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# Development of an reliable analytical method for synergistic extractive spectrophotometric determination of cobalt(II) from alloys and nano composite samples by using chromogenic chelating ligand

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#### ABSTRACT

A synergistic simple and selective spectrophotometric method was developed for the determination of cobalt(II) with 1-(2',4'-dinitro aminophenyl)-4.4.6-trimethyl-1.4-dihydropyrimidine-2-thiol [2',4'dinitro APTPT] as a chromogenic reagent. The proposed method has been described on the basis of synergistic effective extraction of cobalt(II) in presence of pyridine at pH range 9.5-10.2, showed orangered coloured ternary complex having molar ratio 1:2:2 (M:L:Py). The equilibrium time is 10 min for extraction of cobalt(III) from organic phase. The absorbance of coloured organic layer in chloroform is measured spectrophotometrically at 490 nm against reagent blank. The Beer's law was obeyed in the concentration range  $2.5-15 \,\mu g \, m L^{-1}$  of cobalt(II) and optimum concentration range was  $5-12.5 \,\mu g \, m L^{-1}$ of cobalt(II) and it was evaluated from Ringbom's plot. The molar absorptivity and Sandell's sensitivity of cobalt(II)-2',4'-dinitro APTPT-pyridine complex in chloroform are  $1.109 \times 10^3$  Lmol<sup>-1</sup> cm<sup>-1</sup> and 0.053 µg cm<sup>-2</sup>, respectively while molar absorptivity and Sandell's sensitivity of cobalt(II)-2',4'-dinitro APTPT complex in chloroform are  $6.22 \times 10^2$  L mol<sup>-1</sup> cm<sup>-1</sup> and 0.096 µg cm<sup>-2</sup>, respectively. The composition of cobalt(II)-2',4'-dinitro APTPT-pyridine complex (1:2:2) was established by slope ratio method, mole ratio method and Job's method of continuous variation. The ternary complex was stable for more than 48 h. The interfering effects of various cations and anions were also studied, and use of suitable masking agents enhances the selectivity of the method. The method is successfully applied for the determination of cobalt(II) in binary, synthetic mixtures and real samples. A repetition of the method was checked by finding relative standard deviation (R.S.D.) for n = 5 which was 0.15%. The reliability of the method is confirmed by comparison of experimental results with atomic absorption spectrophotometer.

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#### 1. Introduction

Cobalt occurs to the extent of 23 ppm by weight in the earth crusts. Cobalt is present in many ores at micro as well as macro level. Cobalt(II) ores are always found together with nickel and copper ores and sometimes with lead ore [1]. Mainly cobalt is used in metallurgical industries and about 20–25% is used for chemical industries [2]. Cobalt alloys are used in some relative industrial products because of their sufficient hardness and resistivity against oxidation. About 1/3 of cobalt produced is used for high temper-

ature alloys with steels. These alloys find important uses in gas turbine engines and in high speed steels which is used to make cutting tool for lathes. High working speed can be used as these tools retain their hardness and cutting edge even at red heat. Exceptionally hard alloys can be made instead of diamond in rocks, drills, e.g. Stellite (50% Co, 27% Cr, 12% W, 5% Fe, 2.5% C), and Widia metal (tungsten carbide WC with 10% Co).

About 1/3 of cobalt produced is used to make the pigments which are used to make blue ceramic glass and in paint industries. Cobalt is ferromagnetic like iron and nickel; 1/5 of the cobalt produced is used to make the magnetic alloys, such as, Alinico containing aluminium, nickel and cobalt. These alloys make permanent magnetes which are 20–30 times more powerful than Fe. Cobalt is used in cobaltoxide nano materials due to its magnetism and also in semiconducting materials.

Small amounts of cobalt salts of fatty acids from linseed oil and naphthanic acid are used as dryers, to speed the drying of the oil paints. Cobalt is an essential constitutent of fertile soil and is

*Abbreviations:* 4'-chloro PTPT, 1-(4'-chlorophenyl)-4,4,6-trimethyl(1H,4H)-2- pyrimidine thiol; 2',4'-dinitro APTPT, 1-(2',4'-dinitro aminophenyl)-4,4,6trimethyl-1,4- dihydropyrimidine-2-thiol; DMG, dimethylglyoxime; PAR, 4-(2pyridylazo) resorcinol; Py, pyridine.

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**Fig. 1.** (A) Absorption spectra of 2',4'-dinitro APTPT vs. chloroform blank, (B) absorption spectra of Co(II)-2',4'-dinitro APTPT-pyridine complex vs. 2',4'-dinitro APTPT blank. Co(II) = 10  $\mu$ g mL<sup>-1</sup>; pH = 9.7, 2',4'-dinitro APTPT = 5 cm<sup>3</sup> of 0.02 mol L<sup>-1</sup>; pyridine = 5 cm<sup>3</sup> of 1.0 mol L<sup>-1</sup>; solvent = chloroform; equilibrium time = 10 min; wavelength = 300–600 nm.

present in some enzymes and vitamin  $B_{12}$  (cynocobalamine) which are noted for biological activities. Artificial isotopes  $Co^{60}$  is radioactive and undergoes  $\beta$  decay, it gives intense high energy  $\gamma$  radiation, which is used in hospitals for radiotherapy of cancerous tumors. A wide range of cobalt containing compounds finds almost in all real samples, such samples are constant modulus alloys, magnetostrictive alloys, dental and prosthetic alloys, glass to metal seals, electrical resistance, heating elements, nano composite material samples and soft magnetic alloys.

On the other hand, cobalt is a vital trace element in animal nutrition and its deficiency may lead to retarded growth, loss of appetite, anemia and rapid recovery from these symptoms occurs upon feeding them with a cobalt supplemented diet. However, cobalt can irritate the gastro intestinal tract and can cause nausea, vomiting and diarrhea in humans while they are not particularly toxic to animals [3,4]. Therefore, the determination of cobalt is valuable for the quality control of artificial and biological samples, alloys and nano material composites in a simple, selective and sensitive manner.

A literature survey reveals that, there are several techniques and methods such as X-ray fluorescence [5], atomic fluorescence spectrometry [6], polarography [7], chromatography [8], atomic absorption spectrophotometry [9], and inductively coupled plasma-atomic emission spectrophotometry [10]. Among the most



**Fig. 2.** Effect of pH on the extraction of, (A) Co(II)-2',4'-dinitro APTPT-pyridine complex, (B) Co(II)-2',4'-dinitro APTPT complex. Co(II)=10  $\mu$ g mL<sup>-1</sup>; pH=1-14; 2',4'-dinitro APTPT=5 cm<sup>3</sup> of 0.02 mol L<sup>-1</sup>; pyridine=5 cm<sup>3</sup> of 1.0 mol L<sup>-1</sup>; solvent = chloroform; equilibrium time = 10 min,  $\lambda_{max}$  = 490 nm.

widely used analytical methods are those based on the spectrophotometric techniques due to the resulting experimental rapidity, simplicity and wide applications [11–28] (Table 1).

The main goal of the present report is to synthesize 1-(2',4'dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2thiol, as a sensitive chelating agent and developing a simple and proper method for spectrophotometric monitoring of cobalt traces. It was experimentally observed that, 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol reacts with cobalt(II) and produces orange-red coloured complex in presence of pyridine. This method is used for analyzing cobalt(II) from synthetic mixtures as well as alloys and nano composite material samples.

#### 2. Experimental

#### 2.1. Apparatus

Absorption spectra were obtained with an Elico digital spectrophotometer model Systronic 106 using 1 cm quartz cell. The pH values were determined with an Elico digital pH meter model LI-120.

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

#### Table 1

Comparison of the present method with other spectrophotometric methods for the determination of cobalt(II).

Reagent	$\lambda_{max}$ (nm)	Acidity/pH	Beer's law validity range (ppm)	Molar absorptivity $(L \operatorname{mol}^{-1} \operatorname{cm}^{-1} \varepsilon)$	M:L <sup>a</sup>	Remarks	Ref. no.
2-(2-Benzo- thiazolylazo)-2-p-cresol	615	pH 6.50-7.50	0-1.60	$\varepsilon = 1.62 \times 10^4$	1:3	Absorption Increased in presence of TritonX-100	[11]
5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	pH 9.4-10.0	655	0-0.40	$\varepsilon = 1.15 \times 10^5$	1:2	Cobalt(II) and Ni(II) determines simultaneously	[12]
4-(5-Bromo-2-pyridylazo)-1,3-diaminobenzene	2.4 M HCl	573	0.6-25	$\varepsilon = 1.16 \times 10^5$	1:2	10 min waiting for maximum colour absorbance	[13]
2-(2-Thiazolylazo)-4-methyl-5-(sulfo- methylamino) benzoic acid	рН 5.0	655	-	$\varepsilon$ = 6.0 × 10 <sup>4</sup>	-	Interference ions are masked by EDTA	[14]
2-(2-Thiazolylazo)-4-methyl-5-(sulfo- methylamino) benzoic acid	рН 5.0-6.0	655	0-13	$\varepsilon = 1.13 \times 10^5 \text{ s} = 0.52$	1:2	Successfully determined cobalt(II) from reagent grade Ni-salt and glass	[15]
Tetrametylene-bis(triphenyl- phosphonium)	pH 6.5	625	0-130	$\varepsilon = 1.5 \times 10^4$	1:1	Equilibrium time 30 s	[16]
Benzyltributylammonium tetrathiocyanato- cobaltate(II)	pH 7.0	625	0–120	ε = 1327	1:1	Method is sensitive	[17]
2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone	рН 6.0	468.5	0.059-3.299	-	-	Simultaneous determination of cobalt(II) and Ni(II)	[18]
4,4'-Diazobenzene- diazoaaminobenzobenzene	pH 10.2	540	0-7	$\varepsilon$ = 1.72 × 10 <sup>5</sup> s = 0.00035	-	Triton X-114 was used as a surfactant and complex was stable for 24 h	[19]
1-Nitroso-2-naphthol	pH 4.0	425	0.05-2.5	$\varepsilon = 4.62 \times 10^4$	-	Triton X-100 was used as a surfactant	[20]
2-(2-Pyridylazo)-5-ethylaminophenol	pH 1.0	550	0-25	$\varepsilon = 5.5 \times 10^4$	1:1	SDS was used as a surfactant	[21]
Benzeneacetaldehyde-4-hydroxy-α-oxo-aldoxime	pH 8.6–9.4	390	0.05-1.3	$\varepsilon = 2.746 \times 10^4$	1:3	Equilibrium time 1.5 min	[22]
3-Hydroxy-2-methyl-1,4-naphthoquinone 4-oxime	pH 6.0	430	0-19	$\varepsilon = 2.09 \times 10^4$	-	Extarction carried out 60 °C	[23]
Bis(salicylaldehyde) orthophenylene- diamine	0.005 M H <sub>2</sub> SO <sub>4</sub>	458	0.1-15	$\varepsilon = 1.109 \times 10^4 \text{ s} = 6.0$	1:1	Coloured complex stable for 24 h	[24]
Bis(5-bromosalicyl- aldehyde)orthophenylenediamine	pH 3.4–4.0	473	0.01-8.0	$\varepsilon$ = 5.84 × 10 <sup>4</sup> s = 9.0	1:1	Highly sensitive	[25]
5-[3-(1,2,4-Triazolyl-azo)]-2,4-dihydroxy- benzaldehyde	рН 8.0	535, 555	-	$\varepsilon = 2.0456 \times 10^4 \text{ s} = 2.881 \times 10^{-3}$	1:1	Coloured complex stable for 24 h	[26]
Isonitroso-5-methyl-2-hexanone	pH 8.8	400	0.1-5.0	$\varepsilon = 1.135 \times 10^4 \text{ s} = 5.176$	1:3	Equilibrium time 20 s	[27]
2-(2-Quinolinylazo)-5-diethylamino- benzoic acid	pH 4.0	630	0.01-0.32	$\varepsilon = 1.4 \times 10^5$	1:2	CTMAB was used as a surfactant	[28]
2',4'-Dinitro APTPT	pH 9.7	690	2.5-15	$\varepsilon = 2.843 \times 10^3 \text{ s} = 0.053$	1:2	Selective and reproducible	P.M. <sup>b</sup>

<sup>a</sup> Metal:ligand.

<sup>b</sup> Present method.

#### 2.2. Standard cobalt(II) solution

A stock solution of cobalt  $(1 \text{ mg mL}^{-1})$  was prepared by dissolving an accurately weighed amount of cobaltous oxide (4.085 g, Merck) in 1000 mL of water with a few drops of concentrated hydrochloric acid and standardized by a known method [29].

2.3. 1-(2',4'-Dinitro

aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol solution

1-(2',4'-Dinitro aminophenyl)-4,4,6-trimethyl-1,4dihydropyrimidine-2-thiol, [2',4'- dinitro APTPT] was synthesized and recrystallised as reported by Mathes [30]. A 0.02 M stock solution was prepared by dissolving 0.324 g of 2',4'-dinitro APTPT in a 50 cm<sup>3</sup> 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 quantities of their salts in water or dil. HCl. Solutions of anions were prepared by dissolving the respective alkaline metal salts in water. Different synthetic mixtures containing cobalt(II) were prepared by combining with commonly associated metal ions in definite composition. All of the chemicals used were of AR grade. Double distilled water was used throughout the work.

#### 2.5. Recommended procedure

An aliquot of the sample solution containing 100  $\mu$ g cobalt(II) solution was taken in 25.0 mL of calibrated flask and pH was adjusted to 9.7 with dilute hydrochloric acid and sodium hydroxide. The solution was transferred into a 125 mL separatory funnel and thoroughly mixed with 5.0 mL of a 0.02 mol L<sup>-1</sup> 2',4'-dinitro APTPT and 5.0 mL of 0.5 mol L<sup>-1</sup> pyridine in chloroform and made the total volume of organic phase to 10.0 mL by addition of 3.0 mL of chloroform and equilibrated for 10 min. The two phases were allowed to separate and dried over anhydrous sodium sulphate. The organic layer having an orange-red colour was transferred to a 10.0 mL of standard volumetric flask and made upto the mark with chloroform. The absorbance of the coloured complex was measured at 490 nm against reagent blank prepared in similar manner. Percentage extraction (%*E*) and metal distribution ratio (*D*) were calculated according to Eqs. (1) and (2), respectively.

$$%E = \frac{[M]_{\text{org.}}}{[M]_{\text{aq., init.}}} \times 100$$
<sup>(1)</sup>

$$D = \frac{[M]_{\text{org.}}}{[M]_{\text{aq.}}}$$
(2)

where  $[M]_{aq,,init}$  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 coloured complex

A orange-red colour complex formed with 2',4'-dinitro APTPT in presence of pyridine as an auxiliary ligand in chloroform have shown the maximum absorbance at 490 nm. The spectra of the reagent and coloured complex are shown in Fig. 1. And the spectral characteristics are given in Table 2.

#### Table 2

Spectral characteristics and precision data of cobalt(II)-2',4'-dinitro APTPT-pyridine complex.

Optical characteristics and precision	Parameters	
Solvent	Chloroform	
$\lambda_{max}$ (nm)	490	
pH range	9.5-10.2 (9.7)	
2',4'-Dinitro APTPT concentration	$5 \mathrm{mL}(0.02\mathrm{mol}\mathrm{L}^{-1})$	
Pyridine concentration	5 mL (1.0 mol L <sup>-1</sup> )	
Equilibrium time (min)	10	
Stability (h)	>48	
Beer's law range (µg mL <sup>-1</sup> )	2.5-15	
Ringbom optimum conc. range (µg mL <sup>-1</sup> )	5-12.5	
With pyridine		
Molar absorptivity (Lmol <sup>-1</sup> cm <sup>-1</sup> )	$2.843\times10^3$	
Sandell's sensitivity (µg cm <sup>-2</sup> )	0.023	
Without pyridine		
Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )	$6.22  imes 10^2$	
Sandell's sensitivity (µg cm <sup>-2</sup> )	0.096	
Relative standard deviation <sup>a</sup> , (%)	0.15	
Range of error	±0.2	
Mean recovery	$99.9\pm0.06$	
Stoichiometry of the extracted complex	1:2:2 (M:L:Y)	

<sup>a</sup> Average of five determinations.

#### 3.2. Effect of pH

The effect of pH on the formation of the cobalt(II)-2',4'-dinitro APTPT-pyridine complex was investigated by varying the pH of cobalt(II) solution in the range from 1 to 14 before the addition of the organic phase. The result in Fig. 2 showed that the optimal pH for the reaction of cobalt(II) with 2',4'-dinitro APTPT is 9.5–10.2 in the presence and absence of pyridine. However, in the presence of 5.0 mL of 0.5 mol L<sup>-1</sup> pyridine, there was enhancement of absorbance but in absence of pyridine absorbance was decreased in the same pH range. Thus, pyridine showed a synergistic effect on the extraction of cobalt(II) with 2',4'-dinitro APTPT complex. On the other hand, further increase in the pH caused a sharp decrease in the percentage extraction may due to hydrolysis of the complex. Hence, pH 9.7 was recommended for further studies.

#### 3.3. Effect of solvent

Various organic solvents were examined for the extraction of cobalt(II) with 2',4'-dinitro APTPT complex in presence of 5 mL of  $0.5 \text{ mol L}^{-1}$  pyridine. It was observed that, the percentage extraction (%*E*) values increased in the order of kerosene (4.3), *<n*-butanol (15.5)*<* amyl alcohol (23.8)*<* amyl acetate (36.5)*<* toluene (40.1)*<* xylene (54.3)*<* methyl-*iso*-butyl ketone (59.1)*<* 1,2-dichloroethane (73.1)*<* carbon tetrachloride (88.1)*<* chloroform (99.9). Among these, chloroform was used for further extraction.

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

The concentration of 2',4'-dinitro APTPT in chloroform was varied from 0.001 to  $0.01 \text{ mol } \text{L}^{-1}$  for full colour development in presence of 5.0 mL of  $0.5 \text{ mol } \text{L}^{-1}$  pyridine at pH 9.5. In absence of pyridine, absorbance was lowered. Therefore, the extraction of cobalt(II) was complete and reproducible with  $0.007 \text{ mol } \text{L}^{-1}$  2',4'-dinitro APTPT in presence of pyridine. However, 5 mL of  $0.02 \text{ mol } \text{L}^{-1}$  reagent was recommended in order to ensure the complete complexation. There was no significant change in the absorption with excess of the reagent concentration.



**Fig. 3.** Ringbom's plot for determination optimum cobalt(II) concentration. Co(II) = 25-225  $\mu$ g; pH = 9.7; 2',4'-dinitro APTPT = 5 cm<sup>3</sup> of 0.02 mol L<sup>-1</sup>; Pyridine = 5 cm<sup>3</sup> of 1.0 mol L<sup>-1</sup>; solvent = chloroform; equilibrium time = 10 min,  $\lambda_{max}$  = 490 nm.

#### 3.5. Effect of shaking time

The optimum shaking time of 7 min was determined by varying the shaking time from 0.5 to 20 min in absence and presence of pyridine. Prolonged shaking has no adverse effect on the extraction of cobalt(II) in presence of pyridine. Hence, a shaking time of 10 min was selected for subsequent experiment.

#### 3.6. Effect of concentration of pyridine

The effect of pyridine concentration was studied from 0 to 5.0 mL of  $0.5 \text{ mol } \text{L}^{-1}$  and 3.0-5.0 mL of  $1.0 \text{ mol } \text{L}^{-1}$  to obtain the maximum and constant colour development. It was observed that colour of cobalt(II) complex into organic phase increases with the pyridine concentration and remains constant from 3.0 mL of  $1.0 \text{ mol } \text{L}^{-1}$  pyridine. Therefore 5.0 mL of  $1.0 \text{ mol } \text{L}^{-1}$  pyridine was used for further extraction.

#### 3.7. Effect of colour stability of complex

The colour stability was studied at room temperature by measuring the absorbance at regular time intervals. The absorbance of the cobalt(II)-2',4'-dinitro APTPT-pyridine complex in chloroform was stable for more than 48 h. But in absence of pyridine, complex was stable for 9 h. This study indicates that pyridine showed synergistic effect on the extraction of cobalt(II). Hence, the time of measurement of absorbance of complex in presence of pyridine was not critical.



**Fig. 4.** Slope ratio method: with fixed pyridine concentration:  $Log D_{[Co(II)]} - Log C_{[2',4'-dinitro APTPT]}$  plot for determination of composition of extracted species in chloroform,  $Co(II) = 10 \ \mu g m L^{-1}$ ; pH = 9.0 and 10.5; 2',4'-Dinitro APTPT = 0.1–3.5 cm<sup>3</sup> of 0.02 mol L<sup>-1</sup>; Pyridine = 5 cm<sup>3</sup> of 1.0 mol L<sup>-1</sup>; solvent = chloroform; equilibrium time = 10 min,  $\lambda_{max} = 490 \ nm$ .

#### 3.8. Beer's law and sensitivity

The system obeyed Beer's law over the concentration range  $2.5-12.5 \,\mu g \, m L^{-1}$  of cobalt(II) and optimum concentration range is  $5-10 \,\mu g \, m L^{-1}$ , which is shown in Fig. 3 by Ringbom's plot method [31]. The sensitivity of the method defined by Sandell is  $0.023 \,\mu g \, cm^{-2}$  and molar absorptivity was  $2.843 \times 10^3 \, dm^3 \, mol^{-1} \, cm^{-1}$  in presence of pyridine while in absence of pyridine sensitivity and molar absorptivity is  $0.096 \,\mu g \, cm^{-2}$  and  $6.22 \times 10^2 \, dm^3 \, mol^{-1} \, cm^{-1}$ , respectively. The standard deviation calculated from ten determinations in a solution containing  $10 \,\mu g \, m L^{-1}$  of cobalt(II) is 0.02 and relative standard deviation of the method is 0.15%.

#### 3.9. Precision, accuracy of the method

The precision of the proposed method was ascertained from the absorbance values of the actual determinations of five replicates of fixed amounts of the cobalt(II) samples. To determine the accuracy of the proposed method; different amount of samples containing cobalt(II) were taken within the optimum Beer's range limits and analyzed by the recommended procedure. The percentage relative standard deviation was calculated by the proposed method. The results are summarized in Table 2.



**Fig. 5.** Slope ratio method: With fixed 2',4'-dinitro APTPT concentration:  $Log D_{[Co(II)]} - Log C_{[Pyirdine]}$  plot for determination of composition of extracted species in chloroform, Co(II) = 10 µg mL<sup>-1</sup>; pH = 9.0 and 10.5; 2',4'-dinitro APTPT = 5 cm<sup>3</sup> of 0.02 mol L<sup>-1</sup>; pyridine = 0.1-3.5 cm<sup>3</sup> of 1.0 mol L<sup>-1</sup>; solvent = chloroform; equilibrium time = 10 min;  $\lambda_{max} = 490$  nm.

#### 3.10. Stoichiometry of the complex

The composition of extracted species was ascertained by slope ratio method in which graph of  $\log D_{[Co(II)]}$  against  $\log C_{[2',4'-dinitro$  $APTPT]}$  at fixed 0.5 mol L<sup>-1</sup> pyridine concentration is plotted. The plots were linear having the slopes 1.80 and 1.83 at pH 9.0 and 10.5, respectively (Fig. 4). Also plots of  $\log D_{[Co(II)]}$  against  $\log C_{[pyridine]}$ at fixed 0.02 mol L<sup>-1</sup> 2',4'-dinitro APTPT concentration were linear with slopes of 1.9 and 1.8 at pH 9.0 and 10.5, respectively (Fig. 5). 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 Mole ratio [32] (Fig. 6) and Job's method of continuous variation [33].

The reactions of cobalt(II) with the reagent and pyridine may therefore be represented as follows by the Eqs. (3) and (4).

$$[Co(H_2O)_6]^{2+} + 2R - SH \rightleftharpoons [Co(S-R)_2(H_2O)_2] + 2H^+ + 4H_2O$$
(3)

$$[\operatorname{Co}(S-R)_2(H_2O)_2] + 2Py \leftrightarrows [\operatorname{Co}(S-R)_2(Py)_2] \text{adduct} + 2H_2O \qquad (4)$$

Based on the above reactions the probable structure is recommended for the complex as shown in Fig. 7.



**Fig. 6.** Mole ratio method for determination of composition of complex. Co(II)-2',4'-dinitro APTPT-pyridine complex; Co(II)=0.2-1.8 mL of 30  $\mu$ g mL<sup>-1</sup>; pH=9.7; 2',4'-dinitro APTPT=1.0 cm<sup>3</sup> of 5.090 × 10<sup>-3</sup> mol L<sup>-1</sup>; equilibrium time = 10 min; pyridine = 5.0 cm<sup>3</sup> of 5.090 × 10<sup>-3</sup> mol L<sup>-1</sup>; solvent = chloroform;  $\lambda_{max}$  = 490 nm.

#### 3.11. Effect of diverse ions

The selectivity of the method was investigated by the determination of 100  $\mu$ g of cobalt(II) in the presence of number of cations and anions within a relative error of  $\pm 2\%$ . The tolerance limits for cations and anions are summarized in Table 3. The interference of cations was removed by using suitable masking agents, therefore method becomes more selective.



Fig. 7. Structure of Co(II)-2',4'-dinitro APTPT-pyridine complex.

#### Table 3

Effect of diverse ions for the determination of 10  $\mu$ g mL<sup>-1</sup> cobalt(II) with 2',4'-dinitro APTPT at 490 nm (relative error  $\pm 2\%$ ).

Amount tolerated, Mg	Foreign ions
25	Pb(II), Sn(II), Al(III), Mg(II), Ca(II), Ta(V),
	Thiocyanate, Phosphate, Salicyalate
15	Mn(II), Zn(II), Ga(III), Tl(I), Sr(II), Mo(VI)
10	Cr(III), Se(IV), Te(IV), Pd(II) <sup>a</sup> , Hg(II) <sup>a</sup> , Citrate,
	Acetate, EDTA
5	Cr(VI), Bi(III), In(III), Ba(III), Pt(IV), Ni(II) <sup>b</sup> , Sulphate,
	Fluoride, Nitrate, Thiosulphate
3	Fe(III), Sb(III), Cu(II) <sup>a</sup> , Cd(II) <sup>b</sup> , Iodide, Bromide,
	Nitrite, Thiourea
1	Ag(I) <sup>a</sup> , Fe(II), Au(III)
0.5	Nb(V), Zr(IV)
0.3	U(VI)
0.1	Th(IV), Gd(III)

<sup>a</sup> Masked with 3 mg of I<sup>-</sup>.

<sup>b</sup> Masked with 10 mg EDTA.

#### 4. Applications

#### 4.1. Separation of cobalt(II) from associated metal ions

The method was successfully applied for the separation and determination of cobalt(II) from associated metal ions containing Au(III), Sb(III), Cu(II), Pd(II), Fe(III), Ru(III), Ni(II) and Mn(II).

Cobalt(II) separated from Au(III), Sb(III), Fe(III), Ru(III), and Mn(II) by optimized recommended procedure. Under optimized conditions, added metal ions 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 [34–36].

Copper(II), Ni(II), and Pd(II) were co-extracted under the optimum extraction condition of cobalt(II), therefore, separation of cobalt(II) from these metal ions can be achieved by using I<sup>-</sup> for Cu(II) and EDTA for Ni(II) and Pd(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 methods [35,37,38] (Table 4).

#### Table 4

Separation of cobalt(II) from associated metal ions.

Metal ion	Amount taken (µg)	Average % recovery <sup>a</sup>	R.S.D. %	Chromogenic Ref. no. ligand
Co(II)	100	99.8	0.08	
Au(III)	100	99.9	0.09	2′,4′-dinitro [34] APTPT
Co(II)	100	99.9	0.09	
Sb(III)	250	98.7	1.32	Ascorbic [35] acid + KI
Co(II)	100	99.9	0.21	
Cu(II) <sup>b</sup>	300	99.8	0.09	2′,4′-Dinitro [37] APTPT
Co(II)	100	99.9	0.13	
Pd(II)	100	99.7	0.09	4'-Chloro [38] PTPT
Co(II)	100	99.9	0.09	
Fe(III)	100	98.8	0.08	Thiocyanate [35]
Co(II)	100	99.9	0.09	
Ru(III)	200	99.7	0.18	Thiourea [36]
Co(II)	100	99.9	0.09	
Ni(II) <sup>c</sup>	75	98.4	1.51	DMG [35]
Co(II)	100	99.9	0.09	
Mn(II)	100	99.9	0.13	PAR [35]

<sup>a</sup> Average of five determinations.

<sup>b</sup> Masked with 3 mg I<sup>-</sup>.

<sup>c</sup> Masked with 10 mg EDTA.

#### Table 5

Determination of cobalt(II) in a synthetic mixtures.

Composition, µg	Average % recovery <sup>a</sup>	R.S.D. (%)
Co, 100; Au, 100; Ag, 50	99.9	0.14
Co, 100; Cu <sup>b</sup> ,300; Au, 100	99.8	0.18
Co, 100; Ag, 50; Cu <sup>b</sup> , 300	99.8	0.15
Co, 100; Ni <sup>c</sup> , 100; Cu <sup>b</sup> ,300	99.8	0.17
Co, 100; Fe, 100; Mn, 100	99.8	0.20
Co, 100; Ni <sup>b</sup> , 100; Pd, 100	99.9	0.14
Co, 100; Fe, 100; Ru, 100	99.5	0.50
Co, 100; Pd, 100; Au, 100	99.8	0.21
Co, 100; Zn, 100; Cd <sup>c</sup> , 300	99.8	0.20
Co, 100; Hg <sup>b</sup> , 100; Ag, 50	99.9	0.10

<sup>a</sup> Average of five determinations.

<sup>b</sup> Masked with 5 mg I<sup>−</sup>.

<sup>c</sup> Masked with 10 mg EDTA.

#### Table 6

Determination of cobalt(II) from cobalt oxide nano powder and alloy.

Cobalt oxide nano materials/alloy	Amount of Co(II) found <sup>a</sup> mg/gm		Confidence limit $\alpha$ = 0.95	R.S.D. (%)	
	Proposed method	AAS method			
CeCoO <sub>3</sub> <sup>b</sup>	48.77	48.79	1.41	0.006	
ZnCoFe <sub>2</sub> O <sub>4</sub> <sup>b</sup>	32.12	32.11	1.21	0.016	
ZnCoFeDyO4 <sup>b</sup>	29.08	29.09	2.26	0.011	
Nickel-Base alloy (387 BCS) <sup>c</sup>	105.01	105.02	1.16	0.013	

Nickel-Base alloy (387 BCS): Co, 0.21%; Cr, 12.46%; Ti, 2.95%; Al, 0.24%; C, 0.30%; Mo, 5.83%; B, 0.016%; Mn, 0.08%; Si, 0.28%; Fe, 36.0%; Ni, 41.9%; Cu, 0.032%.

<sup>a</sup> Average of five determinations.

<sup>b</sup> Cobalt nano powder, Department of Chemistry, Shivaji University, Kolhapur, India.

<sup>c</sup> Alloy, Department of Chemistry, Shivaji University, Kolhapur, India.

While extracted cobalt(II)-2',4'-dinitro APTPT-pyridine complex estimated spectrophotometrically at 490 nm against reagent blank.

#### 4.2. Determination of cobalt(II) from synthetic mixtures

Several synthetic mixtures of varying compositions containing  $100 \ \mu g$  of cobalt(II) and associated metal ions of known concentration were added, followed by respective masking agents. Extraction of cobalt(II) was analyzed by employing the recommended procedure (Table 5). The results obtained were in perfect and good agreement with the amount added.

#### 4.3. Analysis of cobalt(II) from cobaltoxide nano powder and alloy

The proposed method has been successfully applied for the determination of cobalt(II) from cobalt oxide nano powder and alloy (Table 6). These samples were boiled with 10.0 mL *aqua-regia*, evaporated to moist dryness by gentle heating on hot plate. The solution was boiled with hot water and filtered through Whatmann filter paper No. 1. The residue was evaporated to moist dryness by the addition of  $2 \text{ mL} \times 5 \text{ mL}$  portion of conc. HCl. The filtrate was diluted to required volume with water. An aliquot of cobalt(II) solution was analyzed by the recommended procedure. The results were found to be in good agreement with those obtained by AAS.

#### 5. Conclusion

The newly synthesized 2',4'-dinitro APTPT has been proved to be a selective reagent for cobalt(II) when compared to other spectrophotometric methods. It is successfully applied to the determination of cobalt(II) in synthetic mixtures, nano powder and alloys. Salient features:

- (i) Low reagent concentration is required for quantitative determination of cobalt(II).
- (ii) The extraction procedure is a single stage.
- (iii) 2',4'-Dinitro APTPT forms complex with cobalt(II) in basic medium in presence
- (iv) of pyridine used as a synergent with probable stoichiometry at extracted species is 1:2:2 (M:L:Sy).
- (v) The orange-red coloured ternary complex is stable for more than 48 h.
- (vi) It is free from interference of a large number of foreign ions which are associated with cobalt(II) in its natural occurrence. The selectivity was enhanced by the use of suitable masking agents.
- (vii) The developed method is simple, reproducible, rapid and used for separation and determination of cobalt(II).

#### 5.1. Novelty

Cobalt(II) was extracted and spectrophotometrically determined in basic pH solution by the mixture of 2',4'-dinitro APTPT and pyridine. There was enhancement of absorbance in presence of pyridine which showed the synergistic effect and stability of complex was also increased by chelate formation. The rate of extraction was rapid and allowed large tolerance limit for foreign metal ions. The proposed method is very simple, selective and rapid. The developed analytical method is proved to reliable for analysis of real samples which is confirmed by AAS.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.09.015.

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