CHAPTER - VI

DETERMINATION OF COBALT

6.1 INTRODUCTION

The element cobalt derives its name from the germanic "KOBOLD", since its ores and oxides seemed to behave impishly in resisting early attempts to reduce them to the metal.

Swedish Chemist Brandt, first obtained the metal cobalt in the year 1735. The fact that cobalt minerals impart blue colour to glass was known since early days. Cobalt is an important element because of the industrial uses of metal, alloys and compounds. The chemistry of cobalt and its compounds is extensively investigated and synthetic chemistry of cobalt compounds is also well explored.

The range of uses of cobalt is very wide from industries to medicine and plant physiology, Cobalt is used in ceramic and glass industries, in cemented carbides, in ferrous and non ferrous alloys, in biological and biochemical reactions and also in catalyst and in electroplating. Its alloys with elements such as chromium, tungsten and iron have unique value as high speed cutting tools. Alnico type permanent magnets contain 5 to 35 % cobalt. Special seals contain 18 % cobalt. Ferrous alloys like tool steels contain 5 to 12 % cobalt which improves cutting efficiency at elevated temperature. 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 and surgical alloys, vitallium contain 65 % cobalt. High strength alloys of jet aircraft and gas turbines contain 20 to 65 % cobalt.

Cobalt is undesirable impurity in the nuclear fuel and materials of nuclear reactions. Hence determination of trace amount of cobalt in uranium is important. Cobalt is also found in micro quantities in nickel salts, steel, some pure chemical reagents, in sea water and in silicates. Organic salts of cobalt are used as driers in paints and varnishes. Vitamin B_{12} contains cobalt. Carrots, cheeries, peas, potatoes and cabbages contain 0.005 to 0.2 ppm of cobalt. It is an essential micronutrient for plants and is present in soil. In a normal human being, the body burden of cobalt is 1.5 mg.

Cobalt is determined in a large number of samples. For traces of cobalt, atomic absorption spectrophotometry is used.

The lack of suitable reagents and the experimental conditions for the spectrophotometric determination of this important element is still a problem to analytical chemists. The reagent α - nitroso-β-naphthol[1] was first introduced for the determination of cobalt.

In recent years, although numerous colorimetric reagents for photometric determination of cobalt have been proposed, none of them satisfies the requirement of a good photometric reagent for cobalt.[2-4] Many of them lack either desired sensitivity or selectivity. The classic reagents like thiocyanate[5] for determination of cobalt show less colour intensity in aqueous solution and suffer from numerous interferences.

With some reagents like dimethyl glyoxime,[6] 3-mercaptopropionic acid,[7] pyridine-2,4,6-tricarboxylic acid,[8] azanol A,[9] furil-α-dioxime[10] and 2,4-dimethyl benzamidoxime,[11] method of determination of cobalt is time consuming.

The most important chelating agents used for determination of cobalt are thiooxines,[12-14] and oximes,[15-23] naphthols[24-29] and azonaphthols,[30-32] dithizone[33] and nitro-QDT.[34] With some of these reagents, however, it is not possible to determine traces of cobalt because of the instability of the cobalt complex, poor sensitivity and time consuming procedures.

The reagents 1,2-diaminocyclo-hexane tetra-acetic acid,[35,36] nitroso-R-salt[37,38] 5-aminopyrazole-4-carboxylic acid,[39] sulphosalicylic acid,[40], 3-hydroxy picolin-aldehyde azine[41] and 4-amino-5-nitroso pyrimidine-2, 6-diol[42] at elevated temperature is required for complex formation.

o-Hydroxy acetophenone guanylhydrazone (HAG) was used for spectrophotometric determination of trace amount of cobalt at pH 11 as a yellow complex in aqueous media. The complex was measured at 375 nm. The proposed method is simple, rapid and highly sensitive compared with other photometric methods.

6.2 EXPERIMENTAL

6.2.1 Standard Solutions :

Standard Cobalt Solution :

Standard cobalt solution 1 mg/ml (1.697×10^{-2}M) was prepared from cobalt sulphate heptahydrate and the solution was standardized with EDTA volumetrically.[43] Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

Reagent Solution :

A stock solution of reagent (HAG) 1.92 mg/ml (1.0×10^{-2}M) was prepared by dissolving 192 mg of the reagent in 100 ml distilled water.

Buffer Solution :

Buffer solution of pH 11.0 was prepared from sodium carbonate (0.1 M).

6.2.2 Recommended Procedure :

An aliquot of the solution containing about 10 µg of Co(II) was taken in a 10 ml volumetric flask. To this, was added 3.5 ml reagent (HAG) solution of concentration 1.0×10^{-2}M. The pH of the solution was adjusted to 11 by adding 1.0 ml buffer solution of pH 11.0 and diluted to volume with distilled water. The absorbance of the complex was measured at 375 nm against reagent blank prepared in the same manner excluding metal ion. The concentration of cobalt in an unknown solution was found out from standard calibration curve obtained under identical conditions.

6.3 RESULTS AND DISCUSSION

6.3.1 Spectral Characteristics :

The absorption spectrum of the cobalt (II)-HAG complex of the solution containing 10 µg (1 ml 0.01 mg/ml i.e. 1.697×10^{-4} M) cobalt and 3.5 ml of 1.0×10^{-2}M reagent (HAG) was recorded at pH 11.0 against reagent blank. The absorption measurements were made in the spectral range from 350 to 520 nm. The complex has an absorption maximum at 375 nm at pH 11.0. The spectra of molar extinction coefficient of the complex and reagent are given in fig. 6.1. The observations for the spectra are given in table 6.1.

Table 6.1 : Molar extinction coefficients of the Co(II)-HAG complex and the reagent (HAG)

Wavelength λ, nm	Molar extinction coefficients, ϵ Co(II)-HAG Complex $\epsilon \times 10^4$ l mole^{-1}cm^{-1}	Reagent, HAG $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
350	0.454	0.0300
360	0.707	0.0176
370	0.850	0.0100
375	0.854	0.0078
380	0.825	0.0058
390	0.707	0.0041
400	0.448	0.0036
410	0.253	0.0033
420	0.138	0.0030
430	0.085	0.0026
440	0.059	0.0023
450	0.047	0.0020
460	0.035	0.0016
470	0.029	0.0015
480	0.023	0.0011
490	0.017	0.0010
500	0.011	0.0008
510	0.008	0.0005
520	0.006	0.0005

6.3.2 Effect of pH :

A series of solutions varying in pH were prepared as per the recommended procedure. The complex has maximum and constant absorbance over the pH range 10.5 to 11.5. It falls below pH 10.5 and above 11.5. Hence, the pH value 11.0 was selected for the study of Co(II)-HAG complex. In acidic medium the complex shows comparatively less absorbance. The observations are given in the table 6.2. The plot of observations is shown in fig. 6.2.

Table 6.2 : Effect of pH on the absorbance of Co(II)-HAG complex.

[Co(II)] = 10 ppm; [HAG] = 1.0×10^{-2}M

pH	Absorbance at 375 nm
2.0	0.05
4.0	0.06
6.0	0.06
8.0	0.32
9.0	0.68
10.0	1.02
10.5	1.20
11.0	1.20
11.5	1.20
12.0	0.81
13.0	0.62

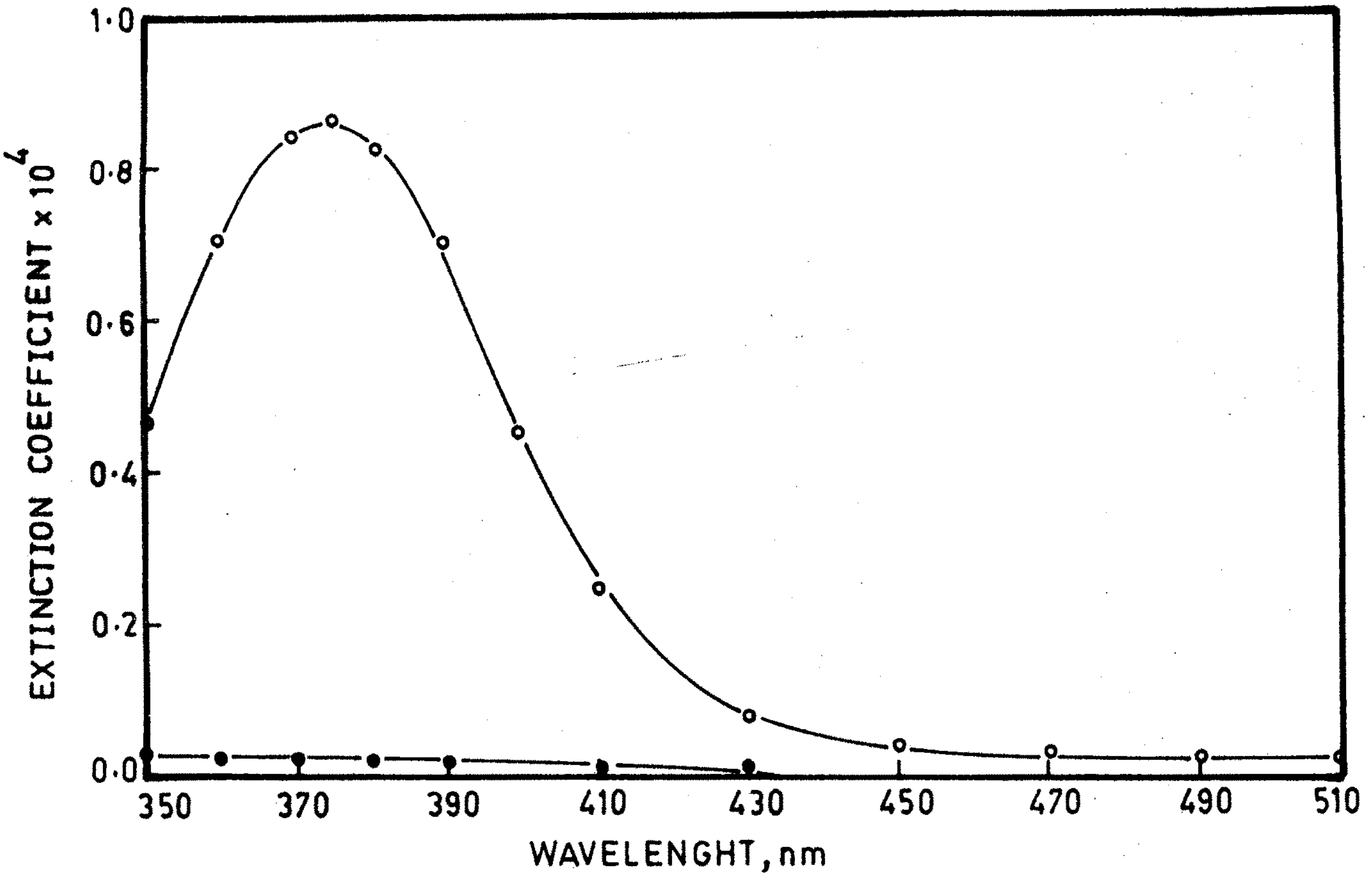


FIG. 6·1 — o—o ABSORPTION SPECTRUM OF COBALT-HAG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (HAG).

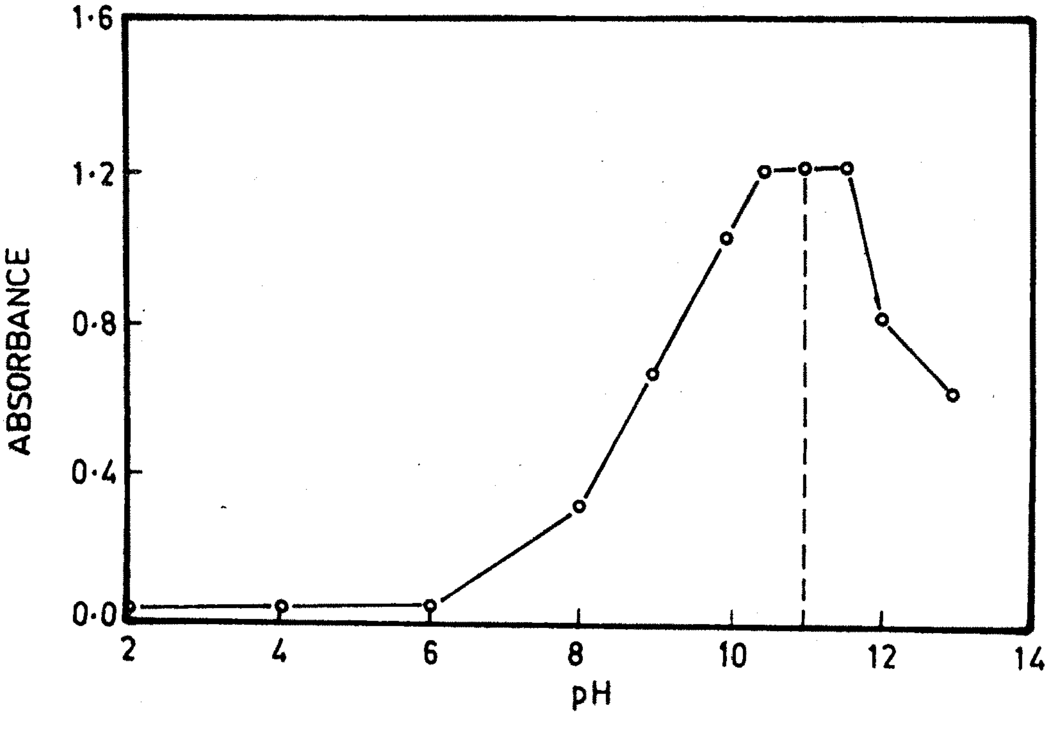


FIG. 6·2 — EFFECT OF pH.

6.3.3 Effect of reagent concentration :

It was observed that the amount of excess of reagent was the least critical. About a three fold excess molar concentration relative to the metal ion concentration was satisfactory. A series of solutions were prepared in which the concentration of reagent was varied from 0.005 M to 0.04 M, while the concentration of cobalt was kept constant at 1.697×10^{-4}M. The pH value was adjusted and the solution was made upto the mark in 10 ml volumetric flask. The absorbance was measured at 375 nm wavelength against reagent blank. The results are given in table 6.3 show that three fold molar excess of the reagent is sufficient for full colour development of 10 ppm cobalt.

Table 6.3 : Effect of reagent concentration on the absorbance of Co(II)-HAG complex.
[Co(II)] = 10 ppm; [HAG] = 1.0×10^{-2}M

Amount of HAG added, ml	Absorbance at 375 nm
0.5	0.64
1.0	1.05
1.5	1.25
2.0	1.35
2.5	1.40
3.0	1.42
3.5	1.45
4.0	1.45

6.3.4 Stability and reaction rate :

Cobalt(II)-HAG complex is stable for several hours. Complex formation is instantareous and is independent of temperature.

6.3.5 Validity of Beer's Law :

The solutions containing different amounts of cobalt and the same amount of reagent (HAG), 3.5 ml of 1.0×10^{-2}M at pH 11 were used to study the validity of Beer's law. It was found that the Beer's law is valid upto 6 ppm of cobalt at 375 nm (Table 6.4, Fig. 6.3).

The optimum concentration range for the determination of cobalt was calculated from the Ringbom plot[44] and was found to be 1.0 to 3.0 ppm at 375 nm (Fig. 6.4).

Table 6.4 : Validity of Beer's law
$[Co(II)] = 1.697 \times 10^{-4}$M; $[HAG] = 1.0 \times 10^{-2}$M

Amount of Cobalt(II) ppm	Absorbance at 375 nm
1.0	0.21
2.0	0.46
3.0	0.70
4.0	0.93
5.0	1.28
6.0	1.40
7.0	1.45

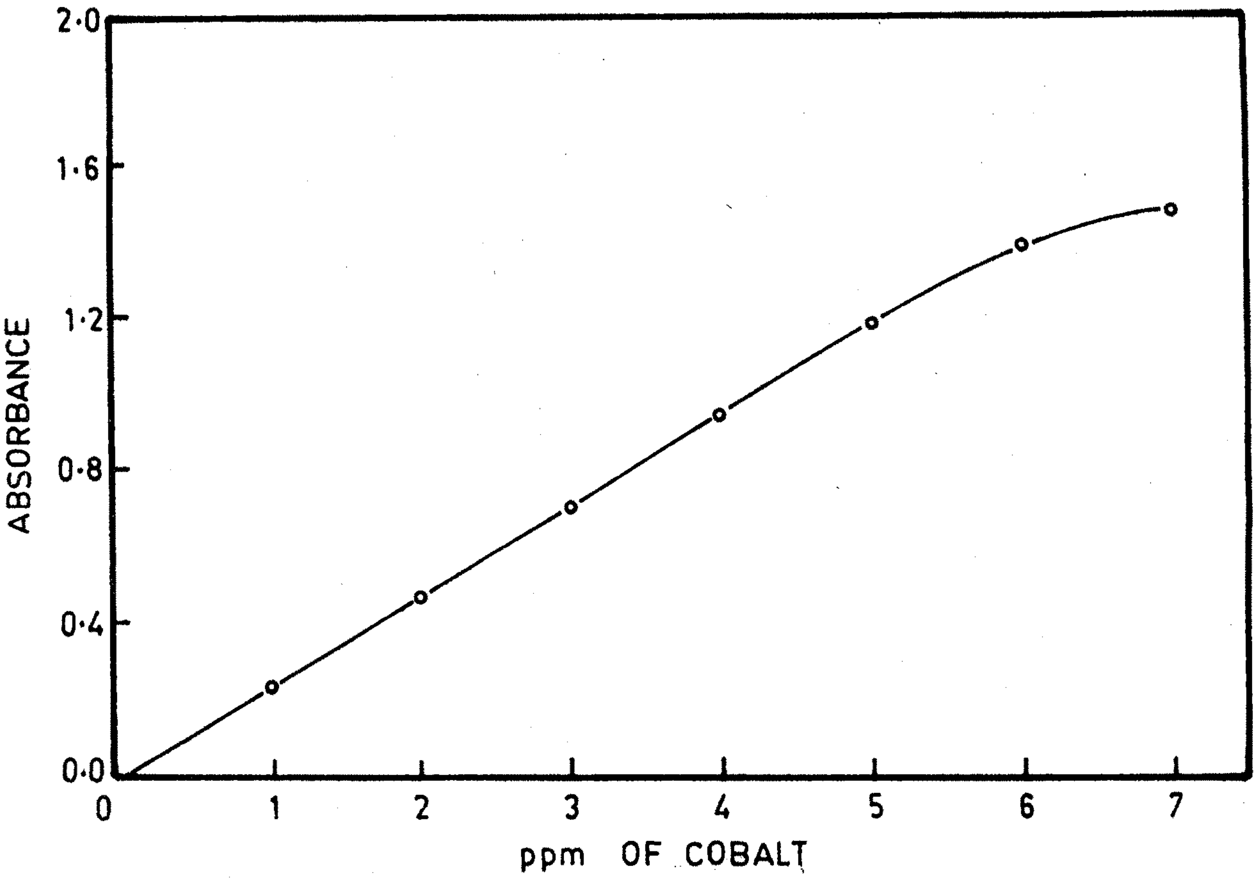


FIG. 6·3 — VALIDITY OF BEER'S LAW.

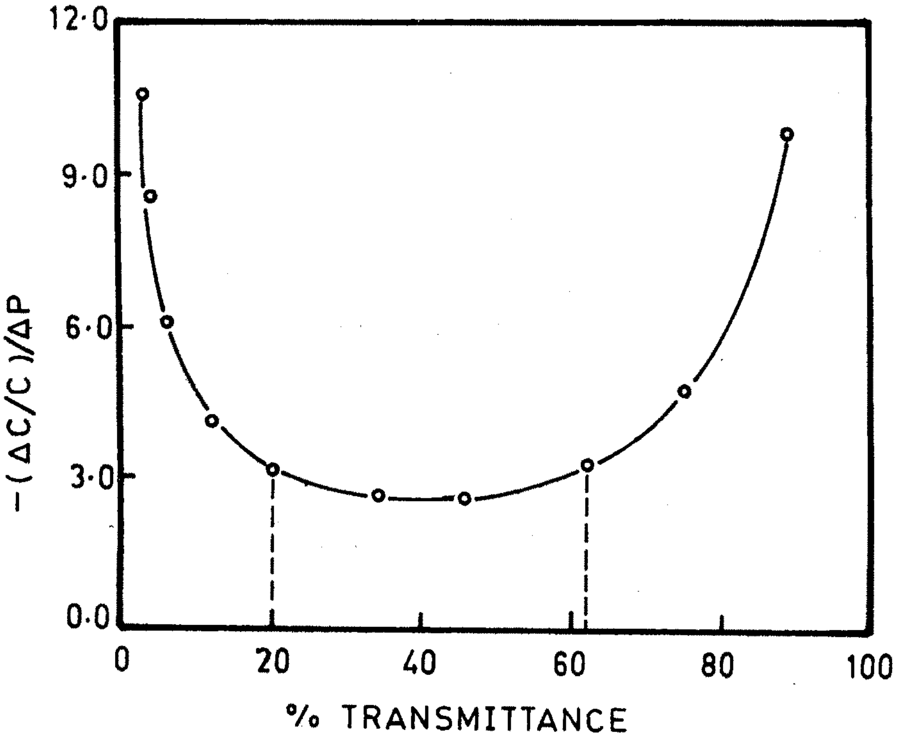


FIG. 6·4 — RINGBOM PLOT.

6.3.6 Composition of the Complex :

The empirical formula for Co(II)-HAG complex was determined by Job's method[45] of continuous variation, mole ratio method[46] and slope ratio method.[47] For these methods equimolar solutions of the concentration 1.697 x 10^{-3} M were used. In Job's method of continuous variation, the absorbances at 375 nm, 385 nm, 390 nm and 400 nm wavelengths against mole fraction of the reagent were plotted which indicate that ligand forms 1:2 complex (Table 6.5; Fig. 6.5). This composition of Co(II)-HAG complex is confirmed by mole ratio method (Table 6.6; Fig. 6.6) and slope ratio method.

Table 6.5 : Job's continuous variation method
[Co(II)] = [HAG] = 1.697 x 10^{-3}M

Cobalt(II) ml	Reagent (HAG) ml	Molar Ratio (M:L)	Absorbances at λ			
			375 nm	385 nm	390 nm	400 nm
0.0	1.8	-	-	-	-	-
0.2	1.6	1:8	0.185	0.140	0.100	0.065
0.4	1.4	2:7	0.335	0.270	0.190	0.120
0.6	1.2	1:2	0.425	0.360	0.245	0.150
0.8	1.0	4:5	0.380	0.325	0.230	0.145
1.0	0.8	5:4	0.310	0.265	0.195	0.120
1.2	0.6	2:1	0.235	0.195	0.150	0.095
1.4	0.4	7:2	0.165	0.130	0.100	0.065
1.6	0.2	8:1	0.080	0.065	0.050	0.030
1.8	0.0	-	-	-	-	-

Table 6.6 : Molar ratio method,
$[Co(II)] = [HAG] = 1.697 \times 10^{-3} M$

Cobalt(II) ml	Reagent (HAG) ml	Molar Ratio M:L	Absorbance at λ	
			375 nm	400 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.030	0.020
0.4	2.0	1:5	0.060	0.040
0.6	2.0	3:10	0.095	0.065
0.66	2.0	1:3	0.125	0.085
0.8	2.0	2:5	0.155	0.110
1.0	2.0	1:2	0.170	0.120
1.2	2.0	3:5	0.185	0.130
1.33	2.0	2:3	0.195	0.135
1.4	2.0	7:10	0.200	0.140
1.6	2.0	4:5	0.205	0.145
1.8	2.0	9:10	0.210	0.145
2.0	2.0	1:1	0.215	0.150

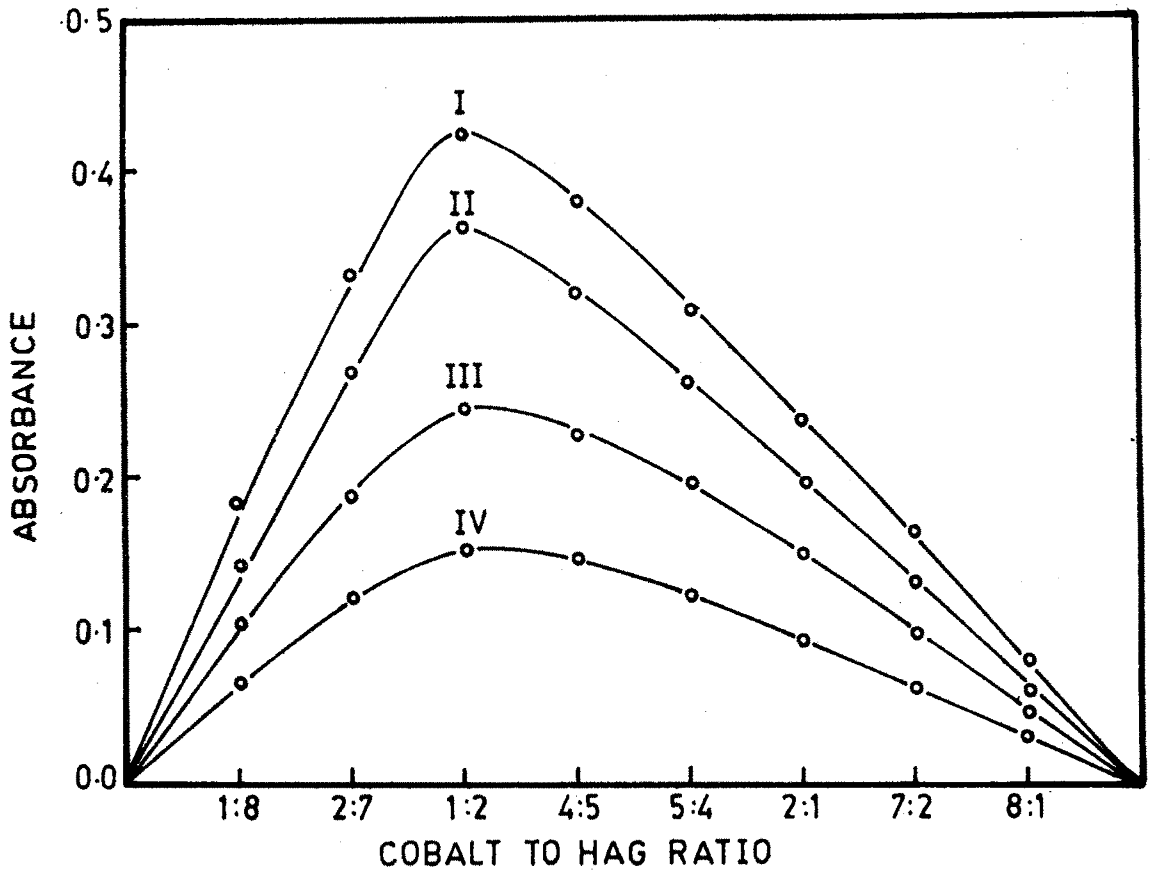


FIG. 6·5 – JOB'S CONTINUOUS VARIATION METHOD.
I – 375 nm, II – 385 nm, III – 390 nm, IV – 400 nm.

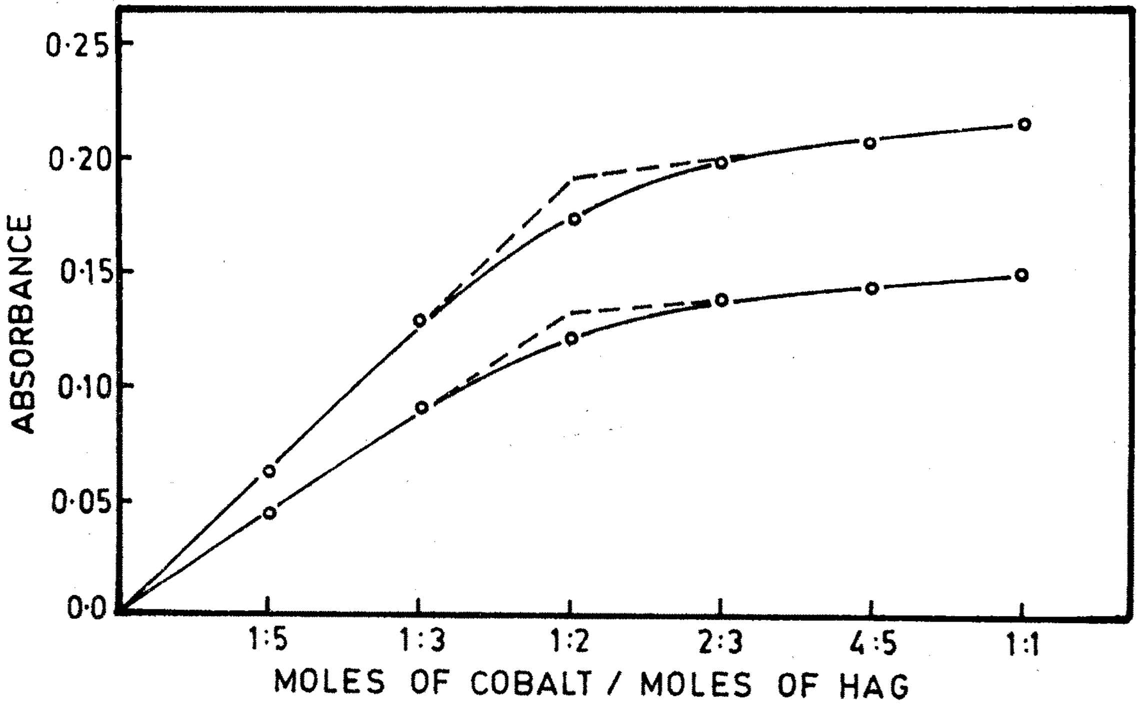
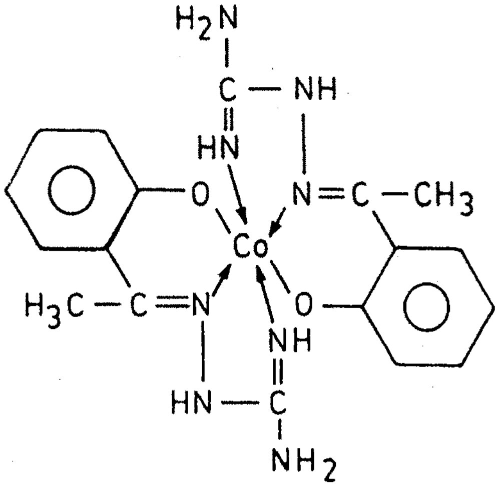


FIG. 6·6 – MOLE RATIO METHOD.
I – 375 nm, II – 400 nm.

The probable structure for Co(II)-HAG complex may be presented as



6.3.7 Sensitivity :

The complex of cobalt is not sensitive to the light. The photometric sensitivity of the method was calculated by the method of Sandell[48] and found to be 0.03289 µg/cm^2.

6.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.[47] The value of α, degree of dissociation was found to be 0.1053.

The apparent instability constant[49] was found to be 1.503×10^{-12} for Co(II)-HAG complex. The change in free energy[50] of the system is -16.283 K cals/mole.

6.3.9 Reproducibility of the method :

The reproducibility of the method was studied by determining cobalt in sets of six observations for each concentration. The table 6.7 summarises the results and shows that the results are reproducible.

Table 6.7 : Reproducibility of the method :

Cobalt(II) ppm	Mean absorbance of six observations	Standard deviation	Coefficient of Variation %
1.5	0.33	0.0015	0.4545
3.0	0.67	0.0032	0.4776
4.5	0.98	0.0044	0.4489

6.3.10 Effect of diverse ions :

The effect of diverse ions was studied using fixed amount of cobalt (1.0 ppm) and developing and measuring the colour intensity as per recommended procedure. An error upto 2 % in absorbance was considered to be tolerable.

It is found that Cr(III), Pd(II), Mn(II), Fe(III), citrate, $EDTA^{-4}$ and tartrate ions interfere seriously. The tolerance limits for the ions are listed in table 6.8.

Table 6.8 : Effect of diverse ions :

[Co(II)] = 1.0 ppm; [HAG] = 1.0 x 10^{-3}M

Foreign ions	Added as	Tolerance limit ppm
Cations		
Cr(III)	$CrCl_3 \cdot 6H_2O$	none
V(IV)	$VOSO_4 \cdot H_2O$	2.0
Ba(II)	$BaCl_2 \cdot 2H_2O$	2.0
Cu(II)	$CuSO_4 \cdot 5H_2O$	0.6
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	0.9
Zn(II)	$ZnSO_4 \cdot 7H_2O$	0.5
Mn(II)	$MnSO_4 \cdot H_2O$	none
Pd(II)	$PdCl_2$	none
Fe(III)	$FeCl_3 \cdot 6H_2O$	none
Ni(II)	$NiSO_4 \cdot 6H_2O$	0.1
Cd(II)	$CdSO_4 \cdot 8/3\ H_2O$	0.8
Cr(VI)	$K_2Cr_2O_7$	0.2
Anions		
Citrate	Citric acid	none
Thiourea	Thiourea	500.0
Oxalate	Potassium oxalate	2.0
$EDTA^{-4}$	Disodium salt	none
Urea	Urea	500.0
Acetate	Sodium acetate	20.0
Tartrate	Tartaric acid	none

6.4 APPLICATIONS

Analysis of cobalt in synthetic mixture of Co(II) and uranyl nitrate :

To an aliquot of the solution containing 25.0 and 50.0 mg of uranium nitrate hexahydrate, was added 9.0 and 12.0 µg of cobalt respectively. Cobalt was then determined as Co(II)-HAG complex as per recommended procedure.

Table 6.9 shows the recoveries of cobalt added to uranyl nitrate. It can be seen from the table that the recovery of added cobalt was quantitative. The results obtained by using 2-nitroso-5-dimethyl amino phenol[51] were in good agreement with this new method.

Table 6.9 : Recovery of added cobalt.

$UO_2(NO_3)_2.6H_2O$ taken, mg	Cobalt added µg	Mean absorbance for five samples at 375 nm	Cobalt recovery in synthetic mixture	
			µg	%
25.0	9.0	0.73	8.98	~100
50.0	12.0	0.95	12.03	~100

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