CHAPTER IV

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

4.1. Introduction

Cadmium is a heavy metal and widely released to the environment by power stations, heating systems, metal working industries, waste incinerators, urban traffic, cement factories and phosphate fertilizer factories[1]. Cadmium occurs in nature as trace amounts and constitutes only 0.0005% of the crust of the earth; it has been listed by UNEP/WHO as a substance dangerous to the environment, because along with such metals as lead, mercury, copper, zinc, and silver it poses a risk of disturbing the balance in ecosystems[2]. The effects of acute cadmium poisoning are manifested in a variety of different symptoms including high blood pressure, kidney damage and destruction of red blood cells[3]. Even at low exposure levels (mg kg^{-1}), the risk of renal tubular damage due to industrial exposure to cadmium can be considerable[4]. Approximately one third of cadmium is used in battery manufacture; other major uses are in pigments and soaps, as an anticorrosive, and as a stabilizer for PVC[5]. The FAO-WHO joint expert committee on food additives recommended a provisional maximum tolerable daily intake for cadmium from all sources is of 1.0-1.2 μg kg^{-1} body mass. Considering the problems caused by the presence of cadmium in the human organism and in the environment, years of effort have been devoted to the development of more effective, fast, precise and accurate approaches to the determination of this element in biological and environmental materials, using numerous analytical methods[6].

4.2. Review of known methods

As per the review of literature some standard, sensitive and/or selective reagents for the spectrophotometric and extractive spectrophotometric determination of cadmium(II) are discussed here.

Ahmed and Chowdhury[7] have reported 5,7-dibromo-8-hydroxyquinoline for the determination of cadmium(II). The molar absorptivity of the complex is found to be 0.53×10^4 lit $mol^{-1}cm^{-1}$ at 396 nm and the Beer's law is obeyed in the range 0.1 to 30 ppm of cadmium(II).

Polyferric sulphate flocculent[8] is used for the spectrophotometric determination of Cd(II). The molar absorptivity of the complex is found to be 4.99×10^5 lit $mol^{-1}cm^{-1}$ at 607 nm and the Beer's law is obeyed in the range 1.0 to 1.5 ppm of cadmium(II).

Chakravrty et al[9] have reported 4-(2-pyridylazo)naphthol for the spectrophotometric determination of cadmium(II). The molar absorptivity of the complex is found to be 3.2×10^4 lit $mol^{-1}cm^{-1}$ at 530 nm and the Beer's law is obeyed upto 1.5 ppm of cadmium(II).

4-(2-pyridylazo)-resorcinol[10] is used for the simultaneous spectrophotometric deter-mination of cadmium(II) and nickel(II). The cadmium complex has the maximum absorbance at 510 nm. The complex shows the molar absorptivity as 2.5×10^4 lit $mol^{-1}cm^{-1}$.

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

2,4-dihydroxyacetophenone benzoylhydrazone[11] is used for the spectrophotometric determination of cadmium(II). The complex shows a maximum absorbance at 306 and 437 nm in the pH range of 3.6-4.4 and the Beer's law is obeyed in the range 0.36-1.40 ppm of cadmium(II).

Di-2-pyridylmethanone 2-(5-nitro)pyridylhydrazone (DPNPH)[12] is used for the spectrophotometric determination of cadmium(II). The complex shows a maximum absorbance at 510 nm in the pH range of 8.8-11.7. The reagent forms 1:2 (M:L) complex with metal ion. The molar absorptivity of the complex is found to be 10.4×10^4 lit $mol^{-1}cm^{-1}$.

Tzivanidou et al[13] have reported 2,2'-dipyridyl-2-pyridylhydrazone(DPPH) for the spectrophotometric determination of cadmium(II). The complex shows a maximum absorbance at 444 nm in the pH range of 12.3±0.2. The reagent forms 1:2 (M:L) complex with metal ion. The molar absorptivity of the complex is found to be 5.5×10^4 lit $mol^{-1}cm^{-1}$ and the Beer's law is obeyed in the range 0.2 to 2.0 ppm of cadmium(II).

Otomo and Singh et al[14] have reported 2,2'-diquinolyl-2-quinolylhydrazone for the extractive spectrophotometric determination of cadmium(II). The cadmium complex has the maximum absorbance at 552 nm. The complex shows the molar absorptivity as 9.15×10^4 lit $mol^{-1}cm^{-1}$ and the Beer's law is obeyed up to 9.0 ppm of cadmium(II).

Other hydrazones used for the spectrophotometric and extractive spectrophotometric determination of cadmium(II) are 2,2'-bipyridil quinolylhydrazone[15], β-cyclodextrin-o-vanillin furfuralhydrazone[16], di-2-pyridyl ketone-2-furancarbothiohydrazone[17], 2,2'-pyridil bis(2-quinolylhydrazone)[18], pyridine-2-aldehyde-2-pyridylhydrazone[19], pyruvaldehyde-2-benzothiazolylhydrazone[20], *o*-vanillin furoylhydrazone[21]etc.,

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

Benzildithiosemicarbazone has been used for the extractive spectrophotometric determination cadmium(II) at pH 10.5 by Reddy et al[22]. The 1:1(M:L) yellow colored complex extracted from isoamylalcohol shows a maximum absorbance at 360 nm in the pH 10.5. Beer's law is obeyed in the range of 1.0-10.0 ppm of cadmium(II). The molar absorptivity of the complex is found to be 0.196×10^4 lit mol^{-1} cm^{-1}. The method has been successfully applied for the determination of cadmium(II) in medicinal leaves and environmental samples.

4-chloroisonitrosoacetophenone thiosemicarbazone has been used for the spectrophotometric determination of cadmium(II) by Lokhande et al[23]. The maximum absorbance of the complex is at 395 nm in the pH range of 8.0-9.0. The composition of the complex is 1:2 (M:L) and the molar absorptivity of the complex is found to be 0.670×10^4 lit $mol^{-1}cm^{-1}$. The method has been successfully applied for the determination of cadmium(II) in biological samples.

Berzas et al.[24] have used 1,3-cyclohexanedione dithiosemicarbazonemonohydrochloride for the spectrophotometric determination of cadmium(II). The maximum absorption of the complex is found to be at 515 nm. The molar absorptivity of the

complex is found to be 1.21 $\times 10^4$ lit mol^{-1} cm^{-1}. The metal-ligand ratio of the complex is determined as 1:1.

2,6-dimethylphenyldiazoaminobenzene[25] is used for the spectrophotometric determination of cadmium(II). The complex has a maximum absorbance at 523nm. The molar absorptivity of the complex is found to be 2.27×10^5 lit mol^{-1} cm^{-1}. The method has been successfully applied for the determination of cadmium(II) in tableware leach solution.

Dipyridylglyoxalbis-(4-phenyl-3-thiosemicarbazone) is used for the spectrophotometric determination of cadmium(II) by Balairon[26]. The determination is carried out at pH 9.7 and the maximum absorption of the complex is found to be at 400 nm and the Beer's law is obeyed in the range 6.0-55.0 ppm of cadmium(II).

Guler et al[27] have used 9-ethyl-3-carbazolecarboxaldehyde-4-phenyl-3-thiosemicarbazone for the spectrophotometric determination of cadmium(II). The maximum absorbance of the complex is at 401 nm in the pH 8.8. The metal to ligand ratio of the complex is 1:2. The molar absorptivity of the complex is found to be 3.6×10^4 lit mol^{-1} cm^{-1}.

Phenanthraquinone monophenylthiosemicarbazone(PMPT)[28] is used for the spectrophotometric determination of cadmium(II). Cadmium(II) reacts PMPT in the pH $\geq$ 6 to from Cd(II)-PMPT complex in 1:2(M:L) ratio. The complex absorbs strongly at 520 nm. The system obeys Beer's law in the concentration range 0.01-0.34 ppm of cadmium(II). The molar absorptivity of the complex is found to be 2.4×10^4 lit $mol^{-1}cm^{-1}$. This method is applied for the determination of cadmium(II) in certificate and human hair samples as well as natural water.

Kamil et al[29] determined cadmium(II) spectrophotometrically by reaction with phenanthrenequinone monosemicarbazone at pH 9.0 in 60-70% DMF medium to form a 1:2 (metal-ligand) complex. The absorbance is measured at 480 nm. The molar absorptivity of the complex is found to be 1.5×10^4 lit $mol^{-1}cm^{-1}$ and the Beer's law is obeyed in the range 1.41-6.13 ppm of cadmium(II).

A thorough literary survey has revealed that a number of thiosemicarbazones are available for the spectrophotometric and extractive spectrophotometric determination of cadmium(II). But many of the thiosemicarbazones are either less sensitive or non-selective. Hence, a new reagent namely 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) is synthesized to the development of a simple, selective and sensitive extractive spectrophotometric method for the determination of cadmium(II). In the present investigation, the researcher has studied the reactivity of 2,6-DAPBPTSC with cadmium (II) and the results are reported in terms of its maximum absorbance, pH, molar absorptivity and stoichiometry, which provides the basis for judging the potential utility of 2,6-DAPBPTSC as an analytical reagent for cadmium(II). Finally, the developed method is successfully applied for the extractive spectrophotometric determination of cadmium(II) in food and water samples.

4.3. Results and Discussion

2,6-diacetylpyridine bis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) forms a 1:1(M: L) yellowish orange coloured complex with cadmium(II), which is extracted into cyclohexanol, from ammonium chloride-ammonium hydroxide(pH 9.5) buffer. The yellowish orange Cd(II)-2,6-DAPBPTSC complex shows a maximum absorbance at 390 nm and is stable for 40 hours. The conditions for effective extraction are established after studying the effects of various factors such as pH, reagent concentration, metal ion concentration and influence of diverse ions, in order to develop a sensitive, selective and rapid spectrophotometric method for the determination of cadmium(II) at micro gram levels.

4.3.1. Absorption spectra of reagent and Cd(II)- 2,6-DAPBPTSC complex

The absorption spectrum of Cd(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. 4.1. From the absorption spectra it is clear that the complex and reagent have shown maximum absorptions at 390 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 cadmium(II). Hence, further absorbance measurements of the complex were recorded at 390 nm.

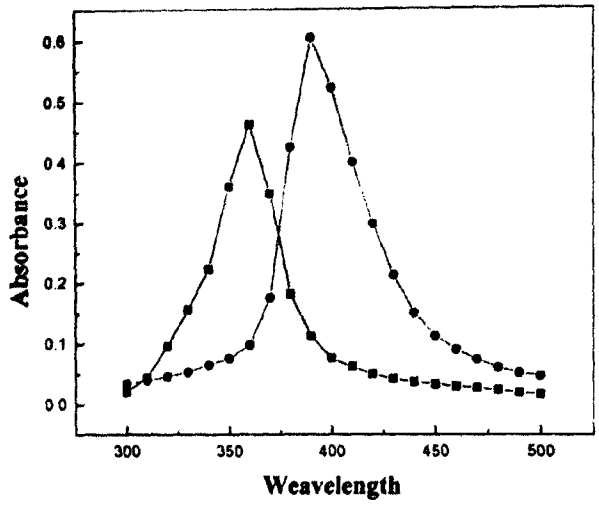

Fig. 4.1 (A) Absorption spectrum of 2,6-DAPBPTSC; (B) Absorption spectrum of Cd(II)- 2,6-DAPBPTSC complex: Cd(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC= 1.0 mL of 1.0×10^{-3} M and pH= 2.0 mL of pH 9.5.

4.3.2. Effect of pH

To arrive at the optimum pH required for maximum colour development, the effect of pH on the colour intensity was studied. In each case, a mixture containing 1.0 mL of 1.0×10^{-4} M cadmium(II), 2.0 mL of suitable buffer, 1.0 mL of 1.0×10^{-3} M 2,6-DAPBPTSC solution was taken and the aqueous phases were adjusted to 10.0 mL with double distilled water. Each aqueous phases was shaken with 10.0 mL of cyclohexanol for one minute. The organic phases are collected into a 25 mL of standard flasks and made upto the mark with cyclohexanol. The same procedure was applied for buffers of different pH values, ranging from 8.0-12.0. The absorbances were measured at 390 nm, using their corresponding reagent blanks and the values are noted in Table 4.1. A plot was executed between the pH and the absorbance, and the same is represented in Fig. 4.2. The plot shows that there is maximum absorbance and constancy in the pH range 9.0-10.0. Hence, pH 9.5 is chosen for further studies, considering this as an optimum pH.

Table 4.1 Effect of pH on Cd(VI)- 2,6-DAPBPTSC complex

S.No.	pH	Absorbance
1	8.0	0.305
2	8.5	0.470
3	9.0	0.610
4	9.5	0.612
5	10.0	0.605
6	10.5	0.510
7	11.0	0.402
8	11.5	0.286
9	12.0	0.172

Cd(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} = 390 nm.

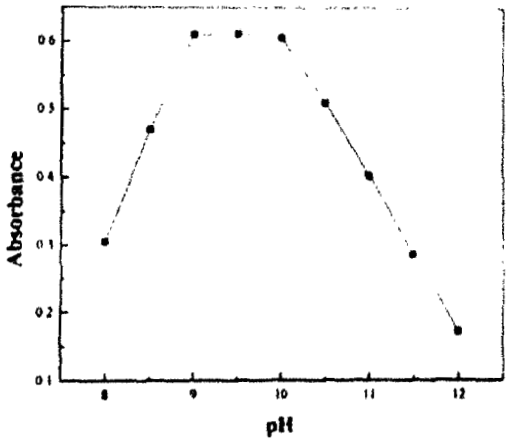

Fig.4.2. Effect of pH on Cd(II)-2,6-DAPBPTSC complex. Cd(II): 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC: 1.0 mL of 1.0×10^{-3} M and λ_{max} = 390 nm

4.3.3. Effect of solvents

The effect of various solvents such as isoamylalcohol, cyclohexanol, chloroform, toulene, benzene, n-butanol, carbontetrachloride, ethyl acetate, butyl acetate, xylene, tributyl phosphate, n-propyl alcohol and isobutyl ketone on the extraction of cadmium(II) with 2,6-DAPBPTSSC is at pH 9.5 for registering the effect of solvent. Among the various solvents studied, cyclohexanol is selected as the suitable solvent, because of its greater

extraction ability, which is indicated by maximum absorbance of the colour in it. The results are reported in Table 4.2.

Table 4.2 Effect of solvent on the extraction of Cd(VI)- 2,6-DAPBPTSC complex

Solvent	Absorbance
cyclohexanol	0.615
Isoamylalcohol	0.550
isobutyl ketone	0.420
n-butanol	0.412
chloroform	0.400
benzene	0.365
carbontetrachloride	0.358
xylene	0.342
hexane	0.325
butyl acetate	0.310
ethyl acetate	0.305
toulene	0.292

Cd(II) = 1.0 mL of 1.0×10^{-4}M, 2,6-DAPBPTSC =1.0 mL of 1.0×10^{-3} M, pH=9.5 and λ_{max} = 390nm.

4.3.4. Effect of reagent concentration

The effect of reagent concentration is studied, using different aliquots containing constant volumes of 1.0×10^{-4} M cadmium(II) solution, 2.0 mL of pH 9.5 buffer solution and 1.0 mL of 2,6-DAPBPTSC solution containing different concentration ranging from 1.0×10^{-4} to 15.0×10^{-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 cyclohexanol in each case and the organic phases are collected into 25 mL standard flasks. The organic phases were made up to the mark with cyclohexanol. The absorbances of the organic phases were measured at 390 nm, against their corresponding reagent blanks and the values are noted in Table 4.3. It is clearly observed from the absorbance values, that a maximum fifteen- fold molar excess of the reagent is sufficient to get maximum colour formation of the complex. The plot is shown in Fig. 4.3.

Table 4.2 Effect of reagent concentration on Cd(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	0.052
2.0	2	0.108
3.0	3	0.183
4.0	4	0.245
5.0	5	0.300
6.0	6	0.365
7.0	7	0.422
8.0	8	0.49
9.0	9	0.543
10.0	10	0.609
11.0	11	0.625
12.0	12	0.638
13.0	13	0.649
14.0	14	0.656
15.0	15	0.660

Cd(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-4} to 15.0×10^{-4} M, pH=9.5 and λ_{max} = 390 nm.

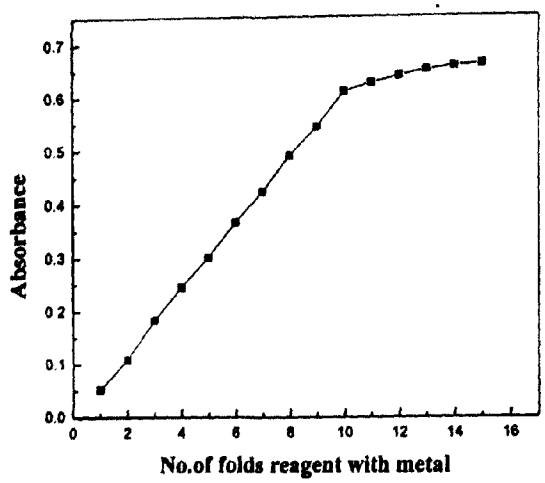

Fig.4.3 Effect of reagent on Cd(II)- 2,6-DAPBPTSC complex: Cd(II)= 1.0 mL of 1.0×10^{-4}M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-4} to 15.0×10^{-4} M; pH=9.5 and λ_{max} = 390 nm.

4.3.5. Applicability of Beer's law

Various aliquots containing different amounts of cadmium(II) 1.0×10^{-5} to 15.0×10^{-5} M (1.2-16.80 ppm), 2.0 mL of pH 9.5 buffer and 1.0 mL of 2,6-DAPBPTSC reagent (15.0×10^{-4} M) solution, were taken and their volumes adjusted 10.0 mL with double distilled water. The aqueous phases were shaken with cyclohexanol in each case and the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with cyclohexanol. The absorbances of all the solutions were recorded at 390 nm, against their corresponding reagent blanks. The obtained results are noted in Table 4.4. A graph plotted between the amount of cadmium(II) and its absorbance is shown in Fig.4.4. It can be observed from the graph that a linear plot passing through the origin obeys Beer's law in the concentration range 0.63-6.30 μg mL^{-1}(ppm) of cadmium(II). The molar absorptivity of the complex is calculated and noted as 6.088×10^{4} L $mol^{-1}cm^{-1}$ and the Sandell's sensitivity of the complex was 0.0018 μg cm^{-2}. The correlation coefficient value of the Cd(II)-2,6-DAPBPTSC complex, with an independent variable as concentration in μg mL^{-1} and a dependent variable as absorbance, is found to be 0.971. This indicates a satisfactory linearity between the two variables.

Table 4.4 Applicability of Beer's law to Cd(II)- 2,6-DAPBPTSC complex

Concentration of metal, $\times 10^{-5}$M	Amount of metal, ppm	Absorbance
1	1.12	0.062
2	2.24	0.120
3	3.36	0.182
4	4.48	0.237
5	5.60	0.304
6	6.72	0.362
7	7.84	0.421
8	8.96	0.485
9	10.08	0.548
10	11.20	0.612
11	12.32	0.635
12	13.44	0.662
13	14.56	0.675
14	15.68	0.690
15	16.80	0.696

Cd(II)=1.0 mL of 1.0×10^{-3} to 15.0×10^{-3} M; 2,6-DAPBPTSC=1.0mL of 15×10^{-4} M; pH=9.5 and λ_{max} = 390 nm.

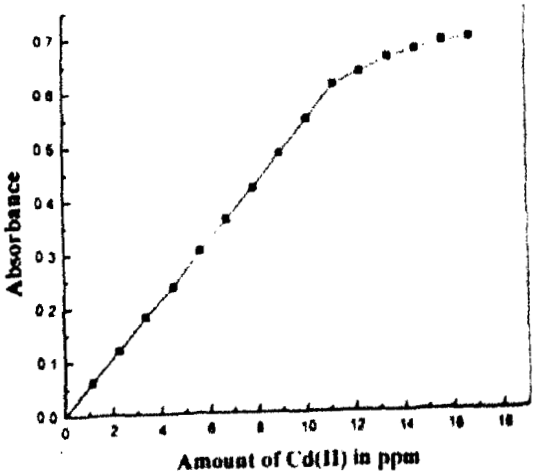

Fig. 4.4 Applicability of Beer's law to Cd(II)-2,6-DAPBPTSC complex: Cd(II)=1.0 mL of 1.0×10^{-4} to 15.0×10^{-3} M (1.2-16.80 ppm); 2,6-DAPBPTSC=1.0 mL of 15.0×10^{-4} M; pH = 9.5 and λ_{max} = 390 nm

4.3.6. Ringbom plot for Cd(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 4.5. The plot is drawn between log C of Cd(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 3.04-3.95 μg L^{-1}. The slope of the plot from Fig.4.5 is 0.80. Based on this value at 1% photometric error, the ratio between the relative error in concentration and the photometric error is 3.59. Hence, the relative error in concentration is 0.0359.

Table 4.5 Ringbom plot for Cd(II)- 2,6-DAPBPTSC complex

Amount of cadmium(II), μg L^{-1}, C	Log C	Absorbance	Transmittance	(1-T)
1120	3.049	0.062	0.939	0.060
2240	3.350	0.120	0.886	0.113
3360	3.526	0.182	0.833	0.166
4480	3.651	0.237	0.788	0.211
5600	3.748	0.304	0.737	0.262
6720	3.827	0.362	0.696	0.303
7840	3.894	0.421	0.656	0.343
8960	3.952	0.485	0.615	0.384
10080	4.003	0.548	0.578	0.421
11200	4.049	0.612	0.542	0.457
12320	4.090	0.635	0.529	0.470
13440	4.128	0.662	0.515	0.484
14560	4.163	0.675	0.509	0.490
15680	4.195	0.690	0.501	0.498
16800	4.225	0.696	0.498	0.501

Cd(II)= 1120-16800 μg L^{-1}; 2,6-DAPBPTSC=1.0 mL of 15×10^{-4} M; pH=9.5 and λ_{max} = 390 nm.

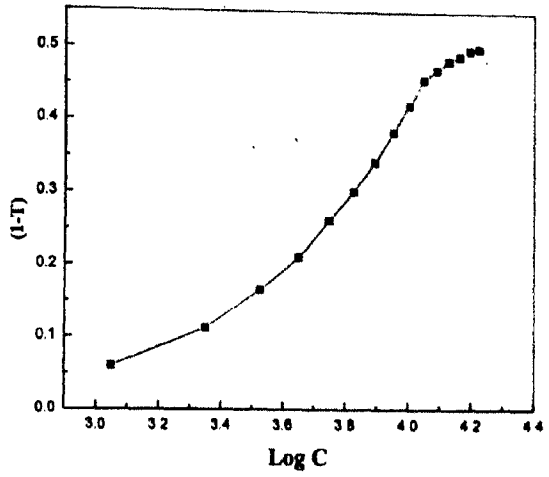

Fig. 4.5 Ringbom plot for Cd(II)- 2,6-DAPBPTSC complex: Cd(II)= 1.12-12.0 ppm; 2,6-DAPBPTSC= 1.0 mL of 15.0×10^{-4} M; pH = 9.5 and λ_{max} = 390 nm

4.3.7. 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 Cd(II), under optimum conditions. Calculations reveal that the standard deviation of method was not more than 0.0017 and the relative standard deviation was less than 0.928%. 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 Cd(II) corresponding to three times the standard deviation of the blank values and a value of 0.006 μg L^{-1} is obtained.

4.3.8. Determination of the composition of Cd(II)- 2,6-DAPBPTSC complex

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

4.3.8.1. Job's method of continuous variation

Equimolar solutions of cadmium(II) and 2,6-DAPBPTSC (1.0×10^{-3} M) were used to determine the metal to ligand ratio by job's method of continuous variation. The absorbance values were recorded at 390 nm against their corresponding reagent blanks.

The values are reported in Table 4.6 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.4.6. From the graph, it is observed that one mole of cadmium(II) reacts with one mole of ligand shows the composition of metal to ligand complex is as 1:1.

Table 4.6 Job's method of continuous variation

Volume of Cd(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	0.183
0.4	1.6	0.2	0.355
0.6	1.4	0.3	0.500
0.8	1.2	0.4	0.636
1.0	1.0	0.5	0.721
1.2	0.8	0.6	0.596
1.4	0.6	0.7	0.465
1.6	0.4	0.8	0.327
1.8	0.2	0.9	0.162

[Cd(II)]= [2, 6-DAPBPTSC] = 1.0×10^{-3} M; pH=9.5 and λ_{max} = 390 nm.

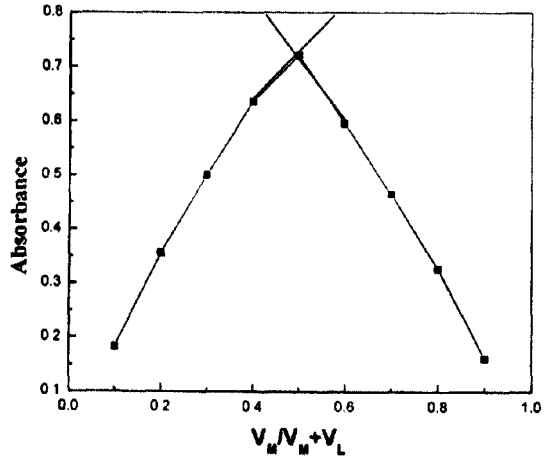

Fig. 4.6 Job's method of continuous variation: [Cd(II)]= [2,6-DAPBPTSC]= 1.0×10^{-3} M; pH = 9.5 and λ_{max}= 390 nm

4.3.8.2. Molar ratio method

In molar ratio method, different aliquots containing 1.0 mL of 1.0×10^{-3} M cadmium(II), 2.0 mL of ammonium chloride-ammonium hydroxide (pH 9.5) 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 390 nm against their respective reagent blanks. The values are noted in Table 4.7. A plot (Fig.4.7.) is drawn between the absorbance and the concentration of the reagent. From the obtained curve, it is confirmed that one mole of cadmium(II) complexes with one mole of 2,6-DAPBPTSC.

Table 4.7 Molar ratio method

No. of moles of 2,6-DAPBPTSC per one mole of Cd(II)	Absorbance
0.25	0.183
0.50	0.372
0.75	0.550
1.00	0.732
1.25	0.750
1.50	0.776
1.75	0.800
2.00	0.817

Cd(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=9.5 and λ_{max} = 390 nm.

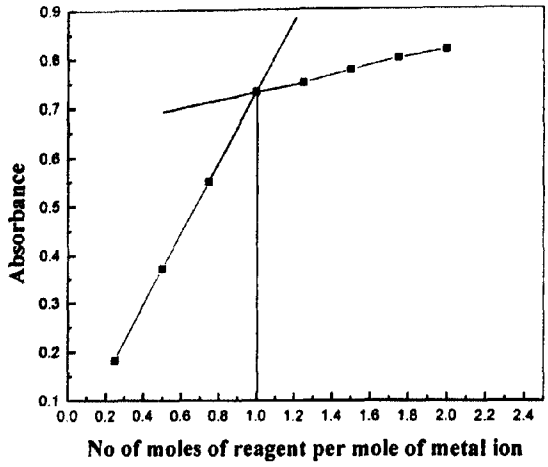

Fig. 4.7 Molar ratio method: Cd(II)= 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC= 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=9.5 and λ_{max}= 390 nm

4.3.8.3. 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 Table 4.8. The plots between 1/m and 1/V, $1/V^2$ and $1/V^3$ are indicated in Fig.4.8. Among the plots between 1/m and 1/V, $1/V^2$ and $1/V^3$, only plot between 1/m and 1/V is linear indicating that the composition of the complex as 1:1 (M: L).

Table 4.8 Asmus' method

S.No.	Volume of 2,6-DAPBPTSC, V, mL	Absorbance m	1/m	1/V	$1/V^2$	$1/V^3$
1	0.50	0.372	1.925	2.0000	4.0000	8.0000
2	0.75	0.550	1.300	1.3333	1.7776	2.3700
3	1.00	0.732	1.024	1.0000	1.0000	1.0000
4	1.25	0.750	0.850	0.8000	0.6400	0.5120
5	1.50	0.776	0.796	0.6666	0.4443	0.2960
6	1.75	0.800	0.734	0.5714	0.3264	0.1860
7	2.00	0.817	0.692	0.5000	0.2500	0.1250

Cd(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=9.5 and λ_{max} = 390 nm

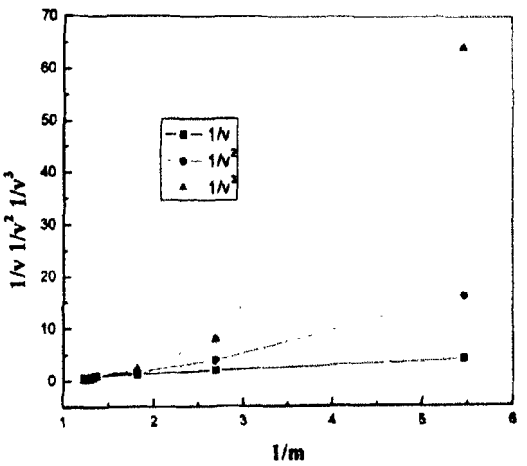

Fig. 4.8 Asmus' method: Cd(II)= 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC= 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=9.5 and λ_{max} = 390 nm

4.3.8. Calculation of instability constant of Cd(II)-2,6-DAPBPTSC complex

The instability constant of Cd(II)-2,6-DAPBPTSC complex was calculated by using Asmus' method. The absorbance values were obtained at 390 nm for the solutions containing fixed volumes of cadmium(II) (1.0 mL of 1.0×10^{-3} M) and 2.0 mL of pH 9.5 buffer with different known volumes of 0.25-2.0 mL of 1.0×10^{-3} M of 2,6-DAPBPTSC. The instability constant of Cd(II)-2,6-DAPBPTSC complex was calculated to be 1.415×10^{-4} at room temperature.

4.3.9. Effect of foreign ions on extraction of Cd(II)- 2,6-DAPBPTSC complex

Interference of a number of cations and anions is studied in the colour absorbance of the Cd(II)-2,6-DAPBPTSC complex. A change in absorbance of ± 0.0025 was taken as the tolerance limit for interference. In respect of some interfering ions, an increased tolerance limit is achieved by the addition of masking agents such as thiosulphate, citrate, acetate and tartate. Increasing the amount of masking agents proportionately could mask higher amounts 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 interfere, 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 upto 3000 μg, but Co(II), Cu(II), Ni(II), Zn(II), Fe(II), Fe(III), Mo(VI) and Pd(II) do interfere with the determination of cadmium(II), when present in more than 2000 μg. The interference of Cu(II) can be eliminated by using 1.0 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), Pd(II) and Ni(II) can be eliminated by using 1.0 mL of 0.5% of citrate solution. The interference of Co(II) can be eliminated by using 1.0 mL of 1.0% of thiocyanate solution. Anions like, bromide, chloride, fluroride, thiosulfate and thiourea do not interfere when present upto 3000 μg, with the determination of cadmium(II) in the method. Oxalate, phosphate and interfere, even present in trace amount. These results are given in Table 4.9.

Table 4.9 Effect of foreign ions on the extraction of cadmium(II)-2,6-DAPBPTSC complex

Foreign Ion	Tolerance Limit, μg/mL	Foreign Ion	Tolerance Limit, μg/mL
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	Thiosulfate	3000
Ba(II)	5500	Thiourea	3000
Zr(IV)	5500	Fluoride	3000
Tl(III)	5500	Citrate	1500
Hg(II)	3000	Borate	1500
Bi(III)	3000		
Be(II)	3000		
Th(VI)	3000		
U(VI)	3000		
Al(III)	3000		

4.4. Applications of the developed method

The developed sensitive and extractive spectrophotometric method for Cd(II) was successfully applied for its determination in food and water samples.

4.4.1. Determination of Cd(II) in food samples

The foods like kakara (Momordica charantia), leafy vegetables and milk samples were analyzed for cadmium(II) using the proposed method. The content of the cadmium(II) present in the solution was determined by using a calibrated plot and results obtained were conformed by direct atomic absorption spectrophotometer. The data obtained in the analyses of medicinal leaves and leafy vegetables and milk samples are given in Table 4.10.

Table 4.10 Determination of cadmium(II) in food samples

Samples	Amount of cadmium(II) [a] found					
	AAS method[b]	Present method[b]	Present method			
			SD	RSD (%)	F-Test	T-Test
Leafy vegetables Name of the samples						
Chilakamukkaku (Impatins balsamina)	0.405	0.403	0.0013	0.322	1.173	2.635
Curry (Murraya koenigil)	0.122	0.121	0.0013	1.074	1.173	1.317
Medicinal leaves Name of the samples						
Bokenaku (Phyla nodiflora greene)	0.971	0.972	0.0014	0.144	1.147	1.129
Neetichamanti (Monochoria vaginalis)	0.123	0.122	0.0013	1.065	1.173	1.131

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

4.4.2. Determination of Cd(II)in water samples

The present method was also applied for the determination of cadmium(II) in water samples. The concentration of cadmium(II) was determined by adopting the procedure described in general procedure. The data obtained in the analyses of water samples were given in Table 4.11.

Table 4.11 Determination of trace amount of cadmium(II) in water samples

Name of the area	Amount of cadmium(II) [a] found					
	AAS method[b]	Present method[b]	Present method			
			SD	RSD (%)	F-Test	T-Test
River water (Penna)	1.51	1.50	0.013	0.880	1.170	1.295
Lake water(Kollate)	2.02	1.99	0.165	0.829	1.090	3.002
Polluted water	2.26	2.23	0.122	0.547	1.677	3.887
Bore water	1.75	1.73	0.013	0.763	1.562	2.395

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

4.5. Conclusions

The present investigations proved that 2,6-DAPBPTSC is a promising complexing agent for Cd(II) and its subsequent determination by spectrophotometry is rapid and precise. The method has good sensitivity when compared to other existing extractive spectrophotometric methods. The selectivity of this method is improved by using masking agents for Co(II), Ni(II), Fe(II), Fe(III), Zn(II), Pd(II), Cu(II) and Mo(VI) . It has been successfully applied for the extractive spectrophotometric determination of cadmium(II) in leafy vegetables, medicinal leaves and water samples.

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