

Development and Optimization of Analytical Method for Synergistic Extraction and Spectrophotometric Determination of Cadmium(II) by using 1-(2',4'- dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol: Analysis of Alloys, Thin Film and Biological Material

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Abstract

A synergistic, simple and selective spectrophotometric method has been developed for 1-(2', 4'-dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2', 4'-dinitro APTPT] as a novel chromogenic reagent. The proposed method is based on the synergistic extraction of cadmium(II) with 2', 4'-dinitro APTPT (0.01 mol L^{-1}) in presence of 0.5 mol L^{-1} pyridine to give orange red coloured ternary complex of a molar ratio 1:2:2 (M:L:Py) in the pH range 9.3 - 9.7. It exhibits a maximum absorption of coloured complex at 425 nm in chloroform against the reagent blank and the absorbance remains stable for at least 20 h. The system obeys Beer's law in the concentration range $1.0 - 12.5 \mu\text{g mL}^{-1}$ of cadmium(II) and optimum range of $2.5 - 12.5 \mu\text{g mL}^{-1}$ of the metal as evaluated by Ringbom's plot. The molar absorptivity and Sandell's sensitivity of cadmium (II) -2', 4'-dinitro APTPT-pyridine complex (1:2:2) was established by Job's method, mole ratio method and slope ratio method. Interference of the foreign ions was investigated and use of suitable masking agent enhances the selectivity of the method. The proposed method is rapid, reproducible and successfully applied for the determination of cadmium(II) in binary and synthetic mixtures, alloys, thin films and tobacco sample. The results of the present study were compared with that of atomic absorption spectrophotometer to test the validity of the method.

Keywords: Cadmium(II); Solvent extraction; 2',4'-dinitro APTPT; Pyridine; Spectrophotometry

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Abbreviations

4'-bromo PTPT	1-(4'-bromophenyl)-4,4,6-trimethyl(1H,4H)- Pyrimidine-2- thiol
2',4'-dinitro APTPT	1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4- dihydropyrimidine-2-thiol
DMG	Dimethylglyoxime
PAR	4-(2-Pyridylazo) resorcinol
Py	Pyridine

1. Introduction

Cadmium is white, lustrous but tarnishable metal, occurs in trace amounts and presents 0.00005 percent of the earth crust. Cadmium minerals are scarce but as a result of its chemical similarity to zinc, cadmium occurs by isomorphous replacement in all zinc ores. The main source is sphalerite [(ZnFe)S] which commonly occurs with galena (PbS). As a consequence cadmium is produced as a byproduct from mining, smelting and refining sulfidic ores of zinc and to a lesser degree lead and copper (Cotton and Wilkinson, 1988; Podgaiskyte and Vaitiekunas, 2009).

Cadmium is an important environmental pollutant and listed as the sixth most poisonous substance jeopardizing human health. Cadmium is toxic at trace level due to disrupting enzyme functions, replacing essential metals in pigments or producing reactive oxygen species. Exposure to lower amounts of cadmium may cause gastrointestinal irritation, vomiting, abdominal pain and diarrhoea. Acute exposure may affect kidneys resulting proteinosis and sometimes fatality (Prasad et al., 2006; Babula et al., 2008). Despite the fact that, cadmium is nonessential element for plant, they can readily uptake and accumulate it in their tissues. This feature makes cadmium a serious problem since the cadmium enriched plant can be incorporated in the food chain therefore this toxic element could be incorporated into human diet through edible plants causing toxicity. A disease especially associated with cadmium poisoning is known as *itai-itai* in which bones become fragile (Pedrero et al., 2008).

Cadmium is also a tetratogenic and carcinogenic agent. Emissions of zinc and copper works contribute 60 percent of anthropogenic sources of pollution with cadmium. Phosphate fertilizers have been responsible for cadmium contamination of agricultural soils. Likewise, sludge from sewage treatment plants has added metals especially cadmium when used as soil amendment. Incineration of solid waste causes an extensive contamination of soil, air and water (Monasterio and Wuilloud, 2009).

Cadmium and its compounds are widely used in various field of industry for example in special alloys, as a pigment, in coating stabilizers, for corrosion resistant plating on steel, in the plastics industry and in rechargeable nickel cadmium batteries (Kocurova et al., 2013). Cadmium improves the mechanical properties of zinc alloys which are used as sacrificial anodes in corrosion protection of structural steel work immersed in seawater (Kaur et al., 2007). Cadmium is used as a barrier to control neutrons in a nuclear fission.

In spite of the applications, toxicity of cadmium necessitates the development of simple, sensitive and reliable method for its determination. A survey of literature reveals that for determination of cadmium(II) various techniques were used including ratio derivative polarography (Ni, 1998), differential pulse polarography (Hussain et al., 2002), adsorptive stripping voltametry (Abbasi et al., 2011), flame AAS (Xiang et al., 2012), EAAS (Li et al., 2009), GF-AAS (Jahromi et al., 2007), ICP-OES (Salahinejad, 2011), ICP-MS (Jia et al., 2010).

Many of these methods are either time consuming or require complicated and expensive instrument. From this point of view, the development of rapid, simple and inexpensive analytical method is one of the areas of growing interest and becomes more accepted especially in environment and industrial field. Spectrophotometry is one of the most frequently used methods for cadmium(II) determination. The automation and feasibility of wide range determination are some of the favorable characteristics of spectrophotometric method (Sandell, 1965; Marczenko, 1976 ; Morrison and Freiser, 1996).

Several spectrophotometric reagents have been used for determination of cadmium(II) (Ling et al., 1996; Zhang, 1998; Amin, 2001; Gao et al., 2001; Lee and Choi, 2001; Hashem, 2002; Bulgariu et al., 2005; Li, 2006; Reddy et al., 2008; Parikh et al., 2009; Gopalakrishna et al., 2010; Meng et al., 2011; Wen et al., 2011; Amin and Gouda, 2012). A comparison of the present method with other solvent extraction and spectrophotometric methods for the determination of cadmium(II) is given in Table 1.

Table 1 Comparison of the present method with other spectrophotometric methods for the determination of cadmium(II)

Reagent	λ_{\max} nm	Acidity / pH	Beer's law validity range, ppm	Molar absorptivity Lit mol ⁻¹ cm ⁻¹ $^1\epsilon$	M:L ^a	Remarks	Reference
Meso-tetra-(2-chloro-4-sulfophenyl) porphyrin	434	2 M NH ₃	0-3.5	5.20×10^5	1:1	Heating required for 6-7 min	Ling et al., 1996
Amidoblack diazoaminoazobenzene	520	10.4	0-8	1.62×10^5	1:2	High pH(10.4)	Zhang, 1998
Thiazolylazo Reagent	616	9.0	0.003-4.0	2.14×10^5	1:2	Use of nonionic surfactant	Amin, 2001
p-Acetyl-benzenediazoaminoazobenzene	475	12.5	0-20	-	1:3	Standing time 10 min and use of high pH	Gao et al., 2001
Ammonium	323	7.0	03-10.0	-	1:2	Use of	Lee and

pyrrolidinedithiocarbamate						Tween 80 surfactant	Choi, 2001
4-(2-Pyridylazo)-resorcinol	510	5.5	0-4.49	2.5×10^5	1:1	Excessive use of HClO_4	Hashem, 2002
<i>p,p'</i> -Dinitro-sym diphenyl carbazid	630-640	0.02N NaOH	0.5-60	2.05×10^4	1:2	Extraction carried out in strong basic media	Bulgariu et al., 2005
2,6-Dimethylphenyl diazoaminobenzene	523	0.2 M NH_3	0-0.48	2.27×10^5	1:3	Reagent solution -in dimethyl-formamide	Li, 2006
Benzildithiosemicarbazone	360	10.5	-	0.196×10^4	1:1	Use of strong basic buffer	Reddy et al., 2008
2-Hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone	440	10.0	5.62-16.86	4.035×10^3	1:2	Color stability one h	Parikh et al., 2009
Cinnamaldehyde-4-hydroxybenzoyl hydrazone	383	9.0	0.056-0.562	5.6×10^4	1:1	Reagent is very sensitive	Gopalakrishna et al., 2010
3,5-Bis(4-phenylazophenyl aminodiazot)	530	10.5	0-12	2.8×10^5	-	Use of nonionic surfactant	Meng et al., 2011
Benzoic acid (BPPABA)	610	3.0	0-25	-	-	Triton X-100	

Dithiozone	610	3.0	0-25	-	-	Narrow pH range	Wen et al., 2011
1-(2- Bezothiazolylaz o)-2-hydroxy-3- naphthoic acid	692	pH 8.5	0.2-3.5	7.05×10^6	1:1	Oxalate interfere seriously	Amin and Gouda, 2012
^b 2',4'- Dinitro APTPT	425	9.5	2.5-17.5	6.463×10^3	1:2	Sensitive and selective	

a = Metal:ligand b = Present method

Derivatives of pyrimidine-2-thiol have long been extensively used for the analytical work, especially for extractive spectrophotometric determination of gold (Kamble et al., 2010), silver (Kamble et al., 2011^a), palladium, osmium, ruthenium (Anuse et al., 1983), copper (Kamble et al., 2011^b), cobalt (Kamble et al., 2011), selenium (Kolekar and Anuse, 1998^a), tellurium (Kolekar and Anuse, 1998^b) and bismuth (Kolekar et al., 1998^c). They act as chelating agents for metal ions bonding through 'S' atoms, sometimes 'N' or possibly both jointly. A measure feature of these reagents is their high selectivity for transition and non transition metal ions.

In this work, we present a highly selective, rapid and sensitive spectrophotometric method for determination of cadmium(II) using a 2,4 dinitrophenyl derivative of pyrimidine-2-thiol as a chromogenic chelating reagent.

The proposed method has been successfully employed for the determination of cadmium(II) in binary and synthetic mixtures, alloys, tobacco sample and thin film and quantum dot nano composite material sample.

2. Experimental

2.1. Apparatus

Elico digital spectrophotometer model Systronic 106 equipped with a quartz cell of 1.0 cm path length was used in these investigations for making absorbance measurements. Elico digital pH meter model LI-127 was used to make pH measurements.

Glass vessels were cleaned by soaking in acidified solutions of potassium dichromate, followed by washing with soap water and rinsed two times with water.

2.2. Standard Cadmium(II) solution

A stock solution of cadmium(II) 1 mg mL^{-1} was prepared by dissolving 1.631 g of cadmium chloride dried at 110°C in water containing 2 mL of concentrated hydrochloric acid and then diluting the solution with double distilled water to 1 litre (Marczenko, 1976). The stock solution was then standardized by EDTA titration (Vogel, 1975) using xylenol orange as an indicator. Working standard solutions were prepared by suitable dilutions of stock solution.

2.3. 1-(2',4'-Dinitroaminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol solution

1-(2',4'-Dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol, [2',4'- dinitro APTPT] was synthesized and recrystallised as reported by R. A. Mathes (Mathes et al., 1948; Mathes, 1953). A 0.01 M stock solution was prepared by dissolving 0.1685 g of 2',4'-dinitro APTPT in a 50 mL of chloroform.

2.4. Solutions of foreign ions

Other standard solutions of different metals used to study the effect of foreign ions were prepared by dissolving weighed quantity of their salts in water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving respective alkali metal salts in water. The synthetic mixtures containing cadmium(II) were prepared by combining with commonly associated metal ion in definite composition.

All the chemicals employed were analytical reagent grade. Double distilled water was used throughout the experiment.

2.5. Recommended procedure

An appropriate volume of the sample solution containing 100 µg of cadmium(II) was placed in 25 mL standard flask and diluted with water and pH was adjusted to 9.5. The resulting solution was transferred into a 125 mL separatory funnel and thoroughly mixed with 5.0 mL of 0.01 mol L⁻¹ 2', 4'-dinitro APTPT reagent in chloroform and 5.0 mL of 0.5 mol L⁻¹ pyridine in chloroform. The volume ratio of the aqueous and organic phases was 25:10 (2.5:1). The resulting mixture was equilibrated for seven minutes and then the two phases were allowed to separate. The organic layer having an orange red color was dried over anhydrous sodium sulphate and was transferred to 10 mL standard flask and made upto the mark with chloroform. The absorbance of the colored complex was measured at 425 nm with 1.0 cm quartz cell against reagent blank prepared in similar manner without addition of metal. Percentage extraction (%E) and metal distribution ratio (D) were calculated according to Eq. (1) and (2), respectively.

$$\% E = \frac{[M]_{org}}{[M]_{aq \text{ init.}}} \times 100 \quad (1)$$

$$D = \frac{[M]_{org}}{[M]_{aq}} \times 100 \quad (2)$$

where, $[M]_{aq \text{ init.}}$ represents the initial concentration of metal ion in the aqueous phase. $[M]_{aq}$ and $[M]_{org}$ are the total concentrations of metal ion in the aqueous and organic phases after equilibrium, respectively.

3. Results and discussion

3.1. Absorption spectra and spectral characteristics of colored complex

The absorption spectra of the reagent and colored complex are shown in Fig. 1. The maximum absorption of the reagent is at 400 nm against chloroform as blank and that of complex is at 425 nm against reagent blank. Therefore all the spectral measurements of the complex have been carried out at 425 nm. Spectral characteristics of the complex are given in Table 2.

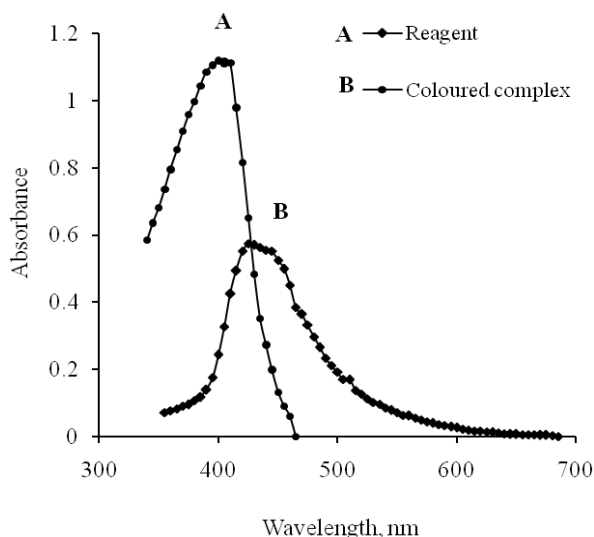


Fig 1. (A) Absorption spectra of 2',4'-dinitro APTPT Vs. Chloroform blank. (B) Absorption spectra of Cd(II)-2',4'-dinitro APTPT-pyridine complex vs. 2',4'dinitro APTPT blank. Cd(II) = 10 $\mu\text{g mL}^{-1}$; 2',4'-dinitro APTPT = 5.0 mL of 0.01 mol L^{-1} ; pyridine = 5.0 mL of 0.5 mol L^{-1} ; pH = 9.5; Shaking time = 7 min

Table 2 Spectral characteristics and precision data of cadmium(II)-2',4'-dinitro APTPT-pyridine Complex

Optical characteristics and precision	Parameters
Solvent	Chloroform
λ_{max} (nm)	425
pH range	9.3–9.7 (9.5)
2',4'-dinitro APTPT concentration	5 mL (0.01 mol L^{-1})
Pyridine concentration	5 mL (0.5 mol L^{-1})
Equilibrium time (min)	7
Stability (h)	> 20
Beer's law range ($\mu\text{g mL}^{-1}$)	1.0–12.5
Ringbom optimum conc. range ($\mu\text{g mL}^{-1}$)	2.5–12.5
Molar absorptivity ($\text{lit mol}^{-1} \text{cm}^{-1}$)	6.436×10^3
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.01739
Relative standard deviation*, (%)	0.11
Range of error	± 0.2
Mean recovery	99.9 ± 0.04
Stoichiometry of the extracted complex	1:2:2 (M:L:Y)

* Average of five determinations

3.2. Effect of pH

The results in Fig. 2 showed that the optimum pH range for the formation of Cd(II)-2', 4'-dinitro APTPT-pyridine complex was in the range of 9.3 - 9.7. At pH values below 9.0 or above 10.0 the

absorbance decreased significantly. For further study, pH 9.5 was used for optimized analytical procedure.

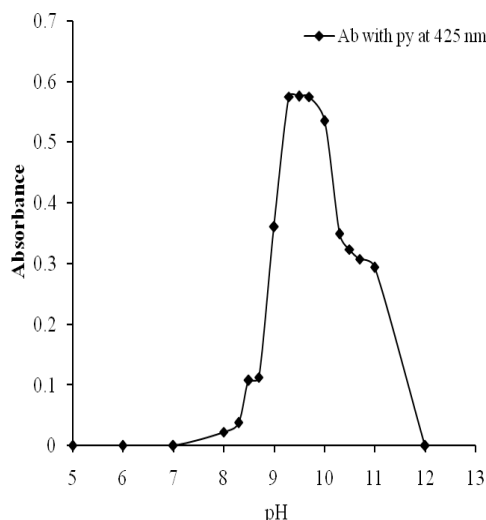


Fig. 2. Effect of pH on the extraction of Cd(II)-2',4'-dinitro APTPT-pyridine complex: Cd(II) = 10 $\mu\text{g mL}^{-1}$; 2',4'-dinitro APTPT = 5.0 mL of 0.01 mol L^{-1} ; pyridine = 5.0 mL of 0.5 mol L^{-1} ; pH = 1 to 14; Shaking time = 7 min; λ_{max} = 425 nm

3.3. Effect of solvent

The main requirement for the liquid-liquid extraction are solvents which have high extraction efficiency for the target analyte, its immiscibility with water, density higher than that of water and minimum absorbance for the blank test. Various solvents which are usually employed were evaluated as the extractant in this work including kerosene (0%), carbon tetrachloride (0.35%), *n*-butanol (1.04%), amyl acetate (1.56%), amyl alcohol (1.74%), xylene (6.08%), toluene (19.96%), methyl iso-butylketone (52.25%), 1,2-dichloro ethane (68.4%), chloroform (99.9%). Percentage extraction (%E) values are given in parenthesis. The experimental results demonstrated that chloroform provided higher extraction efficiency than others. Besides that chloroform has lower toxicity and solubility. Therefore chloroform was selected as extractant in the entire study.

3.4. Effect of 2',4'-dinitro APTPT concentration

The optimum concentration of 2', 4'-dinitro APTPT reagent for maximum color development was determined by carrying out a set of experiments using fixed Cd(II) ion concentration (100 $\mu\text{g mL}^{-1}$). The reagent concentration was varied over a wide range from 0.001 mol L^{-1} to 0.01 mol L^{-1} . It is seen that the absorbance of the extract was highest at concentration of the reagent more than 0.003 mol L^{-1} . A concentration 0.005 mol L^{-1} of reagent was thus chosen for further studies.

3.5. Effect of shaking time and stability

The Cd(II) immediately formed the complex with 2', 4'-dinitro APTPT reagent in presence of pyridine. The optimum shaking time of 7 minutes was investigated by varying the shaking time. Prolonged shaking has no adverse effect on extraction of Cd(II).

The absorbance of Cd(II)-2', 4'-dinitro APTPT-pyridine complex in chloroform remains unchanged for 20 h under 25 °C. This showed that the complex is highly stable.

3.6. Effect of concentration of pyridine

The effect of pyridine concentration on complex formation was studied from 0 to 5.0 mL of 0.5 mol L⁻¹ to obtain maximum and constant color development. It was observed that color of Cd(II) complex into organic phase increases with increase in pyridine concentration. To ensure complete complexation, 5.0 mL of 0.5 mol L⁻¹ pyridine was used as a synergent in the extraction of Cd(II) with 2', 4'-dinitro APTPT reagent.

3.7. Effect of temperature

The effect of temperature on extraction of Cd(II) at pH 9.0 using 5.0 mL of 0.01 mol L⁻¹ 2',4'-dinitro APTPT and 5.0 mL of 0.5 mol L⁻¹ pyridine at varying temperature from 301 to 313 K was studied. It was shown that, the distribution coefficient increases with increase in temperature. The extraction equilibrium constant (K_{ex}) with change in temperature is expressed by Van't Hoff equation.

$$d(\log K_{ex}) / d(1/T) = -\Delta H / 2.303 R$$

The plot of $\log K_{ex}$ versus $1000/T$ is linear with slope value -4.523 (Fig. 3) and the enthalpy change $\Delta H = 86.60$ KJ mol⁻¹. It means that extraction of Cd(II) with 2', 4'-dinitro APTPT reagent in presence of pyridine is endothermic process. The free energy ΔG and entropy ΔS were calculated from the equations (3) and (4), respectively.

$$\Delta G = -2.303 RT \log K_{ex} \quad (3)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (4)$$

The negative values of free energies (ΔG) indicate that reaction is spontaneous. The positive enthalpy (ΔH) value indicates that the extraction of Cd(II) with 2', 4'-dinitro APTPT reagent in presence of pyridine was favorable with rise in temperature.

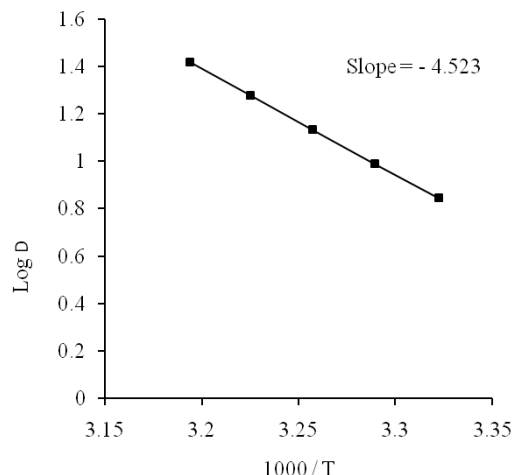


Fig 3. Effect of temperature on the extraction of Cd(II)-2',4'-dinitro APTPT-pyridine complex: Cd(II) = 10 μ g mL⁻¹; 2',4'-dinitro APTPT = 5.0 mL of 0.01 mol L⁻¹; pyridine = 5.0 mL of 0.5 mol L⁻¹; pH = 9.0; Shaking time = 7 min; λ_{max} = 425 nm

3.8. Beer's law and sensitivity

Under the optimum conditions, absorbance of the complex obey Beer's law in the Cd(II) ion concentration range of 1.0-12.5 μ g mL⁻¹, which is shown in Fig. 4. A Ringbom's plot (Ringbom, 1939) showed that the optimum working range for the determination of Cd(II) was 2.5-12.5 μ g mL⁻¹. The molar absorptivity and Sandell's sensitivity were found to be 6.463×10^3 L mol⁻¹ cm⁻¹ and

0.01739 $\mu\text{g cm}^{-2}$, respectively. The standard deviation calculated from ten determinations in a solution containing 10 $\mu\text{g mL}^{-1}$ of Cd(II) is 0.03 and relative standard deviation of the method is 0.11%.

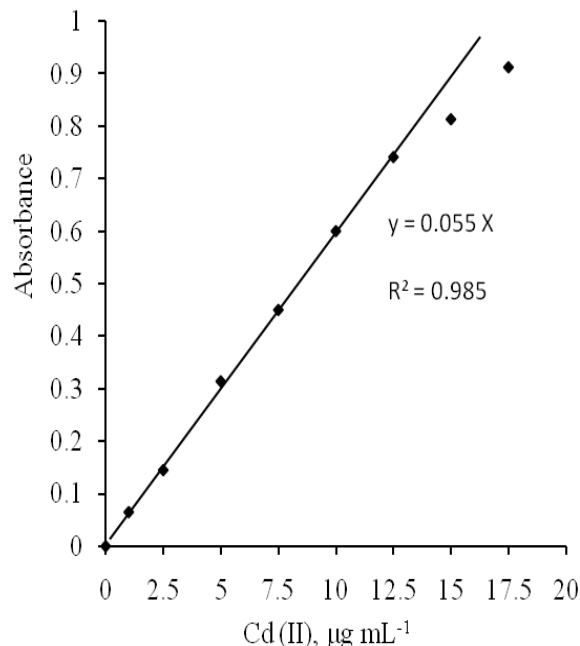


Fig 4. Beer's plot of Cd(II)-2',4'-dinitro APTPT-pyridine complex: Cd(II) = 1.0 – 17.5 $\mu\text{g mL}^{-1}$; 2',4'-dinitro APTPT = 5.0 mL of 0.01 mol L⁻¹; pyridine = 5.0 mL of 0.5 mol L⁻¹; pH = 9.5; Shaking time = 7 min; λ_{max} = 425 nm

3.9. Precision and accuracy of the method

In order to test the accuracy and precision of the methods, five successive measurements were carried out with standard solutions containing 100 μg of Cd(II). The percentage relative standard deviation was calculated by the proposed method. The results are summarized in Table 2.

3.10. Stoichiometry of the complex

The composition of extracted species was ascertained by Mole ratio (Yoe and Jones, 1944) (Figure 5) and Job's method of continuous variation (Job, 1928) (Figure 6). Hence, probable composition of extracted species was calculated to be 1:2:2 (Metal:Thiol:Pyridine). The composition of extracted species was also confirmed by slope ratio method.

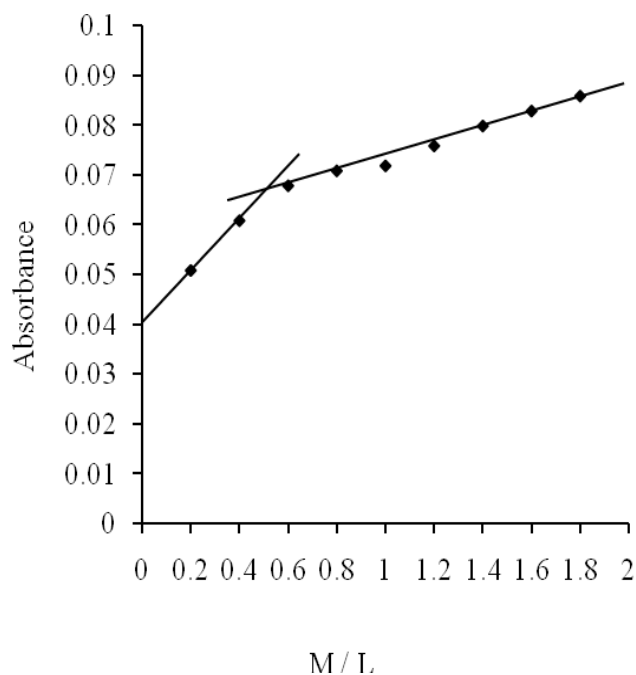


Fig. 5. Mole ratio method: Cd(II) = 0.2 to 1.8 mL of 2.66×10^{-3} mol L⁻¹; 2',4'-dinitro APTPT = 1.0 mL of 2.66×10^{-3} mol L⁻¹; pyridine = 5.0 mL of 0.5 mol L⁻¹; pH = 9.5; Shaking time = 7 min; λ_{\max} = 425 nm

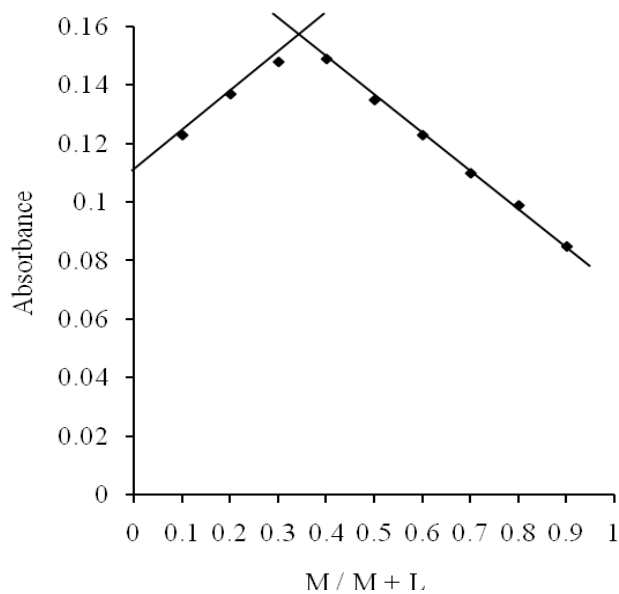
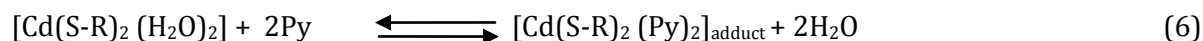
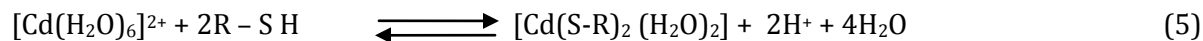


Fig 6. Job's plot method: Cd(II) = 0.2 to 1.8 mL of 2.66×10^{-3} mol L⁻¹, 2',4'-dinitro APTPT = 1.8 to 0.2 mL of 2.66×10^{-3} mol L⁻¹; pyridine = 5.0 mL of 0.5 mol L⁻¹; pH = 9.5; Shaking time = 7 min; λ_{\max} = 425 nm

The reactions of Cd(II) with the reagent and pyridine may therefore be represented as follows by the equation (5) and (6).



Based on these reactions, the probable structure of extracted species in organic phase is shown in Fig. 7.

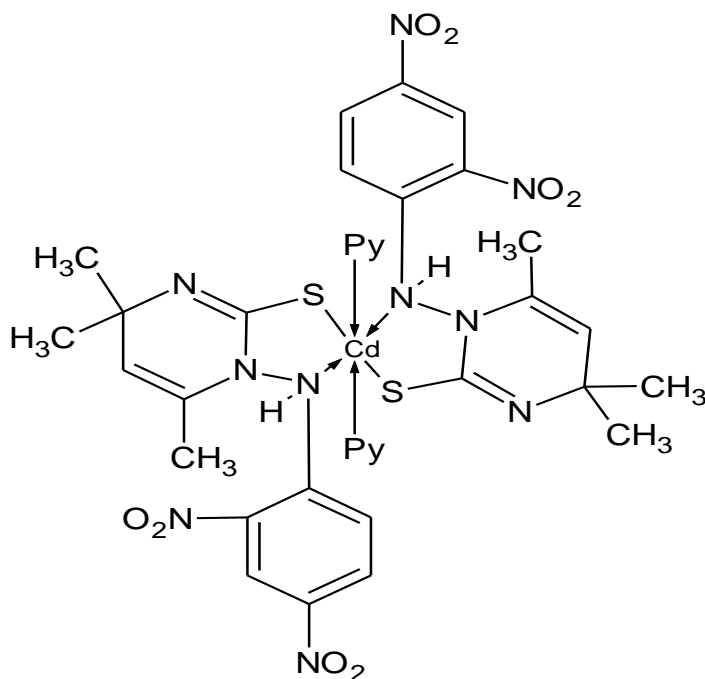


Fig 7. Probable structure of Cd(II)- , 2',4'-dinitro APTPT-pyridine complex (adduct)

3.11. Effect of diverse ions

To assess the possible analytical applications of the proposed method, the effect of diverse ions was examined by carrying out determination of $100 \mu\text{g mL}^{-1}$ Cd(II) with a known amount of diverse ion solutions using the recommended analytical procedure. The tolerance criteria for a given ion was taken as deviation of the absorbance value more than $\pm 2\%$ from the value expected for Cd(II) alone. The results clearly indicate that most of the metal ions can be tolerated in considerable amount (Table 3).

Table 3 Effect of diverse ions for the determination of $10 \mu\text{g mL}^{-1}$ cadmium(II) with 2',4'-dinitro APTPT at 425 nm (relative error $\pm 2\%$)

Amount tolerated (mg)	Foreign ions
75	Iodide, Nitrite, Thiosulphate, Citrate, Oxalate, Succinate, Salicylate, Tartrate, Malonate, Acetate, Thiocyanate
50	Nitrate, Fluoride
25	Bromide, Phosphate, Sulphate, Ascorbate
15	Sn(II), Tl(I)
10	Pb(II), Sb(III), Se(IV), Te(IV), Sr(II), W(VI)
5	Ga(III), Ca(II), Ba(II), Fe(II)
3	Co(II) ^a , Al(III), Mn(II), Thiourea
1	Cr(VI), Bi(III), Ce(IV), Pt(IV), U(VI), Mn(VII), Ag(I) ^b , Au(III) ^b
0.1	Cu(II) ^b , Pd(II) ^b , Hg(II) ^d , Fe(III) ^e , V(V) ^f , Th(IV) ^f
0.05	Ni(II) ^a , Zn(II) ^c

^a Masked with 75 mg citrate

^b Masked with 75 mg thiosulphate

^c Masked with 75 mg thiocyanate

^d Masked with 25 mg sulphate

^e Masked with 75 mg tartrate

^f Masked with 50 mg fluoride

4. Applications

4.1. Separation of cadmium(II) from associated metal ions

In order to validate the methodology, the proposed method was applied for the separation and determination of Cd(II) from associated metal ions containing Cu(II), Fe(III), Ni(II), Bi(III), Hg(II), Se(IV), Te(IV), Co(II), Tl(I), Al(III), Ge(IV), etc. Under optimized conditions the added metal ion remained quantitatively in the aqueous phase which was evaporated to moist dryness by treating with 5.0 ml concentrated hydrochloric acid. The residue was dissolved in water and diluted to appropriate volume. The added metal ions were determined by standard methods. However, Cu(II), Co(II), Ni(II), Hg(II), were coextracted under the optimized extraction condition of Cd(II). Separation of Cd(II) from these metal ions can be achieved by using thiosulphate for Cu(II), citrate for Co(II), Ni(II) and sulphate for Hg(II) as a masking agent. The added metal ions remained in aqueous phase were subsequently demasked by treating with 5.0 ml concentrated nitric acid and determined by reported method (Table 4). The extracted Cd(II)- 2', 4'-dinitro APTPT-pyridine complex estimated spectrophotometrically at 425 nm against reagent blank.

Table 4 Separation of cadmium(II) from associated metal ions

Metal ion	Amount taken (µg)	Average % recovery*	R.S.D %	Chromogenic ligand	Reference
Cd(II)	100	99.9	0.04		
^a Co(II)	100	99.9	0.13	Thiocyanate +Ascorbic acid	Marczenko 1996
Cd(II)	100	99.9	0.13		
^a Ni(II)	50	99.7	0.05	DMG	Marczenko 1996
Cd(II)	100	99.8	0.09		
Bi(III)	300	99.9	0.04	Ascorbic acid + KI	Marczenko 1996
Cd(II)	100	99.8	0.06		
Tl(I)		99.8	0.19	Starch + Iodide	Marczenko 1996
Cd(II)	100	99.9	0.08		
Ge(IV)	50	99.8	0.16	Phenyl fluorone	Marczenko 1996
Cd(II)	100	99.9	0.22		
Fe(III)	100	99.8	0.53	Thiocyanate	Marczenko 1996
Cd(II)	100	99.9	0.06		
^b Cu(II)	50	99.8	0.31	2',4'-dinitro APTPT	Kamble et al.,2011 ^b
Cd(II)	100	99.9	0.09		
Se(IV)	200	99.9	0.14	4'-bromo PTPT	Kolekar and Anuse 1998 ^a
Cd(II)	100	99.8	0.26		
Te(IV)	300	99.9	0.04	4'-bromo PTPT	Kolekar and Anuse 1998 ^b
Cd(II)	100	99.9	0.04		
^c Hg(II)	100	99.6	0.17	PAR	Flaschka and Barnard 1972
Cd(II)	100	99.9	0.12		
Al(III)	25	99.9	0.06	PAR	Flaschka and Barnard 1972

* = Average of five determinations

^a = Masked with 75 mg citrate

^b = Masked with 75 mg thiosulphate

^c = Masked with 25 mg sulphate

4.2. Determination of cadmium(II) from synthetic mixtures

The method was successfully applied to Cd(II) determination in several synthetic mixtures of varying composition containing 100 µg of Cd(II) and associated ions of known concentration followed by respective masking agents (Table 5). The results obtained were in good agreement with the amount added, which clearly indicates high accuracy and precision of the proposed method.

Table 5 Determination of cadmium(II) in a synthetic mixtures

Composition, µg	Average % Recovery*	R.S.D. %
Cd(II), 100; Pb(II), 300; Cu(II) ^a , 50	99.8	0.05
Cd(II), 100; Co(II) ^b , 300; Ni(II) ^b , 50	99.9	0.19
Cd(II), 100; Hg(II) ^c , 100; Au(III), 300	99.8	0.09
Cd(II), 100; Ag(I), 300; Pd(II) ^a , 100	99.9	0.15
Cd(II), 100; Al(III), 300; Tl(I), 300	99.7	0.24
Cd(II), 100; Fe(III) ^d , 50; Co(II), 300	99.8	0.17
Cd(II), 100; Ga(III), 300; Al(III), 300	99.9	0.09
Cd(II), 100; Tl(I), 300; Ga(III), 300	99.9	0.17

* = Average of five determinations

^a = Masked with 75 mg thiosulphate

^b = Masked with 75 mg citrate

^c = Masked with 25 mg sulphate

^d Masked with 75 mg tartrate

4.3. Analysis of cadmium(II) from alloys

To demonstrate the applicability, the proposed method was applied to the determination of Cd(II) in alloys (Table 6). About 0.1gm of alloy was dissolved in 5.0 mL of *aqua regia* and heated almost to dryness. The nitrate was expelled from the residue using 3.0 mL of concentrated hydrochloric acid. Residue was filtered to remove silica and metastannic acid, if present. The solution was boiled with hot water and filtered through Whatman filter paper No 1. The filtrate was diluted to 100 mL with distilled water. An aliquot of the solution was analysed by the proposed method.

Certified samples of bearing metal alloy, Wood's metal alloy, Silver cadmium bearing soft soldering alloy, Braze 053 were not available therefore synthetic mixtures corresponding to the composition to these alloys were prepared. The proposed method was applied to the determination of Cd(II) in synthetic mixtures of alloys.

Table 6 Determination of cadmium(II) from alloy

Alloy	Certified composition (%)	Amount of Cd(II) found* (%)		Confidence limit $\alpha = 0.95$	R.S.D., %
		Proposed method	AAS method		
Bearing metal alloy Sample No.1	Cd, 100; Ni ^a , 1.49; Ag, 4.96	99.89	99.99	0.06	0.09
Bearing metal alloy Sample No.2	Cd, 100; Ni ^a , 2.35; Ag, 2.09	99.99	99.98	0.21	0.06
Braze 053 specialized silver Cadmium bearing soft soldering alloys	Cd, 100; Ag, 5.26	99.98	99.97	0.04	0.16
Silver Cadmium Bearing soft soldering alloy	Cd, 100; Ag, 6.33; Zn ^b , 20.25	99.97	99.95	0.09	0.07
Wood's metal alloy	Cd, 100; Sn, 100; Bi, 400; Pb, 200	99.98	99.99	0.06	0.29
Solder metal alloy	Cd ^{**} , 100; Pb, 40; Sn, 60	99.99	99.89	0.08	0.05

* = Average of five determinations
75 mg citrate

** = Amount added before analysis
^b = Masked with 75 mg thiocyanate

^a = Masked with

4.4. Analysis of cadmium(II) from CdS thin film and quantum dot solution

Thin film sample was boiled with 10 mL *aqua regia* and evaporated to moist dryness by gentle heating on hot plate. The solution was boiled with hot water and filtered through Whatman filter paper No. 1. The residue was evaporated to moist dryness by the addition of 2 x 5 mL portions of concentrated HCl. The solution was boiled with hot water and filtered through Whatman filter paper No 1. Filtrate was collected in 50 mL standard flask and finally diluted to 50 mL with distilled water. A suitable aliquot of the sample solution was analysed for Cd(II) by recommended procedure.

Quantum dot solution of Cadmium(II) sulphide was treated with concentrated sulphuric acid and was appropriately diluted to obtain the concentration in the required range. A suitable aliquot of the sample solution was analysed for Cd(II) by recommended procedure. The results were found to be in good agreement with those obtained by AAS (Table 7).

Table 7 Determination of cadmium(II) from CdS thin film and quantum dot solution

Nanomaterial Sample	Certified value µg/ml	Amount of Cd(II) found* µg/ml		Confidence limit $\alpha = 0.95$	R.S.D., %
		Proposed method	AAS method		
CdS Thin film No.1	120.0	119.40	119.29	0.38	0.25
CdS Thin film No.2	63.0	62.44	62.46	0.31	0.40
CdS Quantum dot solution	112.4	112.01	112.2	0.15	0.10

* = Average of five determinations

4.5. Analysis of cadmium(II) from cigarette tobacco

The tobacco of cigarette was dried in open air, weighed and dissolved in 2 mL of A. R. Grade concentrated sulphuric acid and heated on hot plate for 20 min. The contents were diluted with 20 mL of water and filtered. The filtrate was collected in 50 mL standard flask and diluted upto the mark with distilled water. An aliquot (2 to 5 mL) of the sample was taken and Cd(II) was determined by proposed method and predetermined calibration plot. To validate the accuracy of determination of cadmium(II) from tobacco sample, AAS was used for the comparison with the spectrophotometric determination which showed good consistency (Table 8).

Table 8 Determination of cadmium(II) from cigarette tobacco

Cigarette (Tobacco) Sample	Added µg/ml	Amount of Cd(II) found** µg/ml		Confidence limit $\alpha = 0.95$	R.S.D., %
		Proposed method	AAS method		
Sample No.1	0	ND*	2.3		
	100	102.3	102.3	0.19	0.32
Sample No.2	0	ND*	2.65		
	100	102.65	102.59	0.27	0.16
Sample No.3	0	ND*	3.5		
	100	103.5	103.5	0.34	0.08

* Not detected

** Average of five determinations

5. Conclusion

The present study demonstrates that the newly synthesized, 2', 4'-dinitro APTPT reagent is found to be excellent, selective, sensitive analytical chromogenic reagent for spectrophotometric determination of Cd(II).

Advantages of the proposed method are as follows:-

- i) Reagent is easily synthesized and purified. The solid reagent or its solution in chloroform remains stable for months.
- ii) The extraction procedure is single stage and rapid.
- iii) Very low reagent concentration is required for quantitative determination of Cd(II).
- iv) 2', 4'-dinitro APTPT reagent forms orange red colored ternary complex with Cd(II) in basic medium in presence of pyridine used as a synergent with molar composition 1:2:2(M:L:Py) and is stable upto 20 h.
- v) The proposed method has high selectivity and nearly all of the anions and most of the cations do not interfere with the chromogenic reaction. Use of suitable masking agent enhances the selectivity of the method.
- vi) Simplicity, sensitivity, rapidity besides accuracy and precision are the main advantages of the proposed method and is successfully applied for the determination of Cd(II) in real samples such as alloys, tobacco samples and thin film. The results are found to be in good agreement with those obtained by AAS.

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