CHAPTER-II

DETERMINATION OF COBALT*

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2.1 INTRODUCTION

Among the transition metals cobalt is most important as metals, alloys and compounds. Cobalt is undesirable impurity in the nuclear fuel and materials of nuclear reactors. Hence, determination of trace amount of cobalt in uranium is important. It is used in industry, medicine and plant physiology. It is also used in ferrous and non-ferrous alloys, in ceramics and glass industries, in cemented carbides as a catalyst and in biological and biochemical reactions. Cobalt is also found in micro quantities in nickel salts, steel, some pure chemical reagents, in sea water and in silicates.

Cobalt salts are used to impart blue colour to glasses. It is also used in ceramics and in enamel wears. Cobalt is used in electroplating with nickel. Organic salts of cobalt are used as driers in paints and varnishes. Vitamin B_{12} contains cobalt. Carrots, Cheeries, Peas, Potatoes, Cabbage contain 0.005 to 0.2 ppm cobalt. It is essential micro-nutrient for plants and is present in soil. In a normal being, the body burden of cobalt is 1.5 mg.

Alnico type permanent magnets contain 5 to 35% cobalt. Special seals contain 18% cobalt, while ferrous alloys like tool steels contain 5 to 12% cobalt. Dental or surgical alloy, vitallium contain 65% cobalt. High strength alloys and gas turbines contain 20 to 65% cobalt. Very hard and corrosion resistant alloys, stellite contain 42 to 65% cobalt. In cemented carbides, 3 to 20% cobalt is present.

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

Numerous colorimetric reagents for spectrophotometric determination of cobalt have been proposed, none of them satisfied the requirement of a good photometric reagent for cobalt.[1-3] Many of them lack either desired sensitivity or selectivity. However, because of the lack of suitable reagents and the experimental conditions for spectrophotometric determination of cobalt is still a problem to analytical chemists. Several reagents have been so far suggested for cobalt. The reagent α-nitroso-β-naphthol[4] was first introduced.

The reagents like 4-amino-5-nitroso pyrimidine-2,6-diol,[5] 3-hydroxy picolinaldehyde azine,[6] sulphosalicylic acid,[7] 5-aminopyrazole-4-carboxylic acid,[8] nitroso-R-salt,[9,10] 1,2-diaminocyclohexane tetra-acetic acid,[11,12] at elevated temperature are used for complex formation.

The chelating agents, thiooxines[13-15] and oximes[16-24] naphthols[25-30] and azonaphthols[31-33], dithizone[34] and nitro-QDT[35] are used for determination of cobalt. But it is not possible to determine traces of cobalt with some of these reagents, because of the instability of the cobalt complex, poor sensitivity and time consuming procedures.

For some reagents like 2,3-dimethyl benzamidoxime,[36] furil-α-dioxime,[37] azanol-A,[38] dimethyl glyoxime,[39] 3-mercaptopropionic acid[40] and pyridine-2,4,6-tricarboxylic acid,[41] method of determination of cobalt are time consuming.

Salicylaldehyde guanylhydrazone (SAG) was used for spectrophotometric determination of trace amount of cobalt at pH 8.8 as a yellow complex in aqueous media. The complex was measured at 380 nm. The proposed method is simple, rapid and highly sensitive compared with other photometric methods.

2.2 EXPERIMENTAL

All the chemicals used were of analytical grade.

2.2.1 Standard Solutions

Standard Cobalt Solution :

Standard cobalt solution 1 mg/ml (1.697×10^{-2} M) was prepared from cobalt sulphate hepthaydrate and the solution was standardized with EDTA volumetrically.[42] Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

Reagent Solution :

A stock solution of reagent, salicylaldehyde guanylhydrazone (SAG), 1.78 mg/ml (1.0 x 10^{-2} M) was prepared by dissolving 178 mg of the reagent in 100 ml distilled water.

Buffer Solution :

Buffer solution of pH 11.98 was prepared by mixing appropriate amounts of borax and sodium hydroxide.

2.2.2 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 0.6 ml reagent (SAG) solution of concentration 1.0 x 10^{-3} M. The pH of the solution was adjusted to 8.80 by adding 1.5 ml buffer solution of pH 11.98 and diluted to volume with distilled water. The absorbance of the complex was measured at 380 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.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectral Characteristics :

The absorption spectrum of the cobalt(II)-SAG complex of the solution containing 10 µg (1 ml 0.01 mg/ml i.e. 1.697 x 10^{-4} M) cobalt and 0.6 ml of 1.0 x 10^{-3} M reagent(SAG) was recorded at pH 8.80, against reagent blank. The absorption measurements were made in the spectral range from 3[illegible]0 to 580 nm. The complex has an absorption maximum at 380 nm at pH 8.80. The spectra of molar extinction coefficient of the complex and reagent are given in figure 2.1. The observations for the spectra are given in table 2.1.

2.3.2 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 7.5 to 9.5. It falls below pH 7.5 and above pH 9.5. Hence the pH value 8.80 was selected for the study of Co(II)-SAG complex. In acidic medium the complex shows comparatively less absorbance. The observations are given in the table 2.2. The plot of observations is shown in fig. 2.2.

Table 2.1 : Molar extinction coefficients of the Co(II)-SAG complex and the reagent (SAG)

Wavelength λ,nm	Molar extinction coefficients, ϵ	
	Co(II)-SAG complex $\epsilon \times 10^4$ l $mole^{-1}cm^{-1}$	Reagent, SAG $\epsilon \times 10^4$ l $mole^{-1}cm^{-1}$
340	0.1178	0.055
350	0.6482	0.024
360	0.9723	0.008
370	1.1786	0.002
375	1.2080	0.0015
380	1.2375	0.001
385	1.1401	0.000
390	0.9723	-
400	0.5893	-
410	0.3536	-
420	0.2357	-
430	0.1768	-
440	0.1473	-
450	0.1179	-
460	0.1050	-
470	0.1000	-
480	0.0950	-
490	0.0920	-
500	0.0885	-
510	0.0650	-
520	0.0589	-
530	0.0525	-
540	0.0500	-
550	0.0475	-
560	0.0450	-
570	0.0325	-
580	0.0295	-

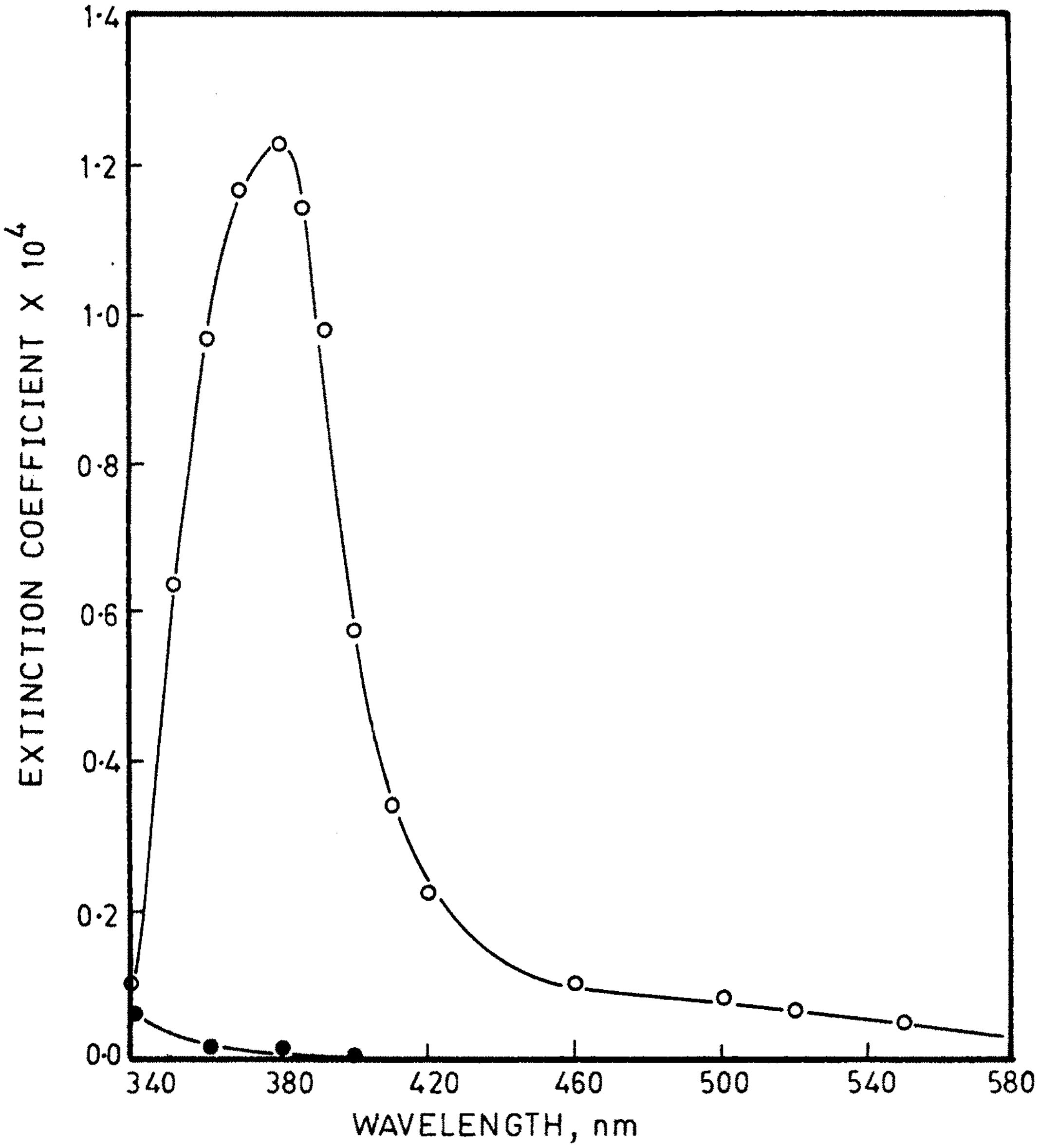


FIG. 2·1 ○—○ ABSORPTION SPECTRUM OF COBALT-SAG COMPLEX
●—● ABSORPTION SPECTRUM OF REAGENT (SAG)

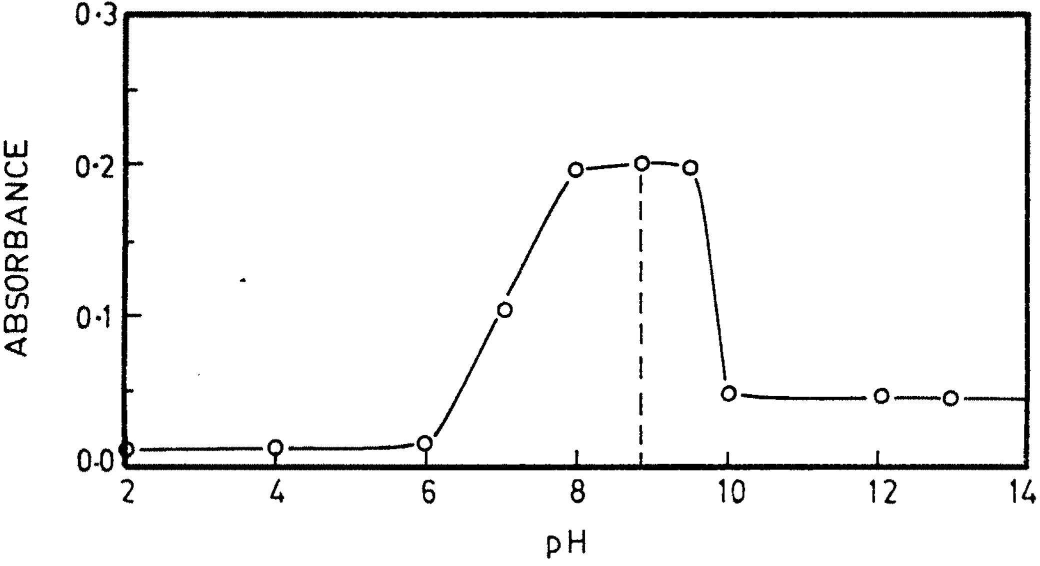


FIG. 2·2 EFFECT OF pH

Table 2.2 : Effect of pH on the absorbance of Co(II)-SAG complex
[Co(II)] = 1 ppm; [SAG] = 6.0×10^{-5}M

pH	Absorbance at 380, nm
3.0	0.01
4.0	0.01
6.0	0.02
7.0	0.10
8.0	0.20
8.8	0.21
9.0	0.20
9.5	0.20
10.0	0.05
12.0	0.05

2.3.3 Effect of reagent concentration :

It was observed that the amount of excess of reagent was the least critical. About a four 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 2.0×10^{-5}M to 1.2×10^{-4}M, while the concentration of Cobalt was kept constant at 1.697×10^{-5}M. The pH value was adjusted and the solution was made up to the mark in 10 ml volumetric flask. The absorbance was measured at 380 nm wavelength against reagent blank. The results are given in table 2.3, show that, four fold molar excess of the reagent is sufficient for full colour development of 1.0 ppm cobalt.

Table 2.3 : Effect of reagent concentration on the absorbance of Co(II)-SAG complex

$[Co(II)] = 1.0$ ppm; $[SAG] = 1.0 \times 10^{-3}M$

Amount of SAG added, ml	Absorbance at 380 nm
0.2	0.08
0.4	0.16
0.6	0.21
0.8	0.21
1.0	0.21
1.2	0.21

2.3.4 Stability and reaction rate :

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

2.3.5 Validity of Beer's Law :

The solutions containing different amounts of cobalt and the same amount of reagent (SAG), 0.8 ml of $1.0 \times 10^{-2}M$ at

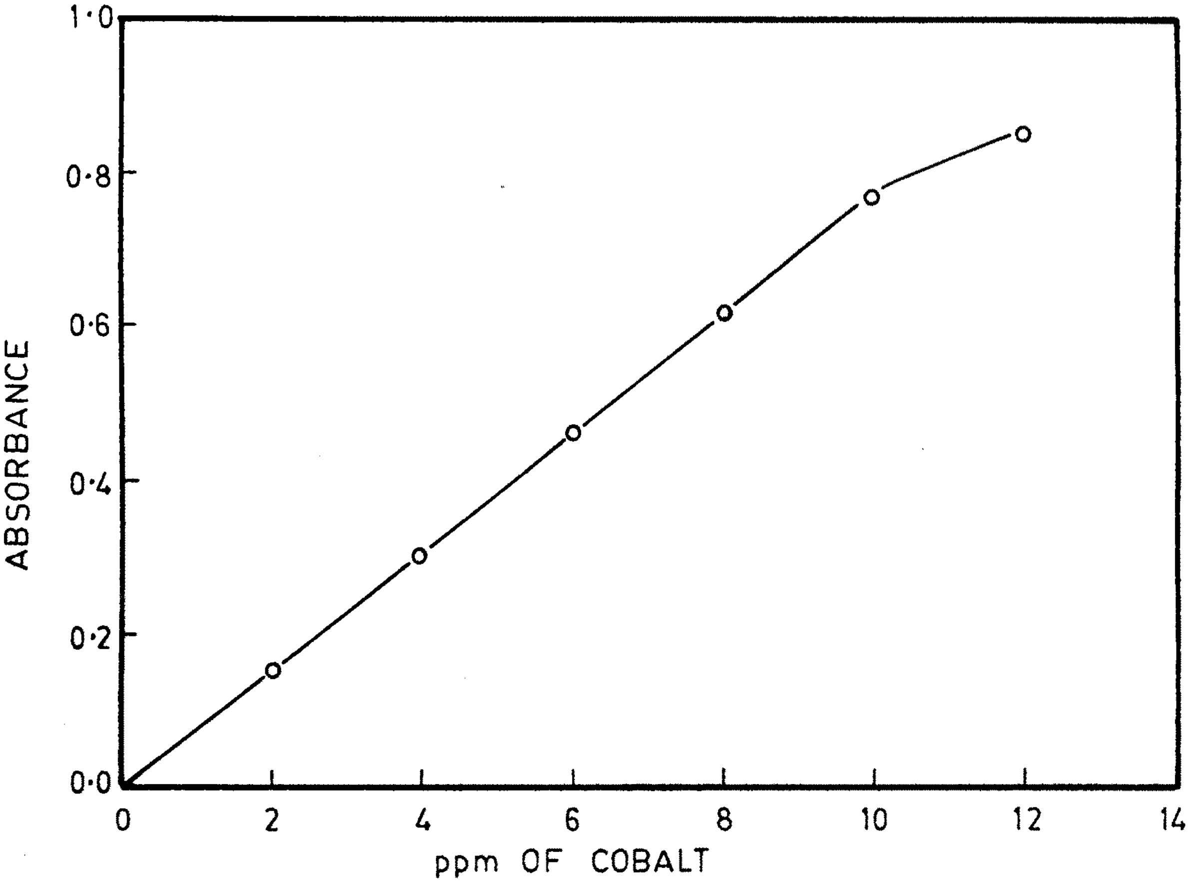


FIG. 2·3 VALIDITY OF BEER'S LAW

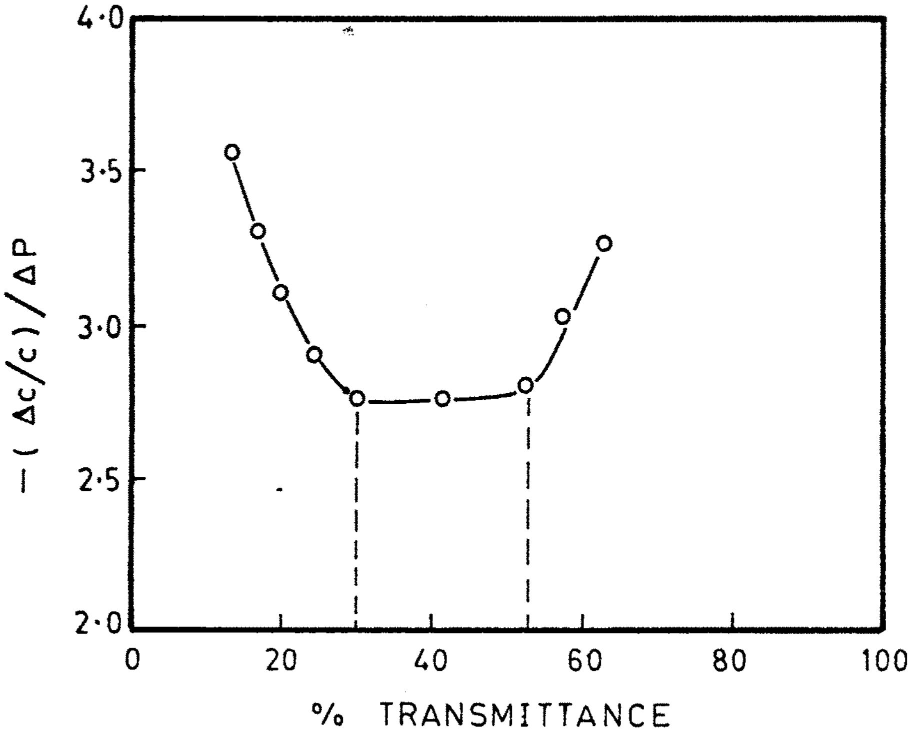


FIG.2·4 RINGBOM PLOT

pH 8.80 were used to study the validity of Beer's law. It was found that the Beer's law is valid up to 10 ppm of cobalt at 380 nm (fig. 2.3).

The optimum concentration range for the determination of cobalt was calculated from the Ringbom plot[43] and was found to be 3.5 to 6.4 ppm at 380 nm (fig. 2.4).

2.3.6 Composition of the Complex :

The empirical formula for Co(II)-SAG complex was determined by Job's method[44] of continuous variation, molar ratio method[45] and slope ratio method.[46] For Job's method of continuous variation, a series of solutions, were prepared by keeping the sum of molar concentrations of cobalt and ligand constant, while their ratio varied in different solutions. For this purpose, equimolar solutions of cobalt and ligand were used (Table 2.4).

The plots of absorbances at 380 nm, 390 nm and 400 nm wavelengths against mole fraction of the reagent indicate that ligand forms 1:2 complex (Fig. 2.5).

In a molar ratio method, ligand concentration (3.4×10^{-5}M) was maintained constant and different concentrations of cobalt ion ranging from 3.4×10^{-6} M to 3.4×10^{-5} M were used. (Table 2.5). The absorbances were measured at 380 nm and 400 nm wavelengths.

Table 2.4 : Job's continuous variation method

$[Co(II)] = [SAG] = 1.7 \times 10^{-4}$ M

Cobalt(II) ml	Reagent (SAG) ml	Molar Ratio M : L	Absorbances at λ		
			380 nm	390 nm	400 nm
0.0	1.8	-	-	-	-
0.2	1.6	1:8	0.045	0.030	0.020
0.4	1.4	2:7	0.083	0.062	0.040
0.6	1.2	1:2	0.090	0.078	0.050
0.8	1.0	4:5	0.080	0.068	0.046
1.0	0.8	5:4	0.065	0.055	0.040
1.2	0.6	2:1	0.052	0.043	0.030
1.4	0.4	7:2	0.038	0.030	0.022
1.6	0.2	8:1	0.023	0.017	0.013
1.8	0.0	-	-	-	-

Table 2.5 : Molar ratio method

$[Co(II)] = [SAG] = 1.7 \times 10^{-4}$ M

Cobalt(II) ml	Reagent(SAG) ml	Molar Ratio M : L	Absorbances at λ	
			380 nm	400 nm
0.0	2.0	-	-	-
0.2	2.0	1 : 10	0.015	0.008
0.4	2.0	1 : 5	0.048	0.030
0.6	2.0	3 : 10	0.065	0.040
0.66	2.0	1 : 3	0.080	0.048
0.8	2.0	2 : 5	0.092	0.060
1.0	2.0	1 : 2	0.100	0.066
1.2	2.0	3 : 5	0.110	0.070
1.33	2.0	2 : 3	0.116	0.076
1.4	2.0	7 : 10	0.120	0.080
1.6	2.0	4 : 5	0.120	0.080
1.8	2.0	9 : 10	0.120	0.080
2.0	2.0	1 : 1	0.120	0.080

Mole ratio plot indicates and confirms the formation of 1 : 2 complex at pH 8.80 (Fig. 2.6).

In slope ratio method, a series of solutions were prepared by keeping the metal concentration variable and

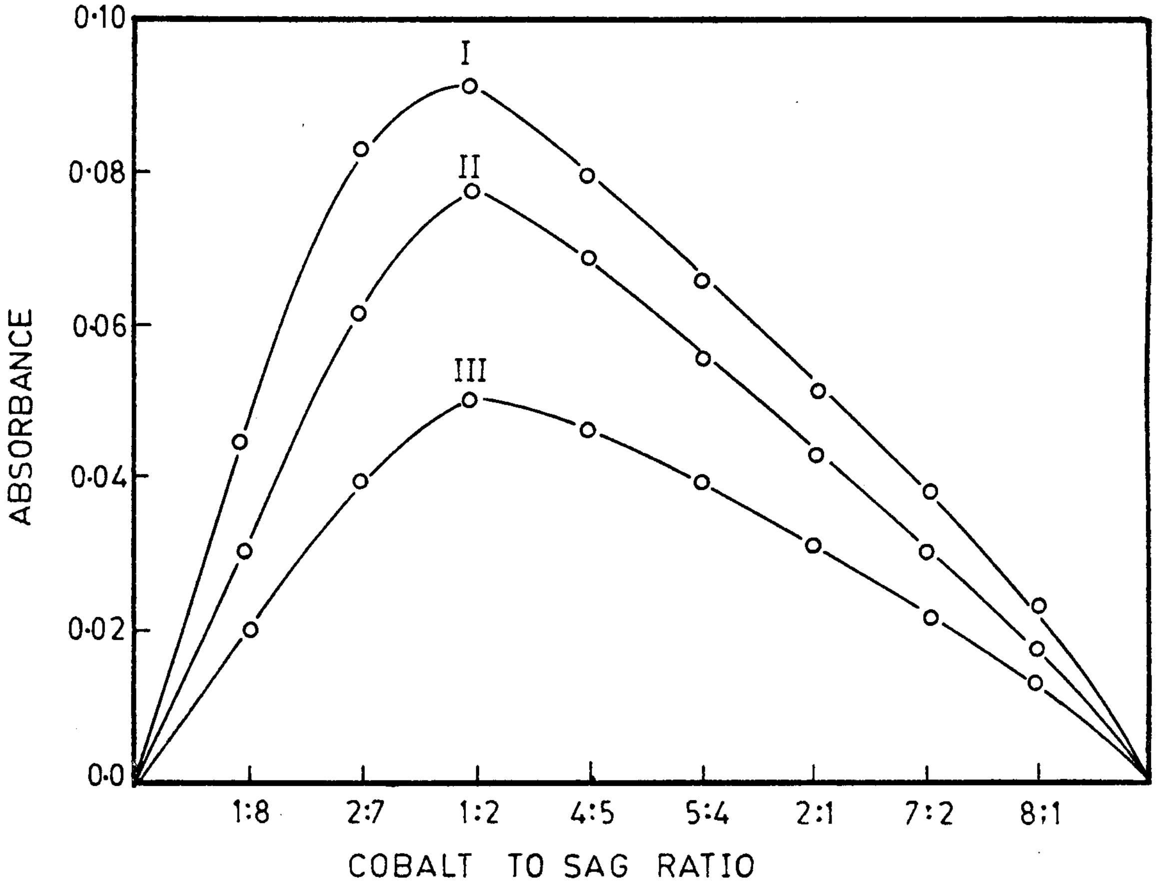


FIG. 2·5 JOB'S CONTINUOUS VARIATION METHOD .
I — 380 nm , II — 390 nm , III — 400 nm

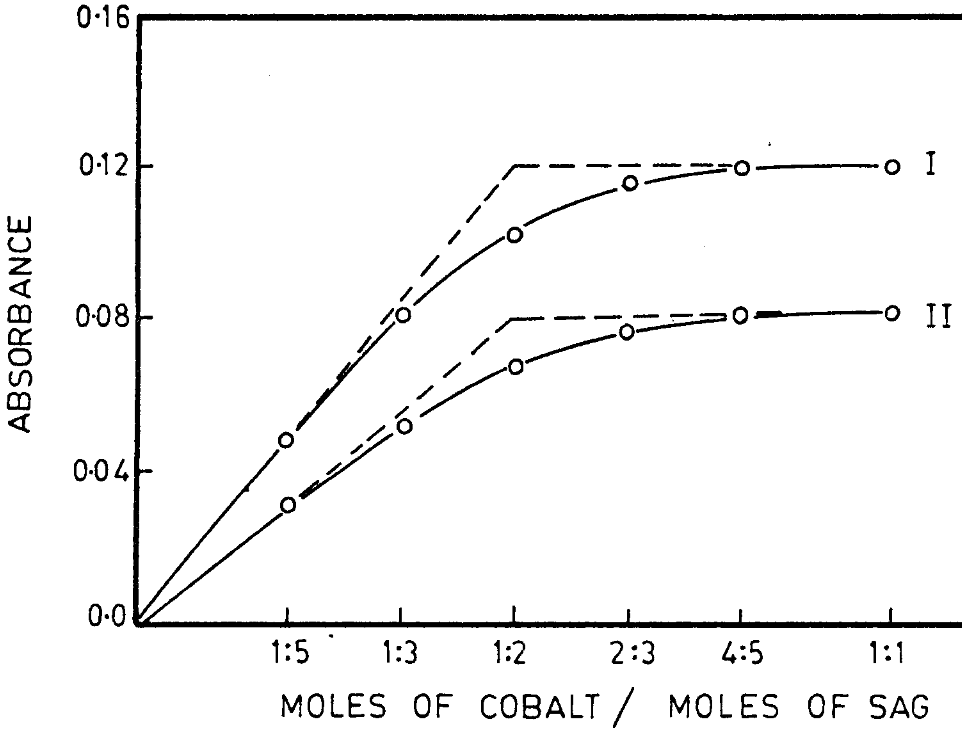
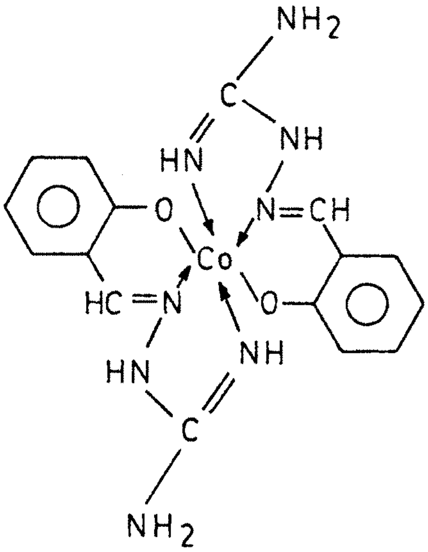


FIG. 2·6 MOLE RATIO METHOD
I — 380 nm , II — 400 nm

a very large excess of ligand concentration and vice versa. Slope ratio method also confirms the 1 : 2 complex.

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



2.3.7 Sensitivity :

The complex of cobalt is not sensitive to the light. The photometric sensitivity of the method was calculated by the method of Sandell[47] and found to be 0.03337 µg/cm^2.

2.3.8 Degree of dissociation and instability constant :

The instability constant[48] is calculated from the mole ratio plot (Fig. 2.6). The equation is

$$K = \frac{(m\alpha c)^m (n\alpha c)^n}{c(1-\alpha)}$$

where,

K = Instability constant

α = Degree of dissociation

c = Concentration of the complex in moles per litre

m and n = 1 and 2 respectively.

The degree of dissociation α, is calculated from the relationship,

$$\alpha = \frac{d_E - d_O}{d_E}$$

where,

d_E = Optical density when complex is completely formed (extrapolated value of O.D.)

d_O = Optical density observed actually at Stoichiometric molar ratio.

The degree of dissociation of the complex at 380 nm was found to be 0.1670.

The apparent instability constant[23] was calculated as 6.445×10^{-12}.

From this value, the change in free energy[48] can be calculated by using the relation,

$$\Delta F = - RT \ln K \text{ at } 25^{\circ}C$$

where,

R = Gas constant

T = Absolute temperature

and K = Instability constant.

The change in free energy of the system is - 15.260 K cals/mole.

2.3.9 Reproducibility of the Method :

The reproducibility of the method was studied by determining cobalt in sets of six observations for each concentration. The table 2.6 summarises the results and shows that the results are reproducible.

Table 2.6 : Standard deviation of the method at pH 8.80 and at 380 nm

Cobalt ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation %
2.0	0.17	0.003	1.765
4.0	0.31	0.005	1.613
6.0	0.50	0.008	1.600

2.3.10 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), Cr(VI), Mn(II), Cu(II), Ni(II), Ag(I) and $EDTA^{-4}$ interfere seriously. The tolerance limits for the ions are listed in table 2.7.

Table 2.7 : Effect of diverse ions
$[Co(II)] = 1.0$ ppm; $[SAG] = 1.0 \times 10^{-3}$ 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)	$BaCl_2 \cdot 2H_2O$	7.0
Al(III)	$AlCl_3 \cdot 6H_2O$	5.0
Cu(II)	$CuSO_4 \cdot 5H_2O$	none
Bi(III)	$Bi(NO_3)_3$	3.0
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	4.0
Ni(II)	$NiCl_2 \cdot 6H_2O$	none
Pb(II)	$Pb(NO_3)_2$	3.0
Zn(II)	$ZnSO_4 \cdot 7H_2O$	6.0
Mn(II)	$MnSO_4 \cdot H_2O$	none

....contd...

Table 2.7 contd...

Foreign ions	Added as	Tolerance limit ppm
Cations (contd..)		
Mg(II)	$MgSO_4 \cdot 7H_2O$	3.0
Cr(VI)	$K_2Cr_2O_7$	none
Cd(II)	$CdSO_4$	8.0
W (VI)	$Na_2WO_4 \cdot 2H_2O$	160.0
Mo(VI)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	55.0
Pd(II)	$PdCl_2$	0.1
Fe(III)	$FeCl_3 \cdot 6H_2O$	1.0
Ag(I)	$AgNO_3$	none
Anions		
Citrate	Citric acid	95.0
Oxalate	Potassium oxalate	18.0
Thiourea	Thiourea	950.0
Persulphate	Ammonium persulphate	10.0
Tartrate	Tartaric acid	74.0
Thiosulphate	Sodium thiosulphate	52.0
$EDTA^{-4}$	Disodium salt	none
Acetate	Sodium acetate	740.0
Bromate	Potassium bromate	128.0
Phosphate	Potassium dihydrogen orthophosphate	62.0
Urea	Urea	900.0

2.4 APPLICATIONS

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

To an aliquot of the solution containing 20.0 and 40.0 mg of uranium nitrate hexahydrate, was added 7.0 and 10.0 μg of cobalt respectively. Cobalt was then determined as Co(II)-SAG complex as per recommended procedure.

Table 2.8 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[49] were in good agreement with this new method.

Table 2.8 : Recovery of added cobalt

$UO_2(NO_3)_2.6H_2O$ taken, mg	Cobalt added μg	Mean absorbance for six samples at 380 nm	Cobalt recovery in synthetic mixture	
			μg	%
20.0	7.0	0.55	6.97	~100
40.0	10.0	0.68	10.02	~100

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