CHAPTER III

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH 2,6-DIACETYLPYRIDINE BIS-4-PHENYL-3-THIOSEMICARBAZONE(2,6-DAPBPTSC)

3.1. Introduction

Cobalt is an essential element for the functioning of many vital processes. It is extremely important in the presence of blood formation, stimulation of hemoglobin synthesis, and the functioning of vitamins, enzymes and hormones. This metal has a very positive influence on the metabolism of vitamins, such as ascorbic acid and vitamin B_{12}[1]. It is present in vitamin B_{12}, which is involved in the production of red blood cells (RBC) and the preventation of pernicious anemia[2].

Cobalt alloys are used in some industrial products because of their sufficient hardness and resistivity against oxidation at high temperatures, for example, in the manufacturing of turbine blades and cutting tools[3] Plants and different diet compositions contain extremely low concentrations of cobalt. Its deficiency is exhibited by a retarded growth rate, loss of appetite and pernicious anemia in human beings[4]. Deficiency of cobalt causes a variety of diseases in animals[5-7]. Over-exposure to cobalt causes irritation of the gastro-intestinal tract, nausea, diarrhea and so on. At high concentrations, it inhibits hemi-biosynthesis and enzyme activities. Moreover, the element is toxic when taken directly. The use of cobalt-60 in medicine as an important radioactive tracer and cancer treatment against as well as its biological activates for examples vitamin B_{12}[8].

3.2. Review of known methods

A number of spectrophotometric and extractive spectrophotometric methods are available in literature[9] for the determination of cobalt(II) in food and other biological materials. They are relatively sensitive and have been widely used.

2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and tetraphenylborate[10] are used for the spectrophotometric determination of cobalt(II). The cobalt complex has the maximum absorbance at 611 nm.

Hayashibe et al[11] have reported 2-(5-bromo-2-pyridylazo)-5-(*N*-propy l-*N*-sulpho propylamino)aniline for the determination of cobalt(II). The cobalt complex has the maximum absorbance at 617 nm.

Jadhav et al[12] have reported isonitroso-5-methyl-2-hexanone for the extractive spectrophotometric determination of cobalt(II). The molar absorptivity of the complex is found to be 1.135×10^4 lit mol^{-1} cm^{-1} at 400 nm. Moreover, the method has been applied for the determination of cobalt in synthetic, pharmaceutical, biological and high speed steel samples.

1-Nitroso-2-naphthol[13] is used for the spectrophotometric determination of cobalt(II). The complex shows maximum absorbance at 420 nm. The molar absorptivity of the complex is found to be 1.14×10^4 lit mol^{-1} cm^{-1} and the Beer's law was obeyed in the range 0.20 to 3.0 ppm of cobalt(II).

Sodium isoamylxanthate[14] is used for the simultaneous spectrophotometric determination of cobalt(II), palladium(II), ruthenium(IV), molybdenum(VI). The cobalt complex has the maximum absorbance at 400 nm in the pH range of 4.5-9.0. The molar absorptivity of the complex is found to be 1.92×10^4 lit mol^{-1} cm^{-1} and the Beer's law is obeyed in the range 3.0-35 ppm of cobalt(II).

Tsuchiya[15] has reported 2-diethylamino-5-nitroso-1,4,5,5,6-tetrahydropyrimidine-4,6-dione for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 385 nm. The molar absorptivity of the complex is found to be 6.3×10^4 lit mol^{-1} cm^{-1}.

Carbonyl derivatives like oximes, hydrazones, thio-and phenylthiosemicarbazones are also used for the spectrophotometric as well as extractive spectrophotometric determination of cobalt(II). Some of the sensitive and/or selective methods are discussed below.

Benzeneacetaldehyde-4-hydroxy-α-oxo-aldoxime has been used for the spectrophotometric determination of cobalt(II) by Jadhav et al[16]. The molar absorptivity of the complex is found to be 2.74×10^4 lit mol^{-1} cm^{-1} at 390 nm in the pH range of 8.6-9.4. The reagent forms 1:3(M:L) complex with the metal ion. The method has been used for the determination of cobalt(II) in synthetic, pharmaceutical, biological and alloy samples.

Eskandari et al[17] have reported α-Benzilmonoxime for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 380 nm. The molar absorptivity of the complex is found to be 3.72×10^4 lit mol^{-1} cm^{-1} at pH 9.0.

2,2'-Diquinolylketoxime[18] is used for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 365 nm. The molar absorptivity of the complex is found to be 5.3×10^4 lit mol^{-1} cm^{-1} at pH 4.5.

1,2,3-Trionetrioxime[19] is used for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 320 nm in the pH range of 4.5-7.5. The molar absorptivity of the complex is found to be 5.32×10^4 lit mol^{-1} cm^{-1} and the Beer's law is obeyed in the range 1.18-23.6 ppm of cobalt(II).

Other oximes like 1,2,3-cyclohexanetrionetrioxime[20], dimedonedioxime[21], 2,2'-dipyridylketoxime[22],1-hydroxyacenaphthonexime[23], nicotinamidoxime[24], phenanthrene-quinonemonoxime[25], pyridyl-2 aldoxime[26] and *p*-tolueneamidoxime[27] are also employed for the spectrophotometric determination of cobalt(II).

Asuero and Rodriguez[28] have reported biacetylmono(2-pyridyl)hydrazone(BPH) for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 505 nm and pH 6.0. The molar absorptivity of the complex found to be 2.3×10^4 lit mol^{-1} cm^{-1}.

Di-2-pyridyl ketone benzoylhydrazone[29](DPKBH) is used for the spectrophotometric determination of cobalt(II). The complex shows a λ_{max} at 370 nm and the Beer's law is obeyed in the range 0.1-2.8 ppm of cobalt(II).

Themelis et al[30] have reported 2,2'-dipyridy-2-pyridylhydrazone(DPPH) for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 500 nm. The method has been successfully applied to the determination of cobalt in cyanocobalamin (vitamin B_{12}).

2-hydroxy-1-naphthaldehyde guanylhydrazone[31] is used for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 416 nm.

The molar absorptivity of the complex is found to be 1.32×10^4 lit mol^{-1} cm^{-1}. The method has been applied for the spectrophotometric determination of cobalt(II) in vitamin preparations, steel and high-purity iron.

Patil and Sawant[32] have reported pyridine-2-acetaldehydesalicyloylhydrazone(PASH) for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbacne at 415 nm in the pH range of 1.0-4.0. The molar absorptivity of the complex is found to be 1.04×10^4 lit mol^{-1} cm^{-1}. The reagent forms 1:2(M:L) complex with the metal ion and the Beer's law is obeyed in the range 0.5-7.0 ppm of cobalt(II).

Thio-and phenylthiosemicarbazones have emerged as very important analytical reagents for the spectrophotometric and extractive spectrophotometric determination of cobalt(II).

Acetylacetonedithiosemicarbazone[33] is used for the spectrophotometric determination of cobalt(II). The complex system obeys Beer's law in the range 0.5-3.5 ppm of cobalt(II). The composition of the complex is determined as 1:2(M:L).

Singh et al[34] have reported acenapthaquinonemonothiosemicarbazone for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 410 nm and pH range of 1.0-10.5. The molar absorptivity of the complex is found to be 0.48×10^4 lit mol^{-1} cm^{-1}. The reagent forms 1:2(M:L) complex with the metal ion.

Benzildithiosemicarbazone has been introduced as an analytical reagent for the spectrophotometric determination of cobalt(II) by Reddy et al[35]. The molar absorptivity of the complex is found to be 7.32×10^3 lit mol^{-1} cm^{-1} at 387 nm and pH 6.5. The reagent forms 1:2(M:L) complex with the metal ion. The complex system obeys Beer's law in the range 1.0-8.0 ppm of cobalt(II). The method has been successfully applied for the determination of cobalt(II) in medicinal and beer samples

1,2-Cyclohexanedionedithiosemicarbazone[36] is used for the spectrophotometric determination of cobalt(II). The molar absorptivity of the complex is found to be 6.4×10^4 lit mol^{-1} cm^{-1}

at 450 nm and pH range of 5.2-6.8. Beer's law is obeyed in the range 2.0-5.5 ppm of cobalt(II).

2,4- Dihydroxyacetophenonethiosemicarbgazone[37] is used for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 390 nm and pH 7.9. The molar absorptivity of the complex is found to be 1.4×10^4 lit mol^{-1} cm^{-1}.

Dipyridylglyoxaldithiosemicarbazone(DPGDT) has been introduced as an analytical reagent for the spectrophotometric determination of cobalt(II) by Bahamonde et al[38]. The molar absorptivity of the complex is found to be 9.1×10^3 lit mol^{-1} cm^{-1} at 410 nm and pH 5.2. The reagent forms 1:2(M:L) complex with the metal ion. The complex system obeys Beer's law in the range 1.0-7.0 ppm of cobalt(II).

Kumar et al[39] have reported 2-hydroxy-3-methoxybenzaldehydethiosemicarbazone for the spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 468 nm and pH 6.0. The complex system obeys Beer's law in the range 0.05-3.29 ppm of cobalt(II).

Picolinaldehyde-4-phenyl-3-thiosemicarbazone has been introduced as an analytical reagent for the extractive spectrophotometric determination of cobalt(II). The complex shows a maximum absorbance at 450 nm and pH 5.0. The molar absorptivity of the complex is found to be 1.40×10^4 lit mol^{-1} cm^{-1}. The system obeys Beer's law in the concentration range 0.5-6.0 ppm of cobalt(II)

A brief review of the methods presented for the determination of cobalt(II) indicated that there are a limited number of procedures established for the extractive spectrophotometric determination of cobalt(II). The researcher observed that 2,6-diacetylphyridinebis-4-phenyl-3-thiosemicarbazone can be successfully utilized for the extractive spectrophotometric determination of cobalt(II). Hence, a detailed investigation with this reagent for the extractive spectrophotometric determination of cobalt(II) has been undertaken.

3.3 Results and Discussion

2,6-diacetylpyridine bis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) forms a 1:1(M:L) reddish brown complex with cobalt(II), which is extracted into isoamylalcohol, from acetic acid and sodium acetate(pH 4.0) buffer. The reddish brawn Co(II)-2,6-DAPBPTSC complex has a maximum absorbance at 400 nm and it is stable for 46 hours. The conditions for effective extraction are established after studying the effects of various factors such as pH, choice of solvent, reagent concentration and influence of diverse ions, in order to develop a rapid and sensitive extractive spectrophotometric method for the determination of cobalt(II) in micro levels.

3.3.1. Absorption spectra of reagent and Co(II)-2,6-DAPBPTSC complex

The absorption spectrum of Co(II)-2,6-DAPBPTSC complex was recorded against the reagent blank. Similarly the absorption spectrum of the reagent (2,6-DAPBPTSC) was recorded against the solvent blank. The absorption spectra of both the complex and reagent are shown in Fig. 3.1. From the absorption spectra it is clear that the complex and reagent have shown maximum absorptions at 400 nm and 360 nm, respectively. The reagent has minimum absorbance at the maximum absorbance of the complex, and the reagent does not interfere with the determination of cobalt(II). Hence further absorbance measurements of the complex were recorded at 400 nm.

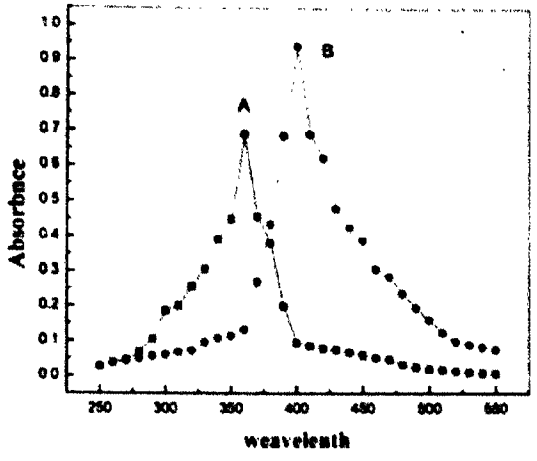

Fig. 3.1 (A) Absorption spectrum of 2,6-DAPBPTSC; (B) Absorption spectrum of Co(II)-2,6-DAPBPTSC complex: Co(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC=1.0 mL of 1.0×10^{-3} M and pH= 2.0 mL of pH 4.0.

3.3.2. Effect of pH

To arrive at the optimum pH required for full colour development, the effect of pH on the color intensity was studied. In each case, a mixture containing 1.0 mL of 1.0×10^{-4} M cobalt(II), 2.0 mL of suitable buffer, 1.0 mL of 1.0×10^{-3} M 2,6-DAPBPTSC solution was taken and the volume of the aqueous phase was adjusted to10.0 ml with double distilled water. It was shaken with 10.0 mL portion of isoamylalcohol for one minute. The organic phase was collected into a 25.0 mL standard flask and made upto the mark with isoamylalcohol. The same procedure is applied for buffers of different pH values, ranging from 1.0 to 6.0. The absorbances were measured at 400 nm, using their corresponding reagent blanks and the values are noted in Table 3.1. A plot is executed between the pH and the absorbance and the same is represented in Fig. 3.2. The plot shows that there is maximum absorbance and constancy in the pH range 3.5-4.5. Hence, pH 4.0 is chosen for further studies, considering this as an optimum pH.

Table 3.1 Effect of pH on Co(II)- 2,6-DAPBPTSC complex

S.No.	pH	Absorbance
1	1.0	0.340
2	1.5	0.375
3	2.0	0.430
4	2.5	0.556
5	3.0	0.742
6	3.5	0.932
7	4.0	0.938
8	4.5	0.936
9	5.0	0.722
10	5.5	0.635
11	6.0	0.520

Co(II) = 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-3} M and λ_{max} = 400 nm.

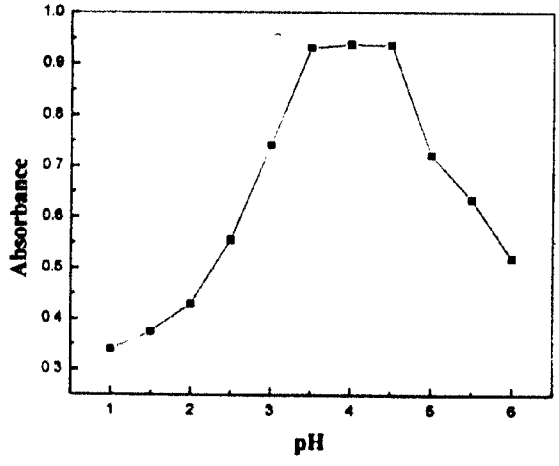

Fig.3.2. Effect of pH on Co(II)-2,6-DAPBPTSC complex: Co(II)=1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC= 1.0 mL of 1.0×10^{-3} M and λ_{max}= 400 nm

3.3.3. Effect of solvents

The effect of various solvents such as isoamylalcohol, chloroform, toulene, benzene, n-butanol, carbon tetrachloride, ethylacetate, butylacetate, xylene, tributyl

phosphate, n-propylalcohol and methylisobutylketone on the extraction of cobalt(II) with 2,6-DAPBPTSSC was studied at pH 4.0 for registering the effect of solvent. Among the various solvents studied, isoamylalcohol is selected as the suitable solvent, because of its greater extraction ability, which was indicated by maximum absorbance of the colour in it. The results are reported in Table 3.2.

Table 3.2 Effect of solvent on the extraction of Co(II)-2,6-DAPBPTSC complex

Solvent	Absorbance
cyclohexanol	0.872
Isoamylalcohol	0.940
isobutyl ketone	0.653
n-butanol	0.845
chloroform	0.489
benzene	0.780
carbontetrachloride	0.638
xylene	0.249
hexane	0.410
butyl acetate	0.356
ethyl acetate	0.452
toulene	0.245

Co(II) = 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-3} M; pH = 4.0 and λ_{max} = 400 nm.

3.3.4. Effect of reagent concentration

The effect of reagent concentration was studied, using different aliquots containing constant volumes of 1.0×10^{-4} M cobalt(II) solution, 2.0 mL of pH 4.0 buffer solution and 1.0 mL of 2,6-DAPBPTSC solution containing different concentrations ranging from 1.0×10^{-4} to 20.0×10^{-4} M, in order to obtain the maximum colour formation. The total volumes of aqueous phases were brought to 10.0 mL with double distilled water. The aqueous phases were shaken with 10.0 mL of isoamylalcohol in each case and the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with isoamylalcohol. The absorbances of the organic phases were measured at 400 nm, against their corresponding reagent blanks and the values are noted

in Table 3.3. It is clearly observed from the absorbance values, that a fifteen-fold molar excess of the reagent is sufficient to get a maximum colour formation of the complex. The plot is shown in Fig.3.3.

Table 3.3 Effect of reagent concentration on Co(II)- 2,6-DAPBPTSC complex

Concentration of reagent, $\times 10^{-4}$ M	No. of folds of reagent concentration with respect to metal	Absorbance
1.0	1	0.080
2.0	2	0.167
3.0	3	0.239
4.0	4	0.362
5.0	5	0.439
6.0	6	0.554
7.0	7	0.640
8.0	8	0.697
9.0	9	0.810
10.0	10	0.919
11.0	11	0.991
12.0	12	1.091
13.0	13	1.184
14.0	14	1.263
15.0	15	1.350
16.0	16	1.371
17.0	17	1.378
18.0	18	1.384
19.0	19	1.386
20.0	20	1.392

Co(II) = 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-4} to 20.0×10^{-4} M; pH= 4.0 and λ_{max} = 400 nm.

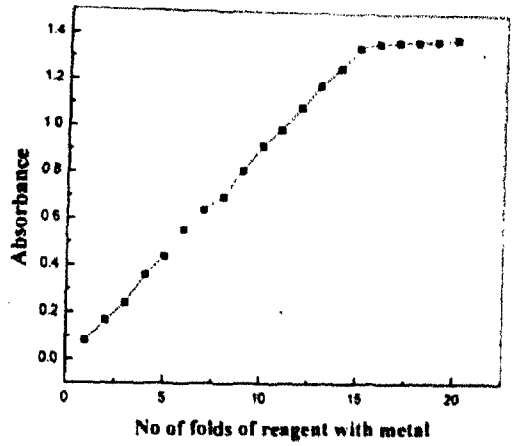

Fig. 3.3 Effect of reagent on Co(II)-2,6-DAPBPTSC complex: Co(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC=1.0 mL of 1.0×10^{-4} to 20.0×10^{-4} M; pH=4.0 and λ_{max} = 400 nm.

3.3.5. Applicability of Beer's law

Various aliquots containing different amounts of cobalt(II) (1.0×10^{-5} to 15.0×10^{-5} M), 2.0 mL of pH 4.0 buffer and 1.0 mL of 2,6-DAPBPTSC reagent (15.0×10^{-4} M), solutions were taken and their volumes adjusted 10.0 mL with double distilled water. The aqueous phases were shaken with 10.0 mL of isoamylalcohol in each case and the organic phases were collected into 25.0 mL standard flasks. The organic phases were made up to the mark with isoamylalcohol. The absorbances of all the solutions were recorded at 400 nm, against their corresponding reagent blanks. The obtained results are noted in Table 3.4. A graph plotted between the amount of cobalt(II) and its absorbance is shown in Fig.3.4. It can be observed from the graph that a linear plot passing through the origin obeys Beer's law in the concentration range 0.6-6.0 ppm of cobalt(II). The molar absorptivity of the complex was calculated and noted as 2.24×10^{4} lit mol^{-1} cm^{-1} and the Sandell's sensitivity of the complex was 0.0026 μg cm^{-2}. The correlation coefficient value of the Co(II)-2,6-DAPBPTSC complex, with an independent variable as concentration in μg mL^{-1} and a dependent variable as absorbance, was found to be 0.969. This indicates a satisfactory linearity between the two variables.

Table 3.4 Applicability of Beer's law to Co(II)- 2,6-DAPBPTSC complex

Concentration of metal, $\times 10^{-5}$M	Amount of metal, ppm	Absorbance
1	0.6	0.132
2	1.2	0.275
3	1.8	0.410
4	2.4	0.550
5	3.0	0.694
6	3.6	0.854
7	4.2	0.955
8	4.8	1.095
9	5.4	1.270
10	6.0	1.365
11	6.6	1.420
12	7.2	1.465
13	7.8	1.482
14	8.4	1.500
15	9.0	1.515

Co(II)=1.0 mL of 1.0×10^{-5} to 15.0×10^{-5} M (0.6-9.0 ppm); 2,6-DAPBPTSC=1.0 mL of 15.0×10^{-4} M; pH=4.0 and λ_{max}= 400 nm.

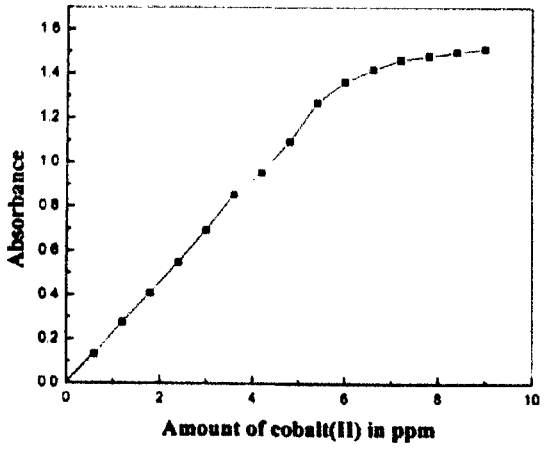

Fig. 3.4 Applicability of Beer's law to Co(II)-2,6-DAPBPTSC complex: Co(II)=1.0 mL of 1.0×10^{-5} to 15.0×10^{-5} M (0.6-9.0 ppm); 2,6-DAPBPTSC=1.0 mL of 15.0×10^{-4} M; pH = 4.0 and λ_{max}= 400 nm

3.3.6. Ringbom plot for Co(II) -2,6-DAPBPTSC complex

Ringbom plot is the standard adopted to know the optimum range of the concentration for a system, which emaciates Beer's law. The values are noted in Table 3.5. The plot is drawn between log C of Co(II) and (1-T) [where T is the transmittance]. The plot has a sigmoid shape with a linear segment at intermediate concentration values ranging from 2.77-3.77 ppm. The slope of the plot from Fig.3.5 is 0.85. Based on this value at 1% photometric error, the ratio between the relative error in concentration and the photometric error is 2.71. Hence, the relative error in concentration is 0.0271.

Table 3.5 Ringbom plot for Co(II)- 2,6-DAPBPTSC complex

Amount of cobalt(II), $\mu g\ L^{-1}$, C	Log C	Absorbance	Transmittance	(1-T)
600	2.77	0.132	0.876	0.124
1200	3.01	0.275	0.759	0.241
1800	3.25	0.410	0.663	0.337
2400	3.38	0.550	0.576	0.424
3000	3.47	0.694	0.499	0.510
3600	3.55	0.854	0.425	0.575
4200	3.62	0.955	0.384	0.616
4800	3.68	1.095	0.334	0.66
5400	3.73	1.270	0.280	0.720
6000	3.77	1.365	0.255	0.745
6600	3.81	1.420	0.241	0.759
7200	3.85	1.465	0.231	0.769
7800	3.89	1.482	0.227	0.773
8400	3.92	1.500	0.223	0.777
9000	3.95	1.515	0.219	0.781

Co(II)= 600-9000 $\mu g\ L^{-1}$; 2,6-DAPBPTSC=1.0 mL of 1.5×10^{-4} M, pH=4.0 and λ_{max} = 400 nm.

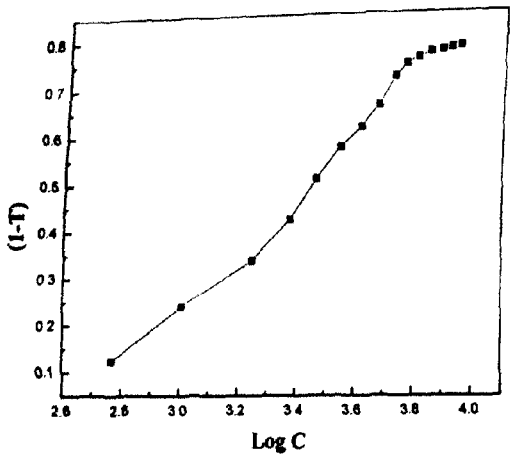

Fig. 3.5 Ringbom's plot for Co(II)-2,6-DAPBPTSC complex: Co(II)= 600-9000 μg L^{-1}; 2,6-DAPBPTSC=1.0 mL of 15.0×10^{-4} M; pH = 4.0 and λ_{max}= 400 nm

3.3.7. Precision, accuracy and detection limit of the method

To assess the precision and accuracy of the method, determinations were carried out for a set of five measurements, with different concentrations of Co(II), under optimum conditions. Calculations reveal that the standard deviation of method was not more than 0.0012 and the relative standard deviation was less than 0.388%. It is evident from these results, that the method is precise, besides being accurate. The detection limit, C_{min} is determined as the amount of Co(II) corresponding to three times the standard deviation of the blank values and a value of 0.0028μg L^{-1} is obtained.

3.3.8. Determination of the composition of Co(II)- 2,6-DAPBPTSC complex

Job's method of continuous variation, molar ratio method and Asums' method were employed to elucidate the composition of the complex.

3.3.8.1. Job's method of continuous variation

Equimolar solutions of cobalt(II) and 2,6-DAPBPTSC(15.0×10^{-4} M) were used to determine the metal to ligand ratio by job's method of continuous variation. The absorbance values were recorded at 400 nm against the reagent blank. The values are

reported in Table 3.6 and the corresponding graph drawn between absorbance and V_M / V_L+V_M (where V_L and V_M are the volumes of the reagent and the metal, respectively) is shown in Fig.3.6. From the graph, it is observed that one mole of cobalt(II) reacts with one mole of ligand and the composition of metal to ligand complex is 1:1.

Table 3.6 Job's method of continuous variation

Volume of Co(II), V_M, mL	Volume of 2,6-DAPBPTSC, V_L, mL	V_M/V_M+V_L	Absorbance
0.2	1.8	0.1	0.650
0.4	1.6	0.2	0.800
0.6	1.4	0.3	1.126
0.8	1.2	0.4	1.373
1.0	1.0	0.5	1.500
1.2	0.8	0.6	1.400
1.4	0.6	0.7	1.230
1.6	0.4	0.8	1.003
1.8	0.2	0.9	0.850

[Co(II)]=[2,6-DAPBPTSC]= 15×10^{-4} M; pH=4.0 and λ_{max} = 400 nm.

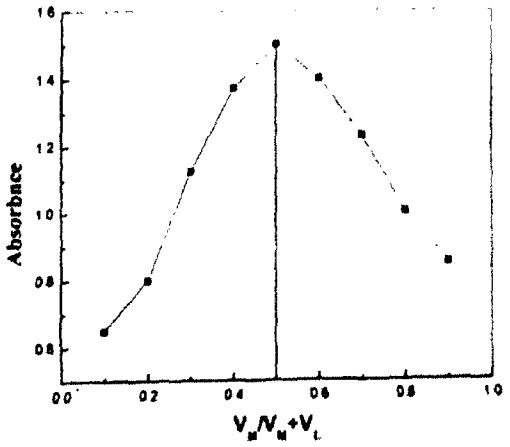

Fig. 3.6 Job's method of continuous variation: [Co(II)]=[2,6-DAPBPTSC]= 15.0×10^{-4}M; pH=4.0 and λ_{max}= 400 nm

3.3.8.2. Molar ratio method

In molar ratio method, different aliquots containing 1.0 mL of 15.0×10^{-4} M cobalt(II), 2.0 mL of sodium acetate-acetic acid buffer (pH 4.0) and varying concentration (0.25×10^{-3} to 2.0×10^{-3} M) of 2,6-DAPBPTSC were used to determine the metal ligand ratio. The absorbances of the solutions were recorded at 400 nm against their respective reagent blanks. The values are noted in Table 3.7. A plot (Fig.3.7) is drawn between the absorbance and the concentration of the reagent. From the obtained curve it is confirmed that one mole of cobalt(II) complexes with one mole of 2,6-DAPBPTSC.

Table 3.7 Molar ratio method

No. of moles of 2,6-DAPBPTSC per one mole of Co(II)	Absorbance
0.25	0.200
0.50	0.620
0.75	1.040
1.00	1.500
1.25	1.520
1.50	1.560
1.75	1.585
2.00	1.600

Co(II)= 1.0 mL of 1.5×10^{-3} M; 2,6-DAPBPTSC=1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=4.0 and λ_{max} =400 nm.

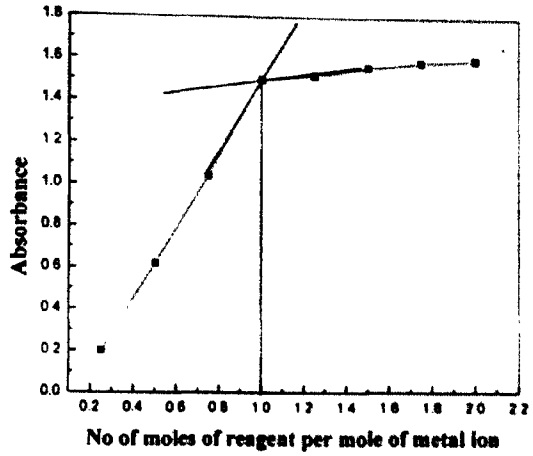

Fig.3.7 Molar ratio method: Co(II)= 1.0 mL of 1.5×10^{-3} M; 2,6-DAPBPTSC=1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=4.0 and λ_{max} = 400 nm.

3.3.8.3. Asmus' method

For Asmus' method the data obtained from molar ratio method was used. 1/m values (where 'm' is extinction modulus) were calculated by dividing the optical density with the cell width, along with 1/V, $1/V^2$, and $1/V^3$ and are given in Table 3.8. The plots between 1/m and 1/V, $1/V^2$ and $1/V^3$ are indicated in Fig.3.8. Among the plots between 1/m and 1/V, $1/V^2$ and $1/V^3$, only the plot between 1/m and 1/V is linear indicating that the composition of the complex is 1:1(M:L).

Table 3.8 Asmus' method

Volume of 2,6-DAPBPTSC, VmL	Absorbance (m)	1/m	1/V	$1/V^2$	$1/V^3$
0.25	0.200	5.00	4.00	16.00	64.00
0.50	0.620	1.61	2.00	4.00	8.00
0.75	1.040	0.96	1.33	1.77	2.37
1.00	1.500	0.66	1.00	1.00	1.00
1.25	1.520	0.65	0.80	0.64	0.51
1.50	1.560	0.64	0.66	0.44	0.29
1.75	1.585	0.63	0.57	0.32	0.18
2.00	1.600	0.62	0.50	0.25	0.12

Co(II)= 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC= 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=4.0 and λ_{max} = 400 nm.

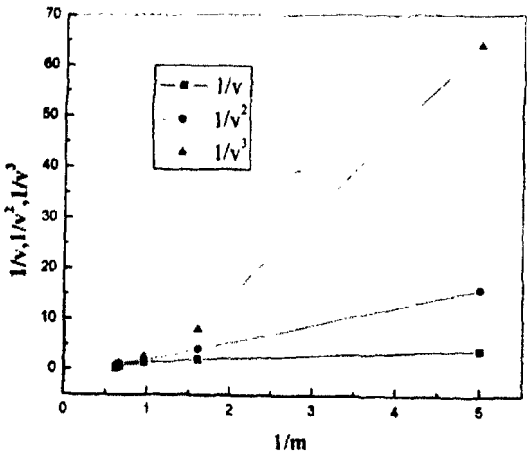

Fig.3.8 Asmus' method: Co(II)= 1.0 mL of 1.5×10^{-3} M; 2,6-DAPBPTSC=1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M, pH=4.0 and λ_{max} =400 nm.

3.3.9. Calculation of instability constant of Co(II) -2,6-DAPBPTSC complex

The instability constant of Co(II)-2,6-DAPBPTSC complex was calculated by using Asmus' method. The absorbance values were obtained at 400 nm for the solutions containing fixed volumes of cobalt(II)(1.0 mL of 1.5×10^{-3} M) and 2.0 mL of pH 4.0 buffer with different known volumes of 0.25-2.0 mL of 1.5×10^{-3} M of 2,6-DAPBPTSC. The instability constant of Co(II)-2,6-DAPBPTSC complex was calculated to be 3.75×10^{-4} at room temperature.

3.3.10. Effect of foreign ions on the extraction of Co(II)-2,6-DAPBPTSC complex

Interference of a number of cations and anions was studied in the colour absorbance of the Co(II)-2,6-DAPBPTSC complex. A change in absorbance of ± 0.0025 is taken as the tolerance limit for interference. In respect of some interfering ions, an increase in tolerance limit was achieved by the addition of masking agents, such as thiosulfate, fluoride, tartrate or thiocyanate. Increasing the amount of masking agents proportionatey could mask higher amount of interfering ions. In this study, cations like As(III), As(V), Mg(II), Mn(II), Zr(IV), Sb(III), Ca(II), Sr(II), Ba(II) and Tl(III) do not interferes, when present upto 5500 μg mL^{-1} and cations like Bi(III), Hg(II), Be(II), Th(VI), U(VI), Al(III) and V(V) are tolerated up to 3000 μg mL^{-1} but Cd(II), Cu(II), Ni(II), Zn(II), Fe(II), Fe(III), Mo(VI) and Pd (II) do interfere with the determination of cobalt(II) when present in more than 200 μg mL^{-1}. The interference of Cu(II) can be eliminated by using 1.0 of mL 0.2% thiosulphate as a masking agent. Fe(II) and Fe(III) are masked with 1.0 mL of 3% of sodium fluoride. The interference of Zn(II) and Cd(II) can be eliminated by using 1.0 ml of 0.5% of thiosulphate solution. Anions like fluroride, thiocyanate, thiosulfate and thiourea do not interfere even when present upto 3000 μg mL^{-1}, with the determination in the method. Citrate and borate are tolerated upto 1500 μg mL^{-1}. Oxalate and phosphate interfere even when present in trace amounts. EDTA masks cobalt(II) completely in the present determination. These results are given in Table 3.9.

Table. 3.9. Effect of foreign ions on the extraction of Co(II)-2,6-DAPBPTSC complex

Foreign Ion	Tolerance Limit, μg mL^{-1}	Foreign Ion	Tolerance Limit, μg mL^{-1}
As(III),	5500	V(V)	3000
As(V)	5500	Zn(II)	2000
Mn(II)	5500	Fe(III)	2000
Mg(II)	5500	Ni(II)	2000
Ca(II)	5500	Cu(II)	2000
Sb(III)	5500	Co(II)	2000
Sr(II)	5500	Thiocyanate	3000
Ba(II)	5500	Thiosulfate	3000
Zr(IV)	5500	Thiourea	3000
Tl(III)	5500	Fluoride	3000
Hg(II)	3000	Citrate	1500
Bi(III)	3000	Borate	1500
Be(II)	3000		
Th(VI)	3000		
U(VI)	3000		
Al(III)	3000		

3.4. Applications of the developed method

The developed extractive spectrophotometric method for cobalt(II) is applied for its determination in real samples such as vegetable, soil, water and standard alloy samples.

3.4.1. Determination of cobalt(II) in vegetable samples

The vegetable samples like Avalu (Brassica nigra), Chama (Colocasia esculenta) Thotakura (Amaranthus gangeticus), Palateega (Ichnocarpus frutescens) and Kakara (Momordica charantia) were analyzed for cobalt(II) using the proposed method. The content of the cobalt(II) present in the solution was determined by using a calibrated plot and results obtained were conformed by atomic absorption spectrophotometer. The data obtained in the analysis of vegetable samples are given in Table 3.10.

Table.3.10. Determination of cobalt(II) in vegetable samples

Name of the vegetable	Amount of cobalt(II) found [a]					
	AAS method [b]	Present method [b]	Present method			
			SD	RSD (%)	F-Test	T-Test
Avalu(Brassica nigra)	0.60	0.54	0.009	1.62	2.60	2.04
Chama(Colocasia esculenta)	1.08	1.09	0.016	1.51	1.33	2.06
Thotakura(Amaranthus ganaeticus)	1.09	1.10	0.017	1.58	1.55	1.84
Pala teega(Ichnocarpus frutescens)	1.48	1.46	0.016	1.51	1.56	1.56
Kakara(Momordica charantia)	1.25	1.23	0.025	2.03	2.04	1.91

[a]Average of five determinations, [b]Concentration in μg/g.

3.4.2. Determination of cobalt(II) in water samples

The present method is also applied for the determination of cobalt(II) in water samples. The concentration of cobalt(II) was determined by adopting the procedure described in general procedure. The content of the cobalt(II) present in the solution was determined by using a calibrated plot and results obtained were conformed by atomic absorption spectrophotometer. The data obtained in the analysis of water samples are given in Table 3.11.

Table 3.11 Determination of Co(II) in water samples

Source of water	Amount of cobalt(II) found [a]					
	AAS method [b]	Present method [b]	Present method			
			SD	RSD (%)	F-Test	T-Test
River water (Swarnamuki)	1.92	2.01	0.01	0.60	1.56	0.53
Waste water (Tiruchanoor)	2.30	2.34	0.02	1.06	1.23	2.11
Sea water (Marina Beach)	1.90	1.85	0.02	1.16	1.21	1.24

[a]Average of five determinations, [b]Concentration in μg/mL.

3.4.3. Determination of cobalt (II) in soil samples

Soil samples were collected from in and around Kadapa, A.P., India. The amount of cobalt (II) was determined by adopting the procedure described in general procedure. The content of the cobalt (II) present in the solution was determined by using a calibrated plot and results obtained were conformed by atomic absorption spectrophotometer. The data obtained in the analysis of soil samples are given in Table 3.12.

Table 3.12 Determination of Co(II) in soil samples

Amount of cobalt(II) found [a]						
Name of the area	AAS method [b]	Present method [b]	Present method			
			SD	RSD (%)	F-Test	T-Test
Kadapa	11.49	11.45	0.16	1.36	1.01	2.12
Mangampeta	11.98	11.81	0.14	1.20	1.25	2.27
Proddutur	10.90	10.82	0.12	1.11	1.29	2.42
Yeeraguntla	10.48	10.42	0.18	1.75	1.12	2.71
Mydukuru	10.00	9.99	0.10	1.01	1.17	1.95
Kondapuram	10.68	10.67	0.19	1.82	1.10	1.23
Anjaneyapuram	11.15	11.16	0.14	1.23	1.17	2.86
Vontimitta	12.28	12.26	0.18	1.44	1.07	1.37
Sidhavatam	10.30	10.28	0.12	1.14	1.20	2.76
Rajampeta	12.80	12.75	0.22	1.73	1.09	1.47

[a]Average of five determinations, [b]Concentration in μg/g.

3.4.4. Determination of cobalt (II) in standard alloy samples

The present method was also applied for the determination of cobalt(II) in alloy samples such as High-speed tool (BCS 484 and 485) and steel alloy samples (BCS 233 AND 266).The amount of cobalt (II) was determined by adopting the procedure described in general procedure. The content of the cobalt(II) present in the solution was determined by using a calibrated plot and results obtained were conformed by atomic absorption spectrophotometer. The data obtained in the analysis of standard alloy samples are given in Table 3.13.

Table.3.13. Determination of cobalt (II) in standard alloy samples

Samples	Amount of cobalt(II) found [a]						
	Certified values[b]	AAS method[b]	Present method[b]	Present method			
				SD	RSD (%)	F-Test	T-Test
High speed tool (BCS 484)	10.20	10.09	10.02	0.15	1.52	1.06	2.11
High speed tool (BCS 485)	5.06	5.05	5.02	0.07	1.51	1.10	1.10
Alloy steel (BCS 233)	23.40	23.25	23.07	0.29	1.26	1.09	1.15
Alloy steel (BCS 266)	23.40	23.34	23.17	0.38	1.67	1.05	1.01

[a]Average of five determination, [b]Concentration in %

3.5. Conclusions

A thorough survey of literature revels, that many thiosemicarbazones and few phenyl thiosemicarbazones are utilized for the determination of cobalt(II). Studies upon the use of 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) as an analytical reagent are however limited. The present investigations are carried out with a view to test the potential of 2,6-DAPBPTSC as a complexing agent for cobalt(II) and its subsequent determination by extraction spectrophotometry. The selectivity of this method is enhanced by using masking agents for Ni(II), Pd(II), Mo(VI), Cu(II), Cd(II), Fe(III) and Zn(II). Finally, it is established that this method is suitable for the determination of cobalt(II) in vegetables, soil, water and standard alloy samples.

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