

Non-Extractive Spectrophotometric Determination of Cobalt (II) using 2-Acetylthiophene Isonicotinoylhydrazone in Environmental and Pharmaceutical Samples

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ABSTRACT

A new chromophore, 2-acetylthiophene isonicotinoylhydrazone (ATINH) has been synthesized and used for non-extractive spectrophotometric determination of cobalt (II). The metal ion reacts with the reagent in aqueous dimethyl formamide (DMF) in wide pH range forming yellowish coloured 1:2 (M:L) soluble complex with λ_{max} at 430 nm. Beer's law obeys in the range 5.893-58.93 $\mu\text{g mL}^{-1}$ of Co (II). The molar absorptivity, Sandell's sensitivity, detection limit, determination limit and relative standard deviation are calculated as $5.0 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, 0.001178 $\mu\text{g cm}^{-2}$, 0.04 $\mu\text{g mL}^{-1}$, 0.012 $\mu\text{g mL}^{-1}$ and 0.998%, respectively. Various diverse ions which generally associated with the determination of Cobalt (II) are also studies. The proposed method is applied for the determination of cobalt(II) in, environmental and pharmaceutical samples and the results were compared with standard dithizone method are quite encouraging and have high precision and accuracy.

Keywords: 2-Acetylthiophene isonicotinoylhydrazone, Cobalt, Spectrophotometry, Environmental and pharmaceutical samples

INTRODUCTION

Cobalt is naturally occurring element found in rocks, soil, water, plants and animals. Cobalt is used to produce alloys used in the manufacture of aircraft engines, magnets, grinding and cutting tools, special cobalt-chromium-molybdenum alloys are used for prosthetic parts such as hip and knee replacements [1]. Iron-cobalt alloys are used for dental prosthetics [2]. Cobalt compounds are also used to color glass, ceramics and paints products [3] and used as a drier for porcelain enamel and paints, fertilizers, feeds and disinfectants. They are important building components in biological systems [4].

Radioactive cobalt is used for commercial and medical purposes. ^{60}Co (read as cobalt sixty) is used for sterilizing medical equipment and consumer products, radiation therapy for treating cancer patients, manufacturing plastics an irradiating food. ^{57}Co is used in medical and scientific research.

Cobalt enters the environment from natural sources and burning of coal or oil or the production of cobalt alloys. In the air, cobalt will be associated with particles that settle to the ground within a few days. Cobalt released in to water or

soil stick to particles. Some cobalt compound may dissolve in water. Cobalt cannot be destroyed. Radioactive decay is a way of decreasing the amount of radioactive cobalt in the environment.

The general population is exposed to low levels of cobalt in air, water and food. Cobalt has both beneficial and harmful effects on health. At low levels, it is part of vitamin B12, which is essential for good health; at high levels it may harm the lungs and heart. This chemical has been found in at least 426 of the 1,636 national priorities. List sites are identified

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by the Environmental Protection Agency (EPA).

Review of literature reveals that a large number of chromogenic reagents for the spectrophotometric determination of cobalt [5-11] were recently proposed are less sensitive and less selective. We are now proposing simple, sensitive and selective, direct and non-extractive spectrophotometric methods for the determination of cobalt (II) in various complex materials using 2-acetylthiophene isonicotinoylhydrazone (ATINH) as chromogenic agent.

EXPERIMENTAL

Chemicals and reagents

Preparation of ATINH: In a 250 ml Erlenmeyer flask, a hot methanolic solution (10 ml) of 2-acetylthiophene (0.05 mol) and isoniazid (0.05 mol), dissolved in 10 ml of hot distilled water were taken. Suitable quantity (~2 ml) of dilute hydrochloric acid was added to the reaction mixture and refluxed for 4 h. On cooling the reaction mixture, pale yellow colored product (ATINH) was separated out. It was collected by filtration and washed several times with hot water and 50% cold methanol. This compound was recrystallized from ethanol and dried in vacuo; Yield 6.6 g; M.P.196°C.

Characterization of ATINH: The compound was characterized by IR and ¹H-NMR, Mass and UV-Visible spectral data. Infrared spectrum of ATINH shows bands at 3281(s), 3059(m), 2927(m), 1666(s), 1599(s), 1548(s), 1500(m), 1482(m), 1297(m) and 747(m) cm⁻¹, respectively corresponding to ν (NH) secondary, ν (C-H) aromatic stretch, ν (C-H) aliphatic stretching, ν (C=O) hydrazine, ν (C=N) azomethine, ν (C-C) aromatic ring, ν (C-C) aromatic ring, ν (C-C) aromatic ring, ν (C-N) stretch, ν (C-H) oop bend(thiophene) aromatic ring vibrations.

¹H-NMR spectrum of ATINH (CDCl₃+DMSO-d₆) showed signals at 2.4 (3H, s), 6.5-8.0 (7H, m) and 10.5 (1H, s) due to CH₃ and isonicotine+thiophene proton, -NH(imino) groups of hydrazine, respectively.

Mass spectrum of ATINH shows molecular ion peak at m/z 246 corresponding to the molecular weight. Other peaks due to loss of methyl radical and thiophene radical are also observed in mass spectrum.

Instrumentation

Shimadzu 160A UV-Visible spectrophotometer equipped with 1.0 pm quartz cell and an Elico model LI-610 pH meter were used in the present study (Figure 1).

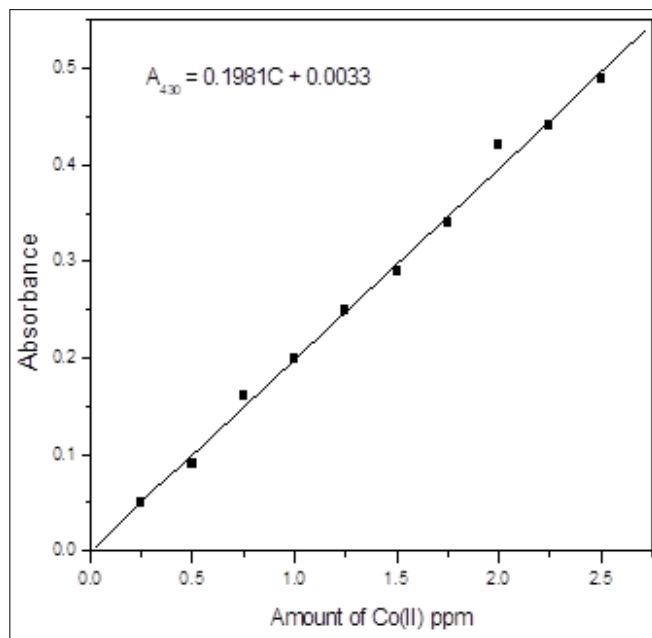


Figure 1. Calibration plot of Co (II) determinations. pH=6.0; [ATINH]=1 × 10⁻⁴ M; Wavelength=430 nm

Preparation of Cobalt (II) solution: Stock solution of Co (II) (1 × 10⁻² M) was prepared from CoCl₂ 6H₂O with doubly distilled water containing few drops of concentrated HCl and made up to 100 ml. The resulting solution was standardized.

Determination of Cobalt (II) in various water, soil and pharmaceutical samples: The present method is applied for the determination of Co (II) in water samples, soil and pharmaceutical samples.

Water samples [12,13]

Each filtered (with whattman No. 40) water sample (250 ml) was mixed with 10 ml of concentrated nitric acid in a 500 ml distillation flask. The sample was digested in the presence of an excess potassium permanganate solution according to the method recommended by Fifield et al. [12]. The solution was cooled and neutralized with dilute NH₄OH solution. The digest was transferred into a 25 ml calibrated flask and diluted up to the mark with deionized water. The results were given in Table 1.

Preparation of soil samples [14]

2 g weight of soil, 5-7 ml of concentrated H₂SO₄ and an excess of KMnO₄ are mixed in a conical flask equipped with a reflux condenser. The crystals of KMnO₄ are added slowly in small portions, while stirring. It is heated until vapors of SO₃ are evolved. After cooling down, 10 ml of distilled water are added. The excess of KMnO₄ and manganese oxides are eliminated by adding H₂O₂. Iron is isolated by precipitation as hydroxide. After filtration, the solution is transferred into 25 ml standard flask and the volume is brought to the mark with distilled water. Aliquots of this

solution were taken for analysis by following procedure given above. The results were given in **Table 1**.

Table 1. Determination of Cobalt (II) in water, biological and soil samples.

Name of the samples	Amount of Cobalt ^a found ($\mu\text{g mL}^{-1}$)	
	ATINH method	Dithizone method
Water Samples		
Effluent water ^b	3.26	3.18
Waste water ^c	3.33	3.29
River water ^d	0.61	0.66
Soil Samples		
Agricultural soil (Red soil) ^e	16.84	17.01
Urban soil ^f	24.03	23.86
Industrial Soil ^g	106.26	105.09

^a Average of three determinations

^b Laboratory effluent water, (Department of Chemistry, S.K.U)

^c Road side water in Anantapur town

^d Tungabhadra River, Kurnool

^e Red soil, Anantapur

^f Urban Soil, Anantapur Town

^g Soil at Electroplating Industry, Anantapur

Preparation of pharmaceutical samples [15]

A known quantity of the pharmaceutical sample (Neurobian Forte/Basiton Forte, Cyanocobalamine - 15 mg of each sample) was taken in a beaker and dissolved in minimum volume of alcohol. Then added 3 mL of 0.01 M nitric acid

and evaporated to dryness. The dried mass was again dissolved in alcohol. This was filtered through Whatman filter paper and the filtrate was diluted to 100 mL with distilled water. The lower concentrations were prepared by the appropriate dilution of the stock solution. The results were given in **Table 2**.

Table 2. Determination of cobalt (II) in pharmaceutical samples.

Sample (mg/Tablet)	Amount of Cobalt(II) ($\mu\text{g mL}^{-1}$)		
	Reported	Found	Relative Error (%)
Neurobian Forte (Cyanocobalmine- 15 mg)	7.45	7.41	-0.04
Basiton Forte (Cyanocobalmine- 15 mg)	7.42	7.39	-0.03

Recommended procedure [16,17]

An aliquot of the solution containing cobalt in Beer's law validity range, 10 ml of NaOAc-AcOH buffer solution (pH 6.0) and 1.0 ml of 0.01 M ATINH were mixed in a 25 ml volumetric flask and resulting solution was diluted to the mark with distilled water. The absorbance of this solution was measured at 430 nm against reagent blank. The measured absorbance is used to compute the amount of

cobalt present in the samples using pre-determined calibration plot.

Dithizone method [18]

As stated in the recommended procedure in a 25 ml volumetric flask 10 ml of buffer (pH 6.0), aliquots of cobalt in beer's law validity range, and instead of reagent ATINH, 1.0 ml dithizone solution is added and the resulting solution

was made up to the mark with distilled water. The absorption is measured at 430 nm against reagent blank.

Composition and stability constant of the complex

The composition of the complex was determined by Job's continuous variation and molar ratio methods. The stability constants of the complexes were calculated by using the data obtained from Job's plot.

Job's continuous variation method

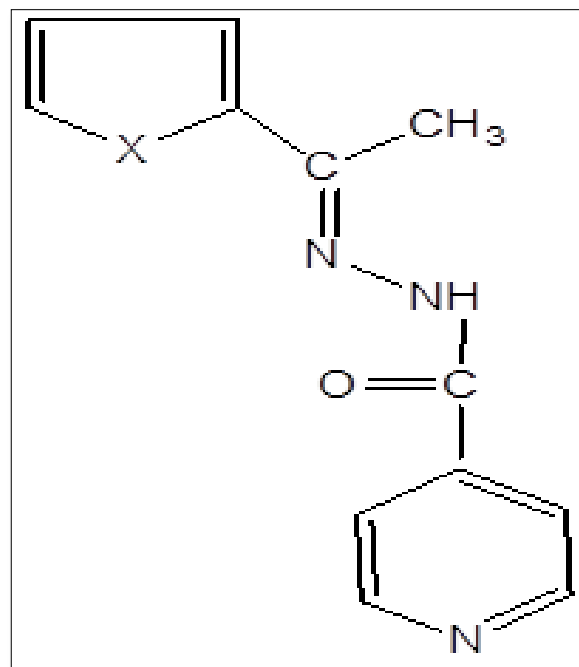
In a set of (nine) 25 ml volumetric flasks, 10 ml of buffer solution and 1.0 ml of DMF were added to each flask. Equimolar solutions of metal ion and reagent in different volume proportions (keeping the volume at 10 ml) were added to each flask. The contents in each flask were made up to the mark with distilled water. The absorbance of the complex in each flask was measured at 430 nm wavelength against a reagent blank. A plot between mole fraction of reagent and the absorbance was made from which the composition of the complex was computed.

Molar ratio method

In a set of (ten) 25 ml calibrated flasks, 10 ml of buffer solution, 1.0 ml of DMF, constant amount of metal ion and varying aliquots of the reagent solutions were added. The contents of each flask were made upto the mark with distilled water. The absorbance of the colored complex in each flask was measured at 430 nm against the reagent blank. From the plot between the absorbance and mole of the reagent per mole of metal ion, the composition of the complex was ascertained.

RESULTS AND DISCUSSION

The reagent ATINH may be easily prepared under reflux conditions. The reagent solutions (0.01 M) are found to be stable for 12 h. The bathochromic shift of absorption band 270-370 nm indicates that in solution are increasing the pH, the acid is neutralized and the C=S group enolised and dissociated [14]. In basic medium (above pH 7.3) the ligand presumably exists in enolic form and coordinates the divalent metal ion as mono anion to give neutral complexes. The structure of ATINH is given in **Figure 2**.



X=S

Figure 2. Structure of ATINH.

The Cobalt (II) reacts with ATINH in acidic pH to give water soluble complexes. The color reactions are instantaneous at room temperature. The change in the order of addition of metal ion, reagent (ATINH) and buffer has no effect in the absorbance of complexes. The solubility of reagents and their metal complexes are low in aqueous medium. But it was observed that the reagents and their metal complexes were more easily soluble in aqueous DMF. In order to arrive at the optimum percentage of DMF required retaining them in solution different aliquots of DMF added to the sample solutions. An analytical characteristic of the complex is summarized in **Table 3**. The stoichiometry of the complex (M:L=1:2) was determined by Job's continuous variation method and molar ratio methods. Sodium acetate (0.2 M) - acetic acid (0.2 M) buffer solution (pH 6.0 and T=300 K) and equimolar 4.8×10^{-5} M solutions of Co (II) or ATINH were used in this method. The stability constant of the complex 5.75×10^{13} M is calculated using α (0.08) and C (2.8×10^{-5} M) values obtained in Job's method using the formula:

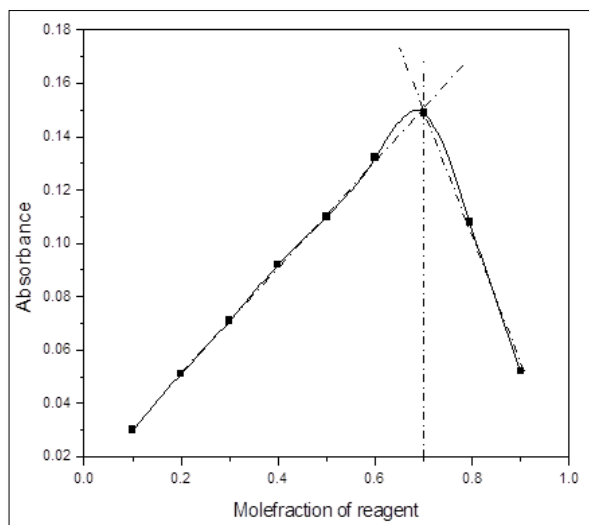
$$\beta_{1:2} = \frac{1 - \alpha}{4\alpha^3 C^2}$$

Table 3. Physico-chemical and analytical properties of Co-ATINH complex.

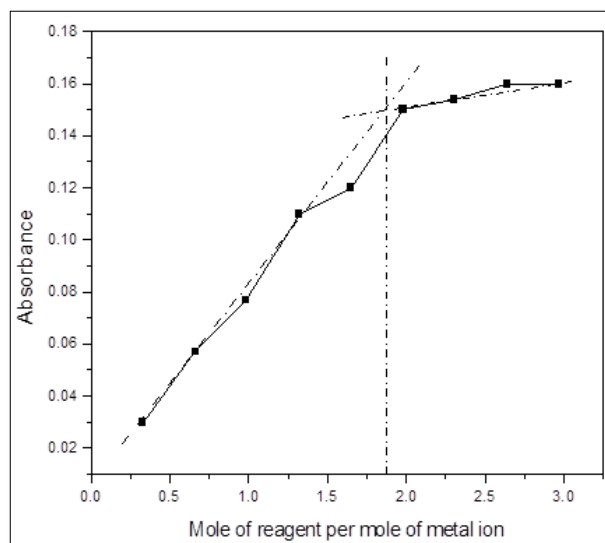
S. No.	Characteristics	Co-ATINH
1	$\lambda_{\max}$ (nm)	420
2	Mean absorbance	0.269 ± 0.0011
3	pH range (optimum)	5.0-8.0
4.	Mole of reagent required per mole of metal ion for full color development	15 fold
5	Time stability of the complex (in hours)	12
6	Beer's law validity range ($\mu\text{g mL}^{-1}$)	5.893-58.93
7	Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	5.0×10^4
8	Specific absorptivity ($\text{mL g}^{-1} \text{cm}^{-1}$)	0.8485
9	Sandell's sensitivity ($\mu\text{g of Co(II) cm}^{-2}$)	0.001178
10	Composition of the complex as obtained in Job's and molar ratio methods (M:L)	1:2
11	Stability constant of the complex	5.75×10^{13}
12	Standard deviation	0.0078
13	Relative Standard deviation (RSD), (co-efficient of variation)	0.998

[‡] In the determination of $5.893 \mu\text{g mL}^{-1}$ of Cobalt (II)

The structure of Co (ATINH)₂ complex is given in **Figures 3-5**.

**Figure 3.** Job's curve.

Co (II) – ATINH = 1×10^{-4} M (stock solution);
Wavelength = 430 nm; pH 6.0

**Figure 4.** Molar ratio plot.

Co (II) = 1×10^{-4} M; Wavelength = 430 nm; pH 6.0

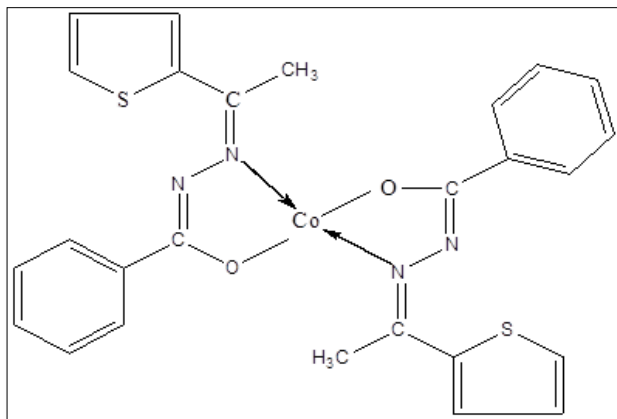


Figure 5. Structure of Co (II) complex of ATINH.

Tolerance limits of foreign ions

The effect of foreign ions was studied with a view to examine the applicability of the method in presence of foreign ions. Interference of various ions was studied with $5.893 \mu\text{g mL}^{-1}$ of cobalt by adopting the procedure. The tolerance limit value was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the absorbance of the Co (II)–ATINH complex (**Table 4**).

Table 4. Tolerance limit of foreign ions in the determination of $5.893 \mu\text{g mL}^{-1}$ of cobalt.

Ion added	Tolerance limit ($\mu\text{g mL}^{-1}$)	Ion added	Tolerance limit ($\mu\text{g mL}^{-1}$)
Citrate	871	W (VI)	110
Tartrate	592	Mn (II)	60
Phosphate	392	Sn (II)	47
Sulphate	384	Cd (II)	27
Carbonate	360	Zr(II)	18
Bromide	318	Cr (VI)	10
Nitrate	248	Pb(II)	5.0
Thiourea	154	Mg (II)	4.8
Iodate	151	Hg (II)	4.8 ^b
Iodide	151	Ag (I)	4.7
Chloride	142	Fe (III)	4.5 ^a
Acetate	94	V (V), Zn (II)	1.62
Fluoride	78	Fe (II)	1.1

^a Masked with $300 \mu\text{g mL}^{-1}$ of Phosphate; ^b Masked with $200 \mu\text{g mL}^{-1}$ of Nitrate

Applications

Cobalt was estimated in various water samples, biological, soil and pharmaceutical samples by employing the present method. The results are presented in **Tables 1 and 2**.

CONCLUSION

The study reveals that the Cobalt content can be determined in ppm level in water, soil and pharmaceutical samples using present method. All these findings cause great concern regarding public health demanding an accurate determination of this metal ion at trace levels and the present study may provide awareness among the public.

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