CHAPTER _ II

DETERMINATION OF COBALT

2.1   <u>INTRODUCTION</u>

Cobalt is one of the important transition metals 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
nonferrous alloys, in biological and biochemical reactions
and also in catalyst and in electroplating.

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 one of the most undesirable impurities in
the nuclear fuel and materials of nuclear reactors because

of its large cross section of neutron absorption. Hence, determination of traces of cobalt in uranium is important. Cobalt is also found in microquantities in nickel salts, steel, some pure chemical reagents, in sea water and silicates.

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 etc. contain 0.005 to 0.2 ppm cobalt. Cobalt is essential micronutrient for the plants and it is present to the extent of 23 ppm in soil.

However, because of the lack of suitable reagents and the experimental conditions for the photometric determination of this important element is still a problem to 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.

The need to determine cobalt in large numbers 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. Colorimetric methods are used in μg to mg ranges, whereas volumetric and gravimetric methods are used for macrodeterminations.

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. In many cases, absorption bands occur in ultraviolet region, where both complex and reagent absorb in the same region. The classic reagents like thiocyanate[5] for determination of cobalt show less colour intensity in aqueous solution and suffer from numerous interferences. However, several modifications have been made in the experimental conditions to get the best results.

With the reagents 1,2-diaminocyclohexane tetra-acetic acid[6,7], nitroso-R-salt[8,9], 5-aminopyrazole-4-carboxylic acid[10], sulphosalicylic acid[11], 3-hydroxy picolinaldehyde azine[12] and 4-amino-5-nitroso pyrimidine-2,6-diol[13] at elevated temperature is required for complex formation.

With some reagents like dimethyl glyoxime[14], 3-mercaptopropionic acid[15], pyridine-2,4,6 - tricarboxylic acid[16], azanol A[17], furil -α-dioxime[18] and 2,4-dimethyl benzamidoxime[19], method of determination of cobalt is time consuming.

The most important chelating agents used for determination of cobalt are thiooxines[20-22] and oximes[23-31], naphthols[32-37] and azonaphthols[38-40], dithizone[41] and nitro-QDT[42]. 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.

2-Benzoyl pyridine guanylhydrazone was used for photometric determination of traces of cobalt at pH 12.5 as a yellow complex in ethyl alcohol. The complex was measured at 422 nm. The preposed method is simple, rapid and highly sensitive.

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 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, 2-benzoyl pyridine

guanylhydrazone (BPG), 0.6 mg/ml was prepared by dissolving 60 mg of the reagent in 100 ml distilled ethanol.

Buffer solution :

Buffer solution of pH 12.5 was prepared by mixing appropriate amounts of caustic soda and glycocoll.

Ethyl alcohol :

Ethyl alcohol used for the experiments was double distilled.

2.2.2   Recommended procedure :

An aliquot of the solution containing about 2.5 μg of Co(II) was taken in a 10 ml volumetric flask. To this was added 0.8 ml of reagent (BPG) solution of concentration 2.511 X 10^{-3}M. The pH of the solution was adjusted to 12.5 by adding 1 ml buffer solution of pH 12.5 and diluted to volume with distilled ethanol. The absorbance of the complex was measured at 422 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-BPG complex of the solution containing 4.241×10^{-5} M cobalt and 2.008×10^{-4} M reagent (BPG) was recorded at pH 12.5, against reagent blank. The absorption measurements were made in the spectral range from 380 to 550 nm. The complex has an absorption maximum at 422 nm at pH 12.5. The molar extinction coefficient of the complex at 422 nm is 0.9196×10^{4} l mole^{-1}cm.$^{-1}$ Absorption spectra of the complex and reagent are given in figure 2.1. The observations for the spectra are given in table 2.1.

Table 2.1 : Molar extinction coefficients of the Co(II)-BPG

Complex and the reagent (BPG).

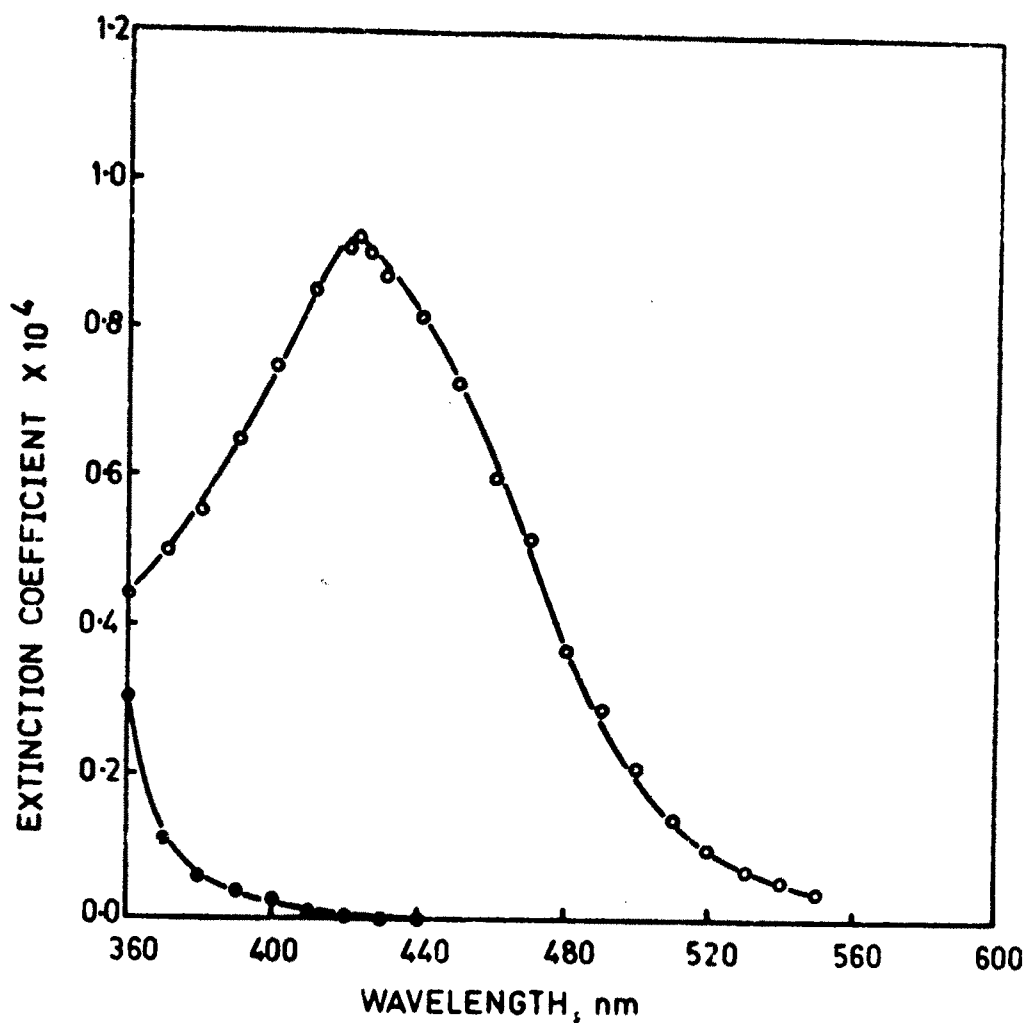| Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Co(II)-BPG complex $\epsilon \times 10^4$ l mole^{-1}cm^{-1}	BPG $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
360	0.4387	0.2948
370	0.4977	0.1115
380	0.5498	0.0509
390	0.6542	0.0387
395	0.6899	0.0318
400	0.7513	0.0298
405	0.7802	0.0199
410	0.8487	0.0174
415	0.8960	0.0124
420	0.9180	0.0049
422	0.9196	0.0000
423	0.9180	0.0000
425	0.9078	-
427	0.8960	-
430	0.8724	-
435	0.8487	-
440	0.8252	-
450	0.7310	-
460	0.6012	-
470	0.5187	-
480	0.3655	-
490	0.2947	-
500	0.2121	-
510	0.1415	-
520	0.1062	-
530	0.0707	-
550	0.0471	-

FIG. 2·1 o——o ABSORPTION SPECTRUM OF COBALT–BPG COMPLEX
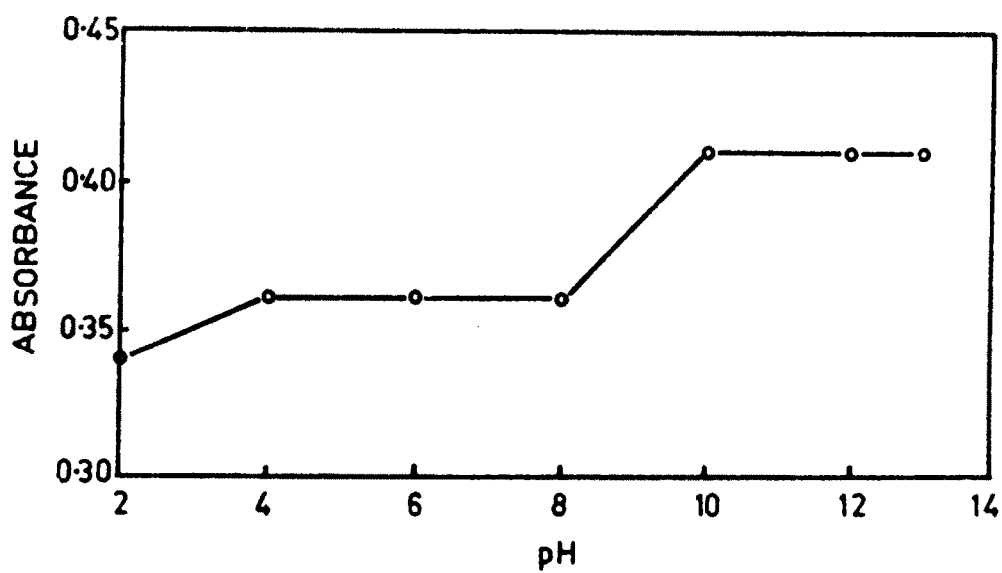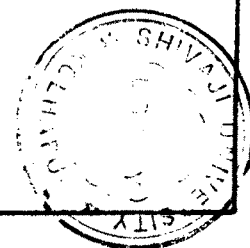●——● ABSORPTION SPECTRUM OF REAGENT (BPG)

FIG. 2·2 EFFECT OF pH

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 10 to 13. Therefore, pH 12.5 was selected for the study of Co-BPG complex. In acidic medium, the complex shows comparatively less absorbance. The plot of observations is shown in fig. 2.2.

2.3.3.   Effect of reagent concentration :

It was found that the amount of excess of reagent used was the least critical. About a six fold excess molar concentration relative to the metal ion concentration was satifactory. A series of solutions were prepared in which the concentration of reagent was varied from 5.02×10^{-5} to 3.514×10^{-4} **M,** while concentration of cobalt was kept constant at 4.241×10^{-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 422 nm wavelength against reagent blank. The results given in the table 2.2 show that, six fold molar excess of the reagent is sufficient for full colour development of 2.5 ppm cobalt.

Table 2.2 : Effect of reagent concentration on the absorbance

   of the CO(II) - BPG complex

   $[Co(II)] = 2.5$ ppm; $[BPG] = 2.511 \times 10^{-3}$ M

Amount of BPG added, ml	Absorbance at 422 nm
0.2	0.21
0.4	0.35
0.6	0.36.
0.8	0.39
1.0	0.39
1.2	0.39
1.4	0.39

2.3.4   Stability and reaction rate :

Cobalt - BPG 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 (BPG), o.5 ml of 1.255×10^{-4} M at pH 12.5 were used to study the validity of Beer's law. It was found that the Beer's law is valid upto 24 ppm of cobalt at 422 nm.
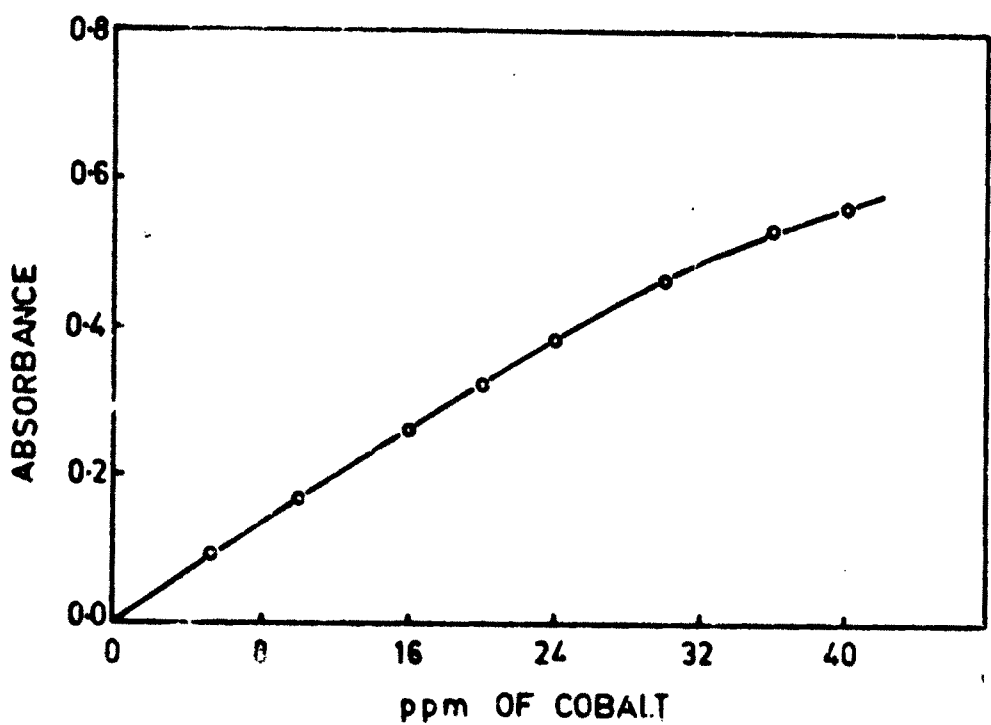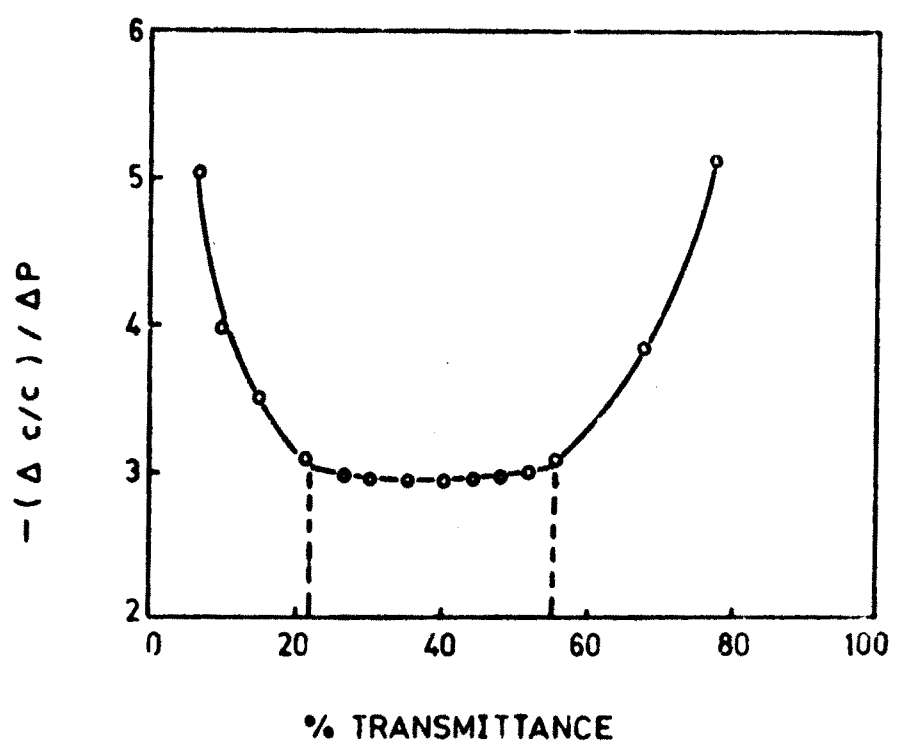
FIG. 2·3 VALIDITY OF BEER'S LAW

FIG. 2·4 RINGBOM PLOT

The optimum concentration range for the determination of cobalt was calculated from the Ringbom plot[44] and was found to be 1.25 to 5 ppm at 422 nm. (Fig.2.4).

2.3.6 Composition of the complex :

The empirical formula for Co(II)- BPG complex was determined by Job's method[45] of continuous variation, molar ratio method[46] and slope ratio method[47] 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. The plot of absorbance at 422 nm, 440 nm, 450 nm and 470 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 (6.3928×10^{-5} M) was maintained constant and different concentrations of cobalt ion ranging from 0.4241×10^{-5} M to 3.3928×10^{-5} M were used. The absorbances were measured at 422 nm and 450 nm wavelengths. Mole ratio plot indicates and confirms the formation of 1:2 complex at pH 12.5 (Fig.2.6). In slope ratio method, a series of solutions were prepared by keeping the metal concentration variable and a very large excess of ligand concentration constant and vice versa. Slope ratio method also confirms the 1:2 complex.
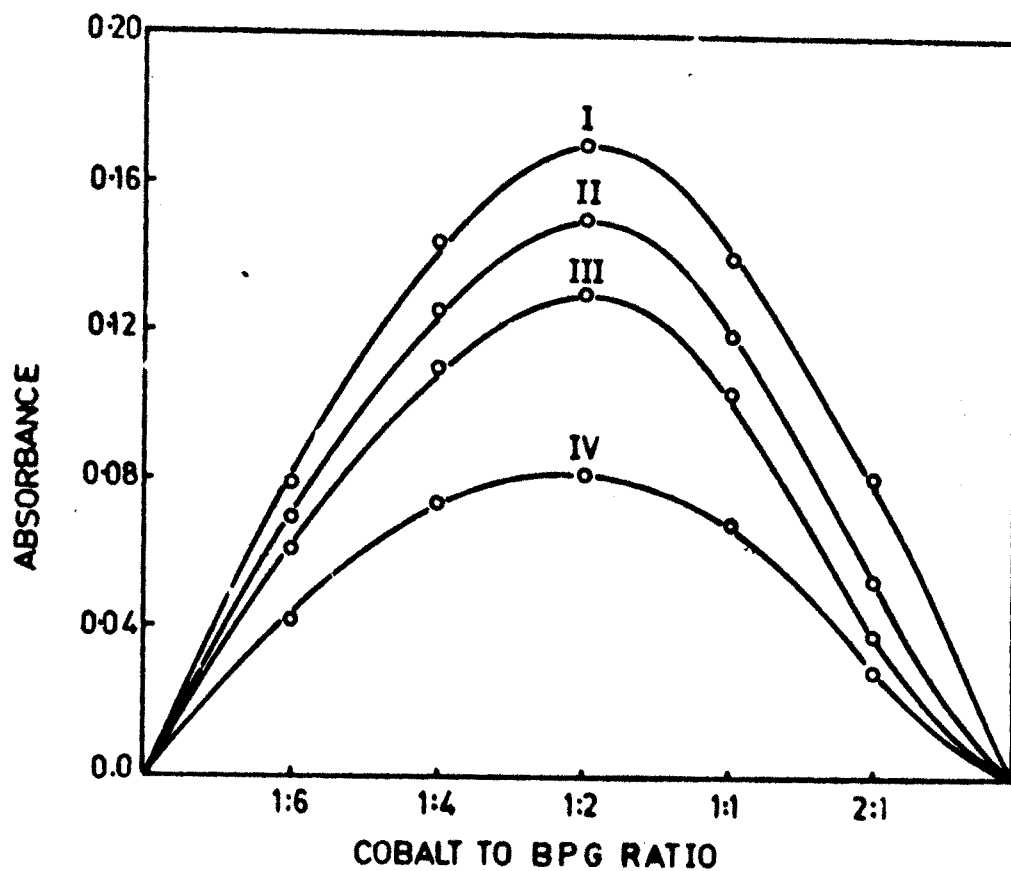
FIG.2·5 JOB'S CONTINUOUS VARIATION METHOD.
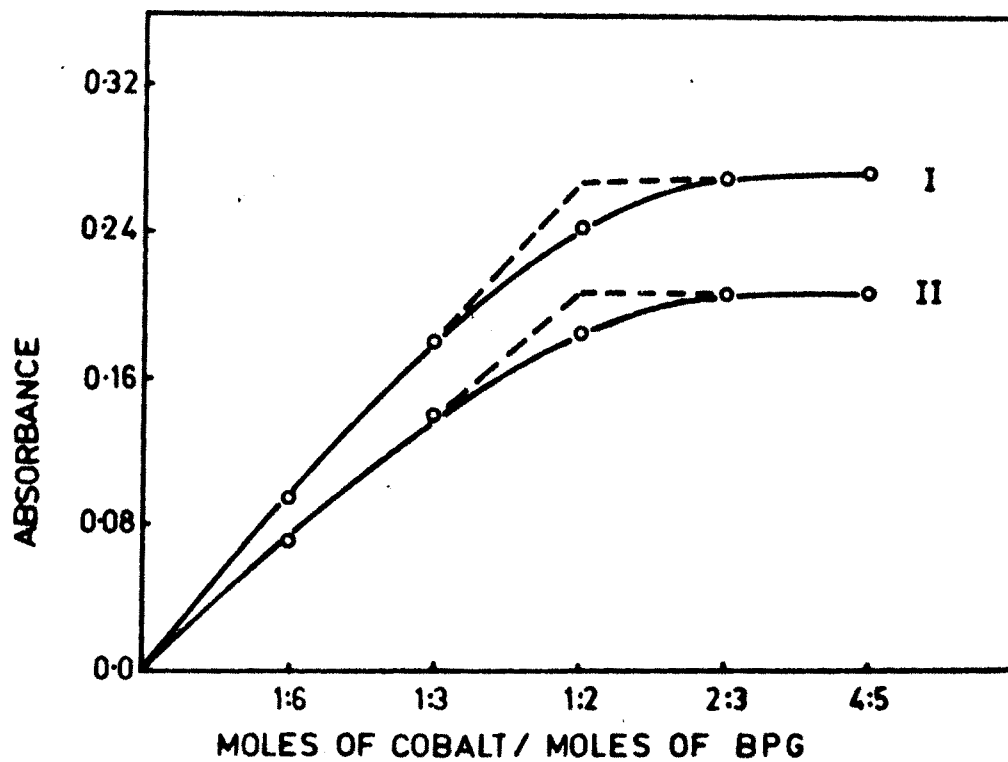I – 422 nm, II – 440 nm, III – 450 nm, IV – 470 nm.

FIG.2·6 MOLE RATIO METHOD.
I – 422 nm, II – 450 nm.

2.3.7   Sensitivity :

The complex of cobalt is not sensitive to light. The photometric sensitivity of the method was calculated by the method of Sandell[48] and found to be 0.0581 μg/ cm^2.

2.3.8   Degree of dissociation and instability constant :

The instability constant[49] 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 mole 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 where complex is completely formed.
      (extrapolated values of O.D.).

   d_O = Optical density observed actually at stoichiometric
      molar ratio.

The degree of dissociation of the complex at 422 nm was found to be 0.0895.

The apparent instability constant[30] was calculated as 1.418×10^{-12}.

From this value, the change in free energy[49] can be calculated by using the relation,

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

where, R - Gas constant

   T - Absolute temperature

and   K - Instability constant.

The change in free energy of the system is - 16.26 K cal/mole.

2.3.9   <u>Reproducibility of the method</u> :

The reproducibility of the method was studied by determining cobalt in sets of ten observations for each concentration. The table 2.3 summarises the results and shows that the results are reproducible.

Table 2.3 : Standard deviation of the method at pH 12.5 and at 422 nm.

Cobalt μg	Mean of 10 observations	Standard deviation	coefficient of variation, %
10	0.17	0.004	2.35
15	0.25	0.007	2.80
20	0.32	0.009	2.81

2.3.10   <u>Effect of diverse ions</u> :

The effect of diverse ions was studied using fixed amount of cobalt (2.5 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 Cu(II) Ce(IV) interfere seriously, while thiourea, acetate ion and thiocyanate ion are tolerated upto 1000 ppm. The tolerance limits for the ions are listed in table 2.4.

Table 2.4 : Effect of diverse ions

$$[CO(II)] = 2.5 \text{ ppm}; [BPG] = 2.008 \times 10^{-4} M$$

Foreign ions	Added as	Tolerance limit ppm
<u>Cations</u>		
Zn(II)	$ZnSO_4 . 7H_2O$	10
Ba(II)	$BaCl_2 . 2H_2O$	1
Hg(II)	$HgCl_2$	2
V (V)	V_2O_5	5
Cu(II)	$CuSO_4 . 5H_2O$	none
Fe(III)	$FeCl_3 . 6H_2O$	0.6
Tl(I)	TlCl	1
W(VI)	$Na_2WO_4 . 2H_2O$	140

....contd. from previous page-

Foreign ions	Added as	Tolerance limit ppm
Ni(II)	$NiSO_4 \cdot 6H_2O$	1
Al(III)	$AlCl_3 \cdot 6H_2O$	0.6
Fe(II)	$FeSO_4 \cdot 7H_2O$	0.5
U(VI)	$UO_2(NC_3)_2 \cdot 6H_2O$	3
Bi(III)	$Bi(NO_3)_3$	2
Cr(VI)	K_2CrO_4	2
Cd(II)	$Cd(NO_3)_3$	50
Mg(II)	$MgSO_4 \cdot 7H_2O$	6
Ca(II)	$CaCl_2$	4
Ce(IV)	$Ce(SO_4)_2$	none
Pb(II)	$Pb(NO_3)_2$	6
Mn(II)	$MnCl_2 \cdot 4H_2O$	6
Anicns		
Thiourea	Thiourea	1000
Fluoride	Ammonium fluoride	20
Oxalate	Potassium oxalate	10
Citrate	Sodium citrate	1
$EDTA^{-4}$	Disodium salt	5
Acetate	Sodium acetate	1000
Phosphate	Potassium hydrogen orthophosphate	2
Tartrate	Antimony potassium tartrate	50
Thiocyanate	Potassium thiocynate	1000

2.4   APPLICATIONS

Analysis of Co(II) in high speed steels :

A sample of high speed steel (Type IV, NBS, U.S.A.), 0.05 g, was dissolved in 10 ml of 1:1 hydrochloric acid with mild heating. A few drops of concentrated nitric acid was added carefully and then the solution was evaporated until its volume has been reduced to 5 ml. Then 10 ml aquaregia was added to ensure complete oxidation of the sample. The solution was evaporated on sand-bath until it appeared syrupy. It was then digested by adding hot 1:1 hydrochloric acid. Tungstic acid was precipitated, which was filtered and washed with hot dilute hydrochloric acid. Original filterate with washings were diluted to 250 ml in volumetric flask.

An aliquot ($\sim$3 ml) was taken. As the alloy contains large amount of iron, it is removed by extraction with IBMK[40] from 6 M hydrocholoric acid medium. Excess hydrochloric acid from aqueous solution was removed by evaporation. Cobalt from this solution was determined as Co(II)- BPG complex by recommended procedure and was measured at 422 nm against the reagent blank. The results are given in table. 2.5.

Table 2.5 : Analysis of high speed steel

Alloy	Certified value of Co,%	Experimental value of Co, %	Relative standard deviation for 5 observations
Type IV	2.90	2.86	0.04

NBS,USA

2.5   R E F E R E N C E S

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