. Comparison of results of Cobalt(II)

Parameter	Zero order	Second derivative
Analytical wave length(nm)	450	482
Beer`s law range(ng/mL)	29.46-132.59	11.78- 70.71
Angular coefficient(m)	0.065	0.013
Y-ntercept(b)	0.005	0.002
Correlation coefficient(r)	0.996	0.998
Standared deviation(s)	0.023	0.028

Table 6. Coparison with other methods

Reagent	λ_{max}(nm)	Molar absorptivity(ε) (L mol^{-1} cm^{-1})	Ref.
3-hydroxy piconaldehyde thiosemicarbazone	450	0.78×10^4	25
Phthaldehyde thiosemicarbazone	385	0.56×10^4	26
Piconaldehyde thiosemicarbazone	410	0.74×10^4	27
Salicylaldehyde thiosemicarbazone	400	1.1×10^4	28
Acenaphthaquinone thiosemicarbazone	410	0.48×10^4	29
Biacetyl monoxime thiosemicarbazone	325	0.49×10^4	30
3,4-Dihydroxybenzaldehyde-1-(3-chloro-2-quinoxalinyl)hydrazone(DHBCQH)	450	4.45×10^5	**Present work**
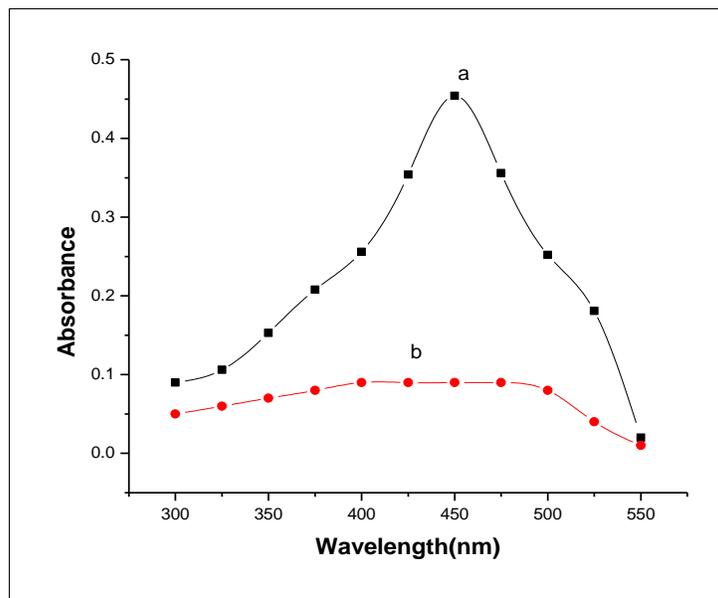
Fig. 1 a and b absorption spectra of Co(II)-DHBCQH and reagent blank system ($\lambda_{max =}$ 450nm) in nonionic micellar medium
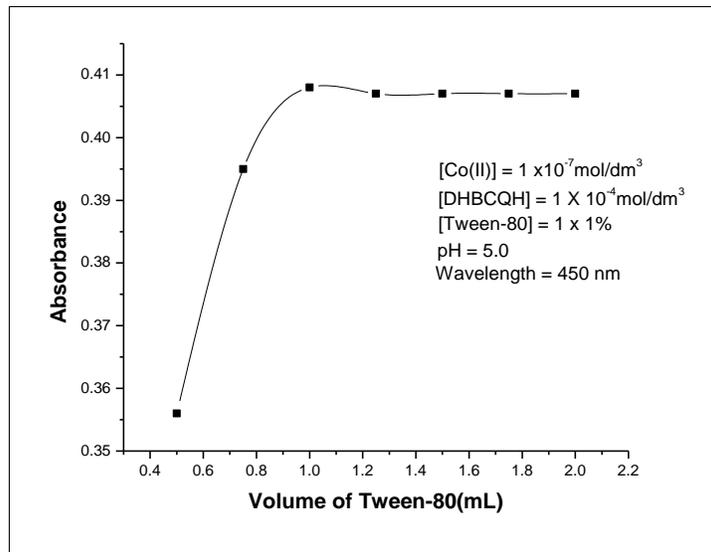
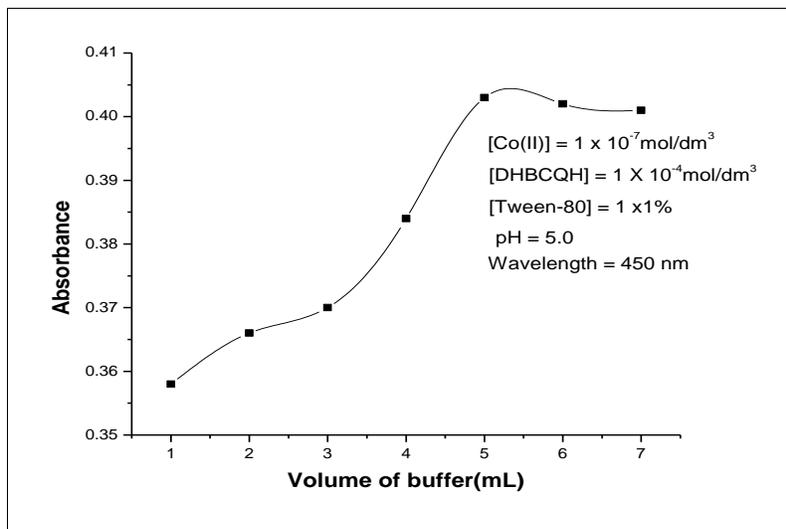**Fig. 2   Effect of surfactant on the absorbance of the Cobalt(II)-DHBCQH system**

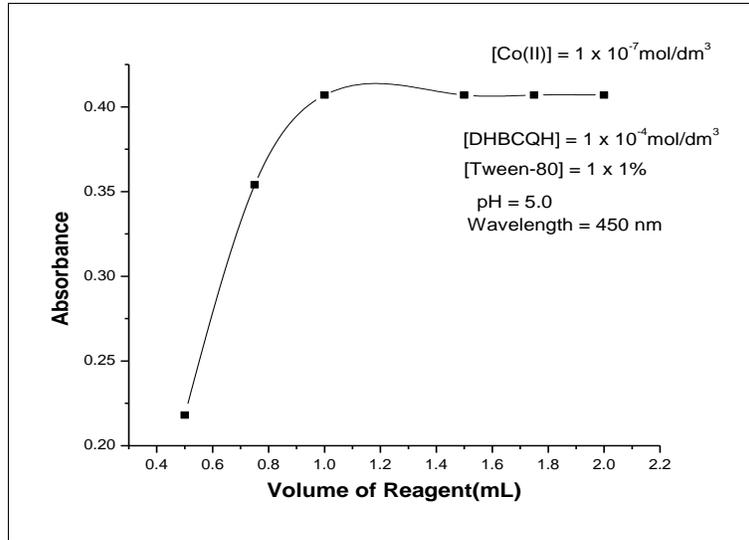**Fig. 3   Effect of Buffer solution on the absorbance of the Cobalt (II)-DHBCQH system**

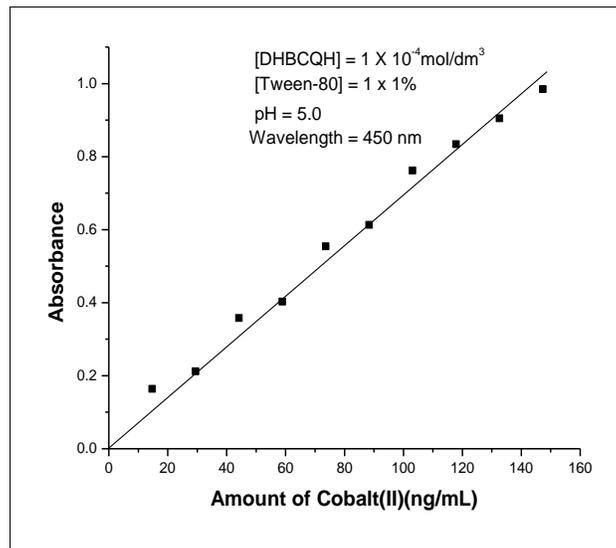**Fig. 4 Effect of reagent(DHBTSC) on the absorbance of the Cobalt(II)-DHBCQH system.**
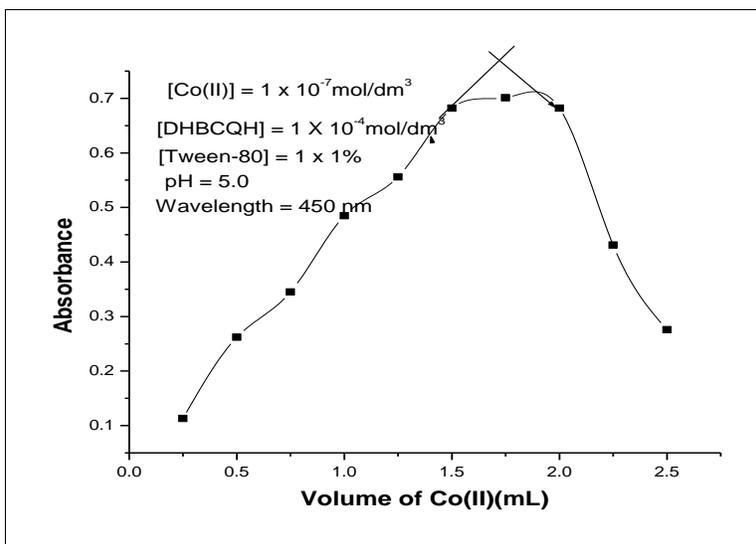

Fig. 5   Calibration graph
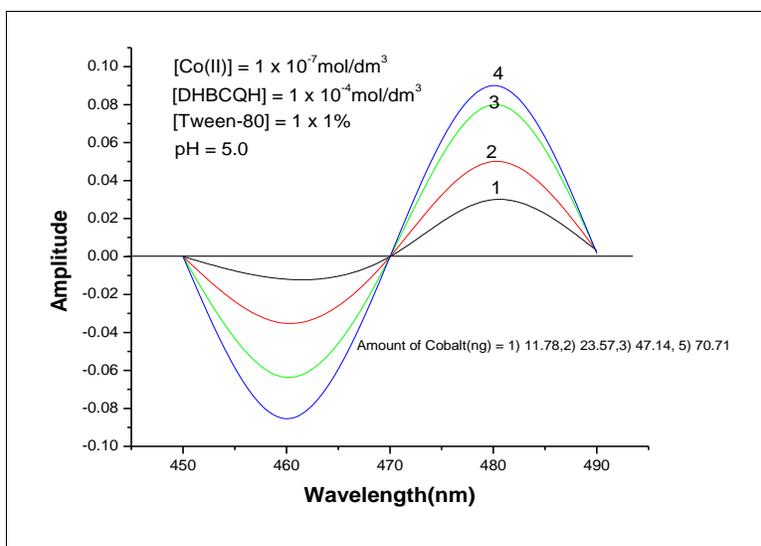
Fig. 6 Job`s curve

Fig. 7 Second derivative spectra of Cobalt (II)-DHBCQH Vs reagent blank