C H A P T E R - III

PHOTOMETRIC DETERMINATION OF COBALT (II)

WITH 2CHLOROQUINOLINE 3 - CARBALDEHYDE

THIOSEMICARBAZONE

INTRODUCTION

The word 'Kobalt' occurs in the writings of B. Valentine and Paracelsus to denote a goblin supposed by the old Teutons and Scandinavians to haunt the mines, destroying the work of mines, and giving them trouble. In 1735 Brandt stated that the blue colouring principle is due to the presence of a peculiar metal or semi-metal he called 'Cobalt rex', hence 'cobalt'. Brandt isolated the metal in 1742.

Cobalt is nearly always found in association with Nickel, chiefly as arsenides. Cobalt ores are principally worked in order to get cobalt salts and not the metal. Cobalt is a white, malleable and ductile metal rather harder than iron. It is feebly magnetic, and melts at 1492°. When in bulk it is not attacked by air at ordinary temperatures, and only reacts slowly with oxygen at a red heat, but in the finely divided state it is sometimes pyrophoric. Dilute hyolrochloric acid and sulphuric acids attack cobalt slowly and nitric acid dissolves it fairly readily.

Cobalt is one of the important transition metals because of the industrial uses of metals, alloys and compounds. A large proportion of studies in co-ordination chemistry are centered around cobalt. As such the chemistry of cobalt and its compounds is extensively investigated and synthetic chemistry of cobalt compounds is also well explored. However because of the lack of suitable reagents and the conditions of experiments the photometric determination of this important element is still a problem confronting the analytical chemists. A multitude of reagents have been so far suggested for cobalt since the introduction of the first reagent α - Nitroso β - naphthol[1], but hardly any one has proved satisfactory. We propose 2-chloroquinoline 3-carbaldehyde thiosemicarbazone as a suitable reagent for photometric determination of cobalt. This method overcomes most of the defects in hitherto reported methods.

The range of uses of cobalt is very wide from industries to medicine and plant physiology. Cobalt is used in ferrous and nonferrous alloys, in ceramic and glass industries, in cemented carbides, as a catalyst in electroplating and in biological and biochemical reactions.

Ferrous alloys like tool steel contain 5 to 12 % cobalt which improves cutting efficiency at elevated temperature. Alnico type permanent magnets contain 5 to 35 % cobalt. Special seals containing 18 % cobalt are made which have the same coefficient of expansion as glass.

Very hard and corrosion resistant alloys, stellites contain 42 to 65 % cobalt. Dental or surgical alloy, Vitallium contain 65 % cobalt. High strength alloys of jet aircraft and gas turbines contain 20 to 65 % of cobalt.

Cobalt is present 3 to 20 % in carbides, sometimes cobalt is used in electroplating with nickel. Cobalt salts are used to impart blue colour to glasses, it is also used in ceramics and in enamel wears. Organic salts of cobalt are used as driers in paints and varnishes. In biological materials also very minute quantity of cobalt is present. Vitamin B_{12} contains cobalt. Human dietaries, carrots, cheeries, peas, potatoes, cabbage, figs contain 0.005 to 0.2 ppm cobalt. Cobalt is essential microneutrient for the plants and it is present to the extent of 23 ppm in soil. In a normal human being (Standard man weighing 70 Kg) the burden of cobalt is 1.5 mg.

Cobalt is an undesirable constituent in the fuel and materials of nuclear reactor. It is also found in microquantities in nickel salts and sea water and silicates. The need to determine cobalt in large number of samples ranging from traces in herbage to 65 % or more in alloys has resulted in the development of many analytical methods. For traces of cobalt atomic absorption spectrophotometry is used, colourimetric methods are used in μg to mg ranges, whereas volumetric and gravimetric methods are used for microdeterminations.

In recent years numerous colourimetric reagents have been proposed for determination of cobalt. Many of them lack either desired sensitivity or selectivity. In many cases absorption bands occur in ultraviolet region where both complex and reagent absorb in the same region. The classic reagents like thiocynate[2] for determination of cobalt show less colour intensity in aqueous solution and suffer from numerous interferences. O-nitrosophenol and O-nitrosocresol[3] are sensitive extraction reagents for cobalt. But the latter reagent is not obtainable in solid form, it is not very stable and special precautions must be taken to prevent the interferences of traces of iron in the procedure.

With the reagents 1:2 diamino cyclohexanetetra-acetic acid[4,5], nitroso-R-salt[6,7], 5-aminopyrazole-4-carboxylic acid[8], salicylic acid[9], 3-hydroxy piconaldehyde azine[10] and 4-amino-5-nitroso pyrimidine-2, 6-diol[11] and elevated temperature is required for complex formation and thiosalicylidene ethylenedimine are less sensitive when compared with 2-acetyl pyridine thiosemicarbazone.

With some reagents like dimethyl glyoxime[12], 3-mercapto propionic acid[13] pyridine-2,4,6 tricarboxylic acid[14] azanol A[15], furil - α - dioxime[16] and 2,4-dimethyl benzamidoxime[17] method of determination of cobalt is time consuming.

Furil α monoxime[18], zephiramine[19], diacetyl monoxime[20], benzil monoxime[20], 2-Nitroso-1-naphthol[21], 2,2',2" terpyridine[22] and 1-Nitroso-2-naphthol[23], though from extractable complexes, suffer from numerous interferences. Prolonged shaking for two hours is required for extraction of cobalt TAR[24] complex. Chromotrope 2R[25], Piconaldehyde thiosemicarbazone.[26]

Recently a few thiosemicarbazone of ketones and aldehydes which act as sensitive reagents for cobalt are reported. Thiosemicarbazones of resorcyl-4-aldehyde[28], benzothiazol-2-phenyl ketone[29], 3-hydroxy piconaldehyde[30] and

3.1 Review of the methods for the photometric determination of Cobalt (II)

Reagent	pH	λ max nm	Molar extinction coefficient, sensitivity, range ppm	Interferences and Remarks	Reference
1	2	3	4	5	6
O-(2-thizolyazo-2-Napthol).	5.0	618	$\epsilon = 24,000$	-	35
Benzoyltrifluro acetone	6.0	390	-	Ca(II), Ni(II), Fe(II) interfere.	36
8-Mercaptohydroxyquinoline.	7.3-8.2	352.7	-	Ni, Citrate, tartarate interfere.	37
8-Mercaptohydroxy quinoline.	-	470	-	Ni, Fe interfere.	38
Di-2-pyridyl keto-oxime	-	388	-	Ni(II), Cu(II), EDTA interfere.	39
Acenaphthene quinone monoxime.	8.0-9.5	400	Sensitivity is 0.005 $\mu g\ Cm^{-2}$, 6-18 ppm.	-	40
STTA	-	490	-	Ni, Cu, EDTA interfere.	41
Thenoyltrifluoro acetone (TTA)	3.2-3.4	460	3-12 ppm.	-	42

1	2	3	4	5	6
2-(5-chloro-2-pyridylazo)-5-diethylamino phenol	5.9	580	$\varepsilon = 106,000$	-	43
Nitroso-R-Salt	-	-	-	-	44
β-Mercaptohydroxy and β-Mercaptocinnamanilide	9.0	640	10-100 ppm	Fe^{3+}, Cu^{2+} intererfere.	45
5-(2-hydroxy-1-naphthylazo) pyrazole-4-carboxylic acid	9.3	580	0.8-6.4 ppm	CN^-, EDTA, Citrate, oxalate, interfere.	46
Picraminazo-4-cyclohexyl resorcinol	2-3	555	$\varepsilon = 28,000$	-	47
Nitroso-R-Salt-4-diphenyl-guanidine.	7.8	520	-	Ni, Cu, Fe, Ti, Sn, In does not interfere.	48
Picolinaldehyde 4-Phenyl-3-thiosemicarbazone	1	430	-	Ag, Pb, Fe, Cu(II), Ni, Zn, Hg, Cd, Au interfere.	49
Furil α-monoxime	2.5-7.0	405-410	-	Ni,Cu,Mn,Pd,Pt interfere.	50
Phenylazobenzoldoxime	-	530	0.6-3.5 ppm	Cu(II), Ni, Pd(II), EDTA interfere.	51
2-Carboxy-2'-hydroxy, 3',5'-dimethyl azobenzene-4-sulphonic acid (CHDMAS)	7.5	630	-	Simultaneous Ni and Co determination.	52

42

1	2	3	4	5	6
Eriochrome black T	-	580	$\varepsilon = 50,000$ S.sensitivity is 1.18 ng Cm^{-2}, 0.03–0.9 ppm	ClO_4^-, NO_3^-, EDTA, interfere.	53
4',5'-dibromo-2',7'-dinitro-Fluorescein	4.6	560	$\varepsilon = 50,000$ 0.06 – 1.68 ppm	-	54
5-(4-diethylamino-2-hydroxy-phenylazo)-1,2,4-triazole-3-carboxylic acid	-	525–540	-	-	55
n-butyl xanthalate	4.3–8.1	355	$\varepsilon = 9.43 \times 10^3$ S.sensitivity is 0.0062 μg Cm^{-2}.	Simultaneous determination of Ni and Co in alloy.	56
1-(2-pyridylazo)-2-Naphthol (PAN)	-	580	Beer's law obeyed upto 0-25 μg/50 ml.	-	57
5-({5-chlor-0-2-pyridyl} azo)-2, 4 diaminotoluene	-	570	1.20×10^5 Beer's law obeyed upto 0-10 μg Co/25 ml	desirable sensitivity and selectivity.	58
1-Nitroso-2-Naphthol	6.8-8.4	-	-	-	59
10-(benzothiazol-2-ylazo) phenthren-9-ol	6.7	560	-	Ni(II), Cu(II), Zn(II), pd(II) and Cd(II) interfere.	60

1	2	3	4	5	6
N-N-dimethyl-4-(2-pyridylazo)-m-phenylene diamine	2.4	603	$\varepsilon = 1.14 \times 10^5$; Beer's law obeyed upto 0.01-0.5 ppm	Cd(II), Cu(II) interfere	61
Cyclohexane-1,3-dione bisthiosemicarbazone monohydrochloride.	-	600	Beer's law obeyed upto 0.5-5 ppm	Several ions interfere	62
4-hydroxy-3-nitroso naphthalene-1-sulphonic acid.	-	307	$\varepsilon = 65,000$; Beer's law obeyed upto 0.5-15 μm	-	63
Sodium alizarin sulphonate	7.0	600	$\varepsilon = 6000$; Beer's law obeyed upto 0-10.6 ppm	-	64
5-(4-diethylamino-2-hydroxyphenylazo)-1,2,4-triazole-3-carboxylic acid.	2.4 M HCl	510	Beer's law obeyed for 0.04-0.4 μg ml^{-1}	-	65
2-(5-chloro-2-pyridyl-azo)-5-dimethylamino aniline.	6	570	$\varepsilon = 114,000$; Beer's law obeyed for 0 to 0.5 ppm.	-	66
2,4-dichlorobenzyl triphenyl phosphonium tetrathiocyanate.	-	625	$\varepsilon = 1800$	Fe(III) interferes.	67

1	2	3	4	5	6
4-(2-amino-3-hydroxy-4-pyridylazo) benzene Sulphonic acid.	8-9.7	540	$\varepsilon = 34,100$ S.sensitivity is 1.7 ng Cm^{-2}. Beer's law is obeyed for 0.16 to 1.5 ppm.	-	68
Salicylaldehyde thiosemicarbazone.	5	400	$\varepsilon = 11,000$ Beer's law is obeyed for 0.3 to 6 ppm.	-	69
3-(4-sulphophenylazo chromotropic acid (SPADNS)	5.5 to 6	580	$\varepsilon = 14,000$ S.sensitivity is 0.06 μg Cm^{-2}	Be, Zn, Cd, Zn, Al interfere.	70
ethylene diamine-N,N'-dipropionic acid	7.5 - 9	550	Beer's law obeyed for 36-195 μg ml^{-1}	Cr(VI), Mn(II), Cu(II), Fe(III) interfere.	71
2,6-diamino-3-(4-methyl-2-thiazolylazo) Pyridine.	-	610	Beer's law obeyed for 0.2 to 1.5 ppm	-	72
4-Methyltetrahydrazo benzofurano(6,7-b)-Coumarin.	8 or 10	380	$\varepsilon = 19,100$ Beer's law obeyed for 2.0 to 7.5 ppm of Co	-	73
2-(3'-sulphobenzoyl) Pyridine thiosemicarbazone	-	420	Beer's law obeyed for 1 to 3.5 ppm	-	74

1	2	3	4	5	6
2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol.	Acidic	580	$\epsilon = 1.03 \times 10^5$. Beer's law obeyed for 0-12.5 μg Co/25 ml.	Commonly other elements present do not interfere	75
Pyridine-2-carboxaldehyde 2-pyridylhydrazone.	—	350-390	—	—	76
Pyridoxal thiosemicarbazones	—	440	—	Pd(II), Au(III) interfere.	77
Salicylaldehyde thiosemicarbazone.	—	400	—	V(V) interfere.	78
1-2 diaminoanthraquinone	—	690	—	Interference by 24 cations.	79

1	2	3	4	5	6
di-2-Pyridyl(ketone) pyrimidin-2-ylhydrazone	-	460	ϵ = 29,500 Beer's law obeyed upto 2.1 ppm	-	80
		440	ϵ = 31,500 Beer's law obeyed upto 2.2 ppm		
(-4-(6-chlorindazol-3-ylazo)-3-hydroxynaphthalene-2,7 disulphonic acid)	-	638	Sandell sensitivity is ~2 ng cm^{-2}	Cu^{2+}, CN^- interfere	81
2-amino-5-nitroso-1,4,5,6-tetrahydropyrimidine-4,6-dione.	4.8 to 4.6	375	ϵ = 5.3 x 10^4 Beer's law obeyed upto 0 to 2 µg ml^{-1} Sandell sensitivity 1.11 ng cm^{-2}	Cu^{2+}, Fe^{3+} interefere	82
N-Methylaminothioformyl-N'-phenyl hydroxylamine	8	470	ϵ = 16,500 Beer's law obeyed upto 6 to 60 µm	Zn,Cd,Pb do not interfere	83
3-hydroxy Picolinealdehyde azine	4.3 to 4.6	545 570	ϵ = 3.04 x 10^4 ϵ = 2.66 x 10^4	-	84

1	2	3	4	5	6
Salicylaldehyde azine	7.8 to 8.1	530	$\epsilon = 1356$ Beer's law is obeyed for 4–11 ppm	–	85
Picolinealdehyde azine	7.4 to 9.5	400	$\epsilon = 3560$ Beer's law is obeyed for 3–11 ppm	–	86
Furidioxime	8	350	$\epsilon = 1.84 \times 10^4$	–	87
2,2',2"-Terpyridine	–	510	$\epsilon = 2900$ Beer's law is valid for 0.5 to 50 ppm.	Cu, Ni, Fe, CN interfere.	88
Sulphosalicylic acid	9.5 to 10.5	380	$\epsilon = 4265$ Beer's law is valid for 2–8 ppm.	–	89
2,2'-dipyridylketone 2-pyridylhydrazone (DPPH)	2	514	$\epsilon = 3.9 \times 10^4$ Sandell sensitivity 0.0015 μg/cm2 Beer's law is obeyed for 4 μg/ml.	–	90
isonitrosothiocamphor	–	350	$\epsilon = 1.7 \times 10^4$ Sandell sensitivity is 0.0025 μg Cm^{-2}. Beer's law is obeyed for 0.2–1.5 ppm.	Tolerates thousand fold excess of diverse ions.	91

1	2	3	4	5	6
Trifluro ethylxanthalate	3.8 to 10	352	$\epsilon = 2.9 \times 10^4$ Beer's law is obeyed for 0.0 – 1.7 μg Co/ml.	–	92
3-Bromo-2-hydroxy-5-methyl acetophenoneoxime (BHAMAO)	7.0 to 8.5	400	$\epsilon = 1190$ Beer's law is obeyed for 2–31 ppm. Sandell sensitivity 0.049 μg.	–	93

kethiazone[31] and phthaldehvde bithiosemicarbazone[32] piconaldehyde 4-phenyl 3 thiosemicarbazone[33], and di-2-pyridyl glyoxal dithiosemicarbazone[34] are used for trace determination of cobalt but most of them suffer due to one or another earlier discussed drawbacks.

The detailed summary of reported photometric methods for cobalt determination is given in table 3.1.

The present work accounts for spectrophotometric determination of cobalt (II), cobalt (II) gives yellow coloured complex with 2-chlroquinoline-3-carbaldehyde thiosemicarbazone. For cobalt (II) optimum pH is 6.5 and λmax is 415 nm. Beer's Law is obeyed upto 6 ppm for cobalt(II). The effect of pH, reagent concentration, and diverse ions have been studied. The molar absorptivity and Sandell sensitivity are 3.211×10^{4} Lmole^{-1} cm^{-1} and .01 μg cm^{-2} respectively. For cobalt (II), Mn (II), Mg(II), Ni(II), Cu(II) interefere seriously but Na, Fe does not interefere. The dissociation constant of complex Co(II) - QAT is 7.960×10^{-6}.

However, the proposed reagent QAT overcomes most of the above difficulties and act as a suitable reagent for cobalt.

EXPERIMENTAL

1. **Standard Cobalt Solution :**

Standard Cobalt Solution 1 mg/ml was prepared from cobaltous Nitrate hexahydrate and the solution was standardized with EDTA volumentrically.[94] Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

2. **Reagent Solution :**

0.055 gm QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the solution is 2.07×10^{-4} M. The solution is found to be stable for more than a week.

Recommended Procedure :

To an aliquot of solution containing upto 2.5 ppm of cobalt, add 1.2 ml of 2.07×10^{-4} M reagent solution and a buffer solution of pH 6.5. Dilute this to 10 ml with DMF and water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

Spectral Characteristics :

Figure 3.1 shows the absorption spectrum of the

cobalt (II) QAT Complex containing $1.697 \times 10^{-4}M$ of cobalt and $2.07 \times 10^{-4}M$ reagent at pH 6 using reagent blank. Absorption measurements were made in the spectral region 390 nm to 700 nm and recorded in table. From the group it was found that 415 nm will be suitable wavelength for the cobalt determination. The molar absorptivity of the complex is 3.211×10^3 L mole^{-1} cm^{-1} at 415 nm.

Table 3.2 : Molar Extinction Coefficients of
Co(II) - QAT Complex

λ nm	Molar Ext. Coefficient of Complex 10^4 L Mole^{-1} Cm^{-1}
390	1.296
400	2.593
410	3.153
415	3.211
420	3.194
430	3.005
440	2.593
450	2.240
460	1.886
470	1.679
480	1.592
490	1.544
500	1.503

λ nm	Molar Ext. Coefficient of complex x 10^4 L mole^{-1}Cm^{-1}
510	1.444
520	1.355
530	1.237
540	1.119
550	0.9900
560	0.8249
570	0.7071
580	0.5892
590	0.4883
600	0.4125
610	0.3418
620	0.2828
630	0.2357
640	0.1768
650	0.1473
660	0.1179
670	0.08839
680	0.05892
690	0.02946

FIG. 3·1 — ABSORPTION SPECTRUM OF

Co (II) — QAT COMPLEX .
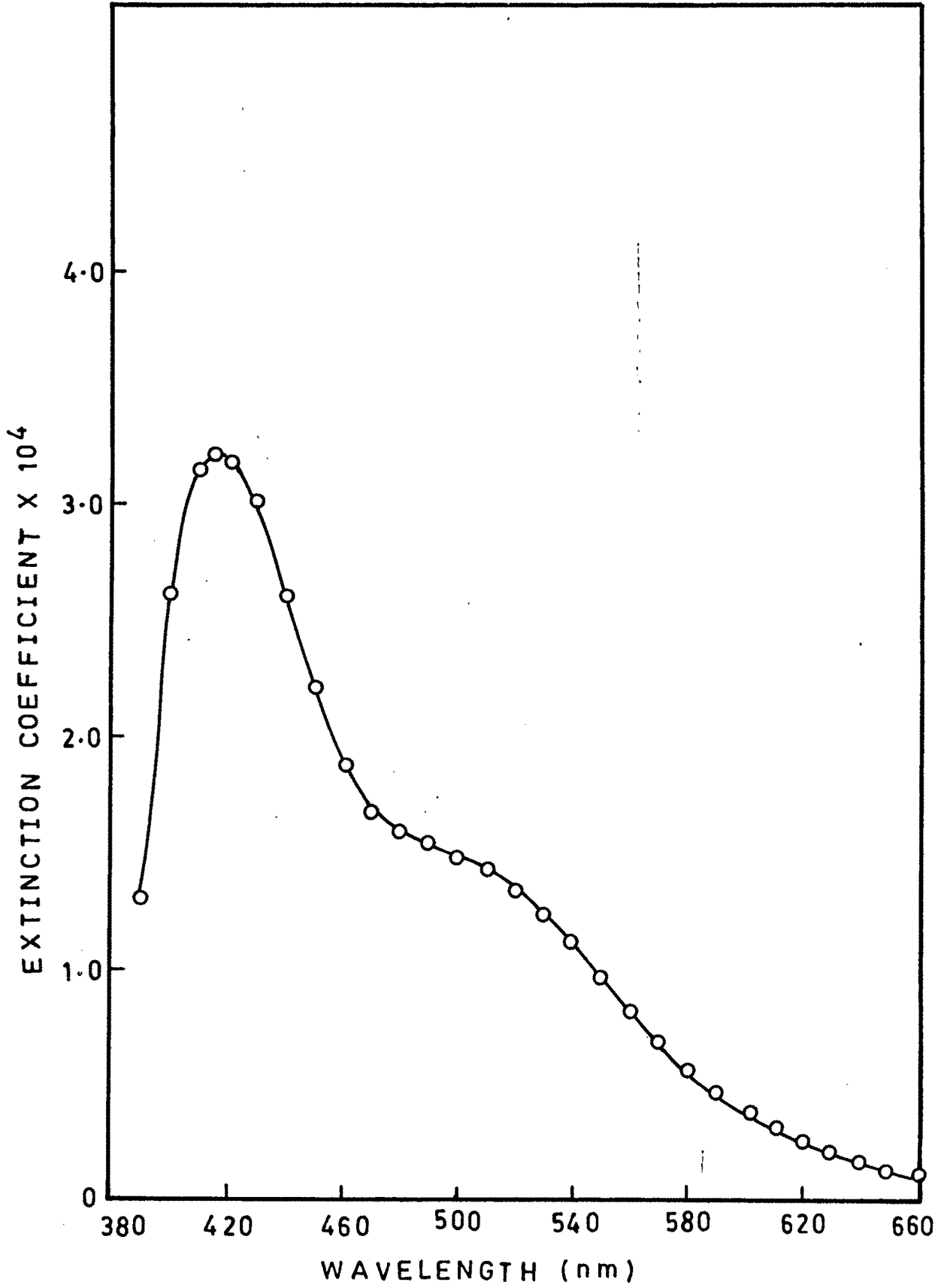
Effect of Time on absorbance :
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In order to study effect of time on the absorbance of Cobalt (II)-QAT complex containing 1.697×10^{-4}M Co(II) at pH 6.5, the absorbance measurements were recorded at different time intervals at 415 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 24 hours and decreases after that. Hence the complex is stable for atleast 24 hours.

Effect of Reagent Concentration :
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Solutions containing the same amount of cobalt (1.697×10^{-4}M) but different amounts of reagent varying from 0.1 to 1.4 ml of 2.07×10^{-4}M reagent solutions were prepared. The pH 6.0 buffer was added and the solution was made upto 10 ml with DMF : water (3:2). Absorbance measurements were recorded at 415 nm against the simultaneously prepared reagent blank. The data given in table (3.3, fig. 3.2) shows that 1.697×10^{-4}M cobalt solution required minimum 1 ml of 2.07×10^{-4}M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in absorbance. However, 1.2 ml of 2.07×10^{-4}M reagent solution was employed for further studies to ensure maximum colour intensity of the cobalt complex.

Table 3.3 : Effect of Reagent Concentration on
the absorbance of Co(II) - QAT Complex

(Co) = 1.697 x 10^{-4}M, (QAT) = 2.07 x 10^{-4}M, pH=6.5

Reagent ml	Absorbance at 415 nm.
0.2	.020
0.4	.050
0.5	.120
0.6	.200
0.7	.260
0.8	.340
1.0	.460
1.2	.540
1.4	.545

Effect of pH :

A series of solutions containing 1.697 x 10^{-4}M

Co(II) and 2.07 x 10^{-4}M of the reagent but varying in pH

from 2 to 9 were prepared and the absorption measurements

were recorded at 415 nm. The results are summarised in the

table 3.4. It was observed that maximum absorvance was

obtained at the pH 6.5. The absorbance of the solutions

decrease at higher or lower pH values than this which is shown in figure (3.3). Hence the pH 6.5 was maintained in further studies.

Table 3.4 : Effect of pH on the absorbance of
Co(II)-QAT Complex

$(Co)=1.697 \times 10^{-4}M; \quad (QAT)=2.07 \times 10^{-4} M$

pH	Absorbance at 415 nm
2	.290
3	.370
4	.420
5	.480
5.5	.510
6	.530
6.5	.540
7	.525
8	.450
9	.370

Validity of Beer's Law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of cobalt and the same amounts of reagents with the pH maintained at pH 6.5 were used for the study. The

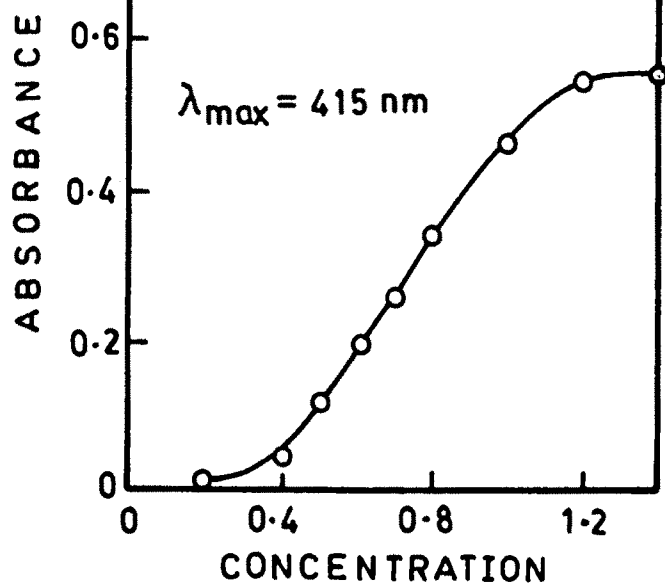FIG. 3·2 — EFFECT OF REAGENT CONC . ON Co(II)- QAT COMPLEX .

λmax = 415 nm

ABSORBANCE

CONCENTRATION

FIG. 3·3 — EFFECT OF pH ON Co(II) — QAT COMPLEX .

λmax = 415 nm

ABSORBANCE

pH

FIG. 3·4 — VALIDITY OF BEER'S LAW .

λmax = 415 nm

ABSORBANCE

CONCENTRATION, Co(II) PPm

FIG. 3·5 — RINGBOM'S PLOT.

λmax = 415 nm

$-(\Delta c/c)/\Delta P$

TRANSMITTANCE (%)
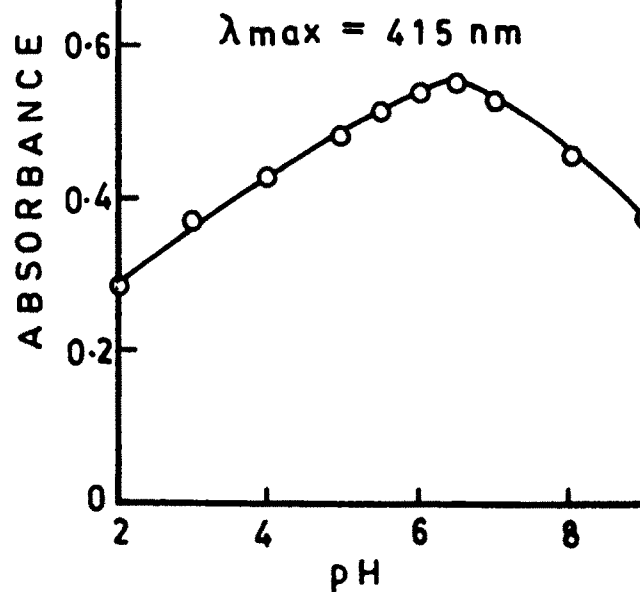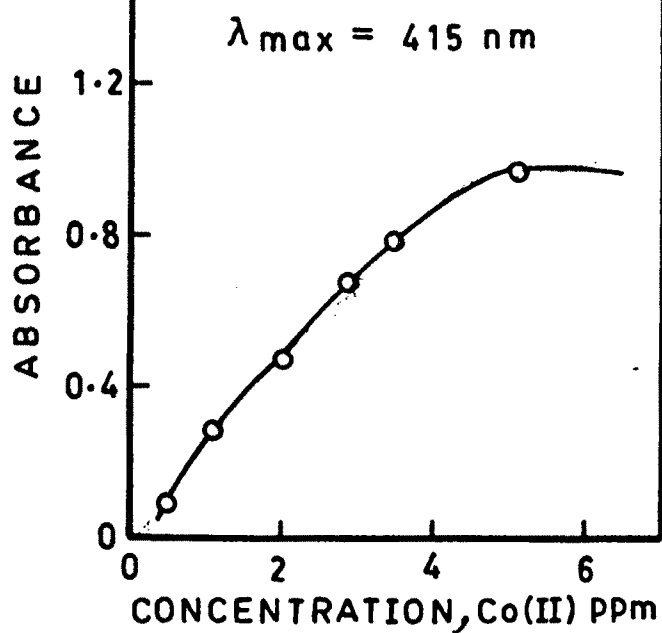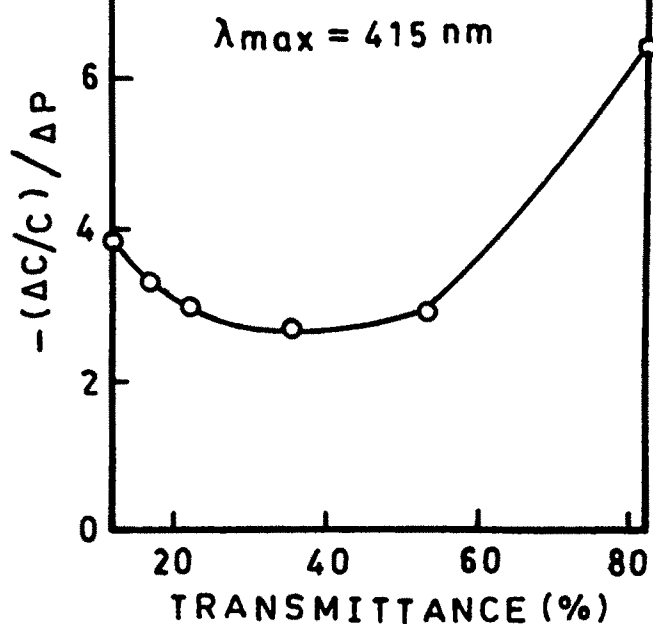
absorption measurements were recorded against reagent

blank at 415 nm (Table 3.5, Fig.3.4) Beer's law is obeyed

upto a concentration of 6.0 ppm of Cobalt (II). The

Sandell sensitivity[95] of the reaction is 0.1 ng/cm^2 of

Co(II).The Ringbom's plot (Fig.3.5) indicates that the optimum
range is 1 to 3 ppm of Cobalt (II).

Table 3.5 : Verification of Validity of Beer's Law

(QAT = 2.07 x 10^{-3}M, pH = 6.5

Co taken ppm	Absorbance at 415 nm
0.5	0.08
1.0	0.28
2.0	0.45
3.0	0.66
4.0	0.78
5.0	0.90

Composition of the complex :

The combining ratio of metal to reagent was

ascertained by Job's method of continuous variations[96] and

Mole ratio method.[97] For Job's method of continuous

variation, a series of solution were prepared by mixing

equimolar solutions of Cobalt (II) and the reagent

(2.07 x 10^{-4}M). The pH of the solutions was adjusted to

6.5. The absorbance of the solutions after diluting to

10 ml in volumetric flask were recorded at 415 nm against simultaneously prepared reagent blank (Table 3.6, Fig. 3.6). The plot indicates the existance of 1:1 complex with respect to metal and reagent represented as ML.

Table 3.6 : Determination of the formula by Job's
Method of continuous Variation

$(Co) = (QAT) = 2.07 \times 10^{-3}M$, pH=6.5

Metal ion ml	reagent ml	Mole fraction of metal	Absorbance at 415 nm
0.1	0.9	0.1	0.28
0.2	0.8	0.2	0.45
0.3	0.7	0.3	0.54
0.4	0.6	0.4	0.65
0.5	0.5	0.5	0.68
0.6	0.4	0.6	0.62
0.7	0.3	0.7	0.46
0.8	0.2	0.8	0.30
0.9	0.1	0.9	0.195

The dissociation constant of the complex k, is calculated from the mole ratio plot by using the following equation

$$k = \frac{\alpha c(n\alpha c)}{c(1-\alpha)}$$

where   n = 1,

   c = Molarity of the solution of complex and

   α = degree of dissociation defined by

$$\alpha = \frac{Am - As}{Am}$$

Am is the maximum absorption obtained from horizontal portion of the curve and As is the absorbance of stoichiometric molar ratio of reagent to cobalt in the complex. The value of k comes out to be 7.960×10^{-6}.

Mole Ratio method :

For mole ratio method, solutions containing the same final metal concentration ($2.07 \times 10^{-3}M$) and different amounts of reagent ranging from concentration were prepared keeping pH 6.5 Absorbances of the solutions were measured at 415 nm against reagent blank. The curve showed break at the metal to ligand ratio 1:1, confirming the results obtained by application of Job's method of continuous variations. (Table 3.7, Fig. 3.7).
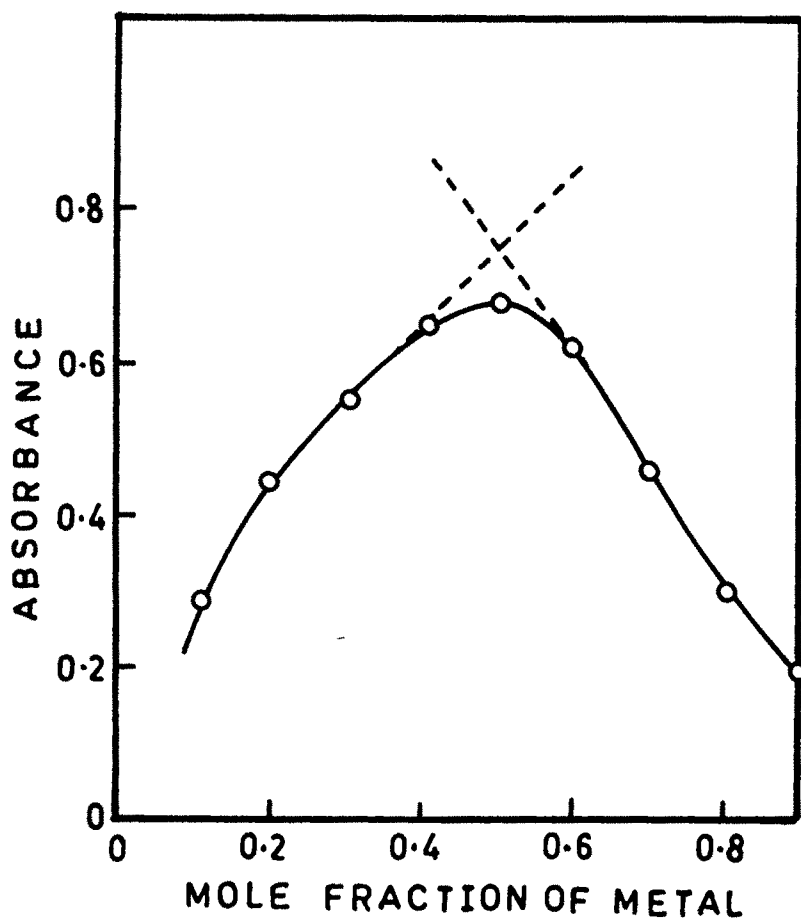
FIG. 3·6 —
JOB'S PLOT FOR
Co(II)-QAT COMPLEX.

$\lambda_{max} = 415$ nm

FIG. 3·7 —
MOLE RATIO PLOT
FOR Co(II)-QAT
COMPLEX.

$\lambda_{max} = 415$ nm

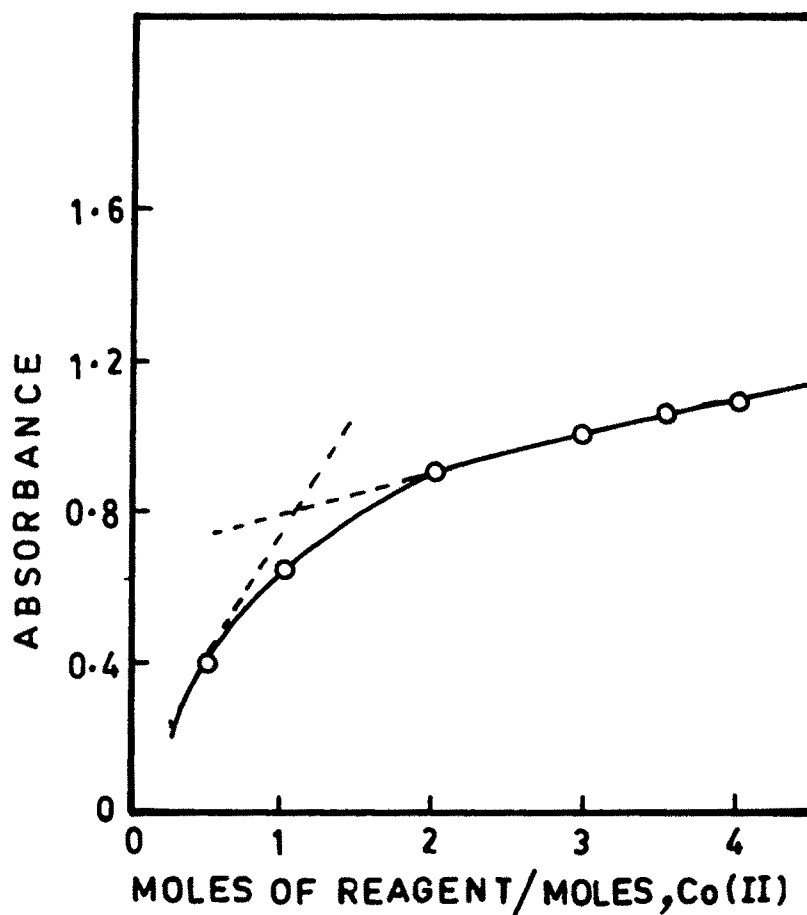Table 3.7 : Determination of the formula of Co(II)-
QAT Complex by Mole Ratio Method

$$(Co) = (QAT) = 2.07 \times 10^{-3}M, \quad pH = 6.5$$

Metal ion ml	reagent ml	Reagent to Metal Ratio	Absorbance at 415 nm
0.4	0.2	0.5	0.40
0.4	0.4	1.0	0.68
0.4	0.8	2.0	0.90
0.4	1.2	3.0	1.00
0.4	1.4	3.5	1.05
0.4	1.6	4.0	1.10

Effect of diverse ions :

The effect of diverse ions was studied using 2 ppm of cobalt and 2.07×10^{-4}M reagent in a final volume of 10 ml at pH 6.5. The results indicated that Mn(II), Ni(II), Cu(II) and anions like citrate and cynide interfere strongly. The tolerance limit for various foreign ions tested has been shown in the table.

Effect of diverse ions :

Co(II) = 2 ppm, QAT = 2.07×10^{-4}M, pH = 6.5

Metal ion	Tolerance limit μg
Ga(III)	100
Mo(VI)	100
Ca(II)	100
Cu(II)	None
Mn(II)	None
Ni(II)	None
Fe(II)	None
CN^-	None
Acetate	1000
SCN^-	1000
Oxalate	1000
Thiourea	1000
Citrate	None
PO_4^{3-}	1000
F^-	1000

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