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Antipyryl Azo(2,7)-Naphthalindiol as Spectrophotometric Reagent for Micro-determination of Cobalt (II)

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Abstract:

A new, simple, sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of cobalt (II). The method is based on the formation of a 1:2 complex with 1-(4′- antipyryl azo) 2,7-naphthalendiol (1-APANDOL) as a new reagent is developed . The complex has a maximum absorption at 542 nm and ε_{max} of 1.15×10^4 L. $mol^{-1}.cm^{-1}$. A linear correlation (0.1–2.5 μg. mL^{-1}) was found between absorbance at λ_{max} and concentration. The accuracy and reproducibility of the determination method for various known amounts of cobalt (II) were tested . The results obtained are both precise (RSD was better than 0.44 %) and accurate (relative error was better than 0.35 %). The stability constant of the product was 1.6×10^8 L. moL^{-1}.

Key Word: Cobalt (II) determination, spectrophotometry, antipyryl azo (2,7)-Naphthalindiol.

Introduction:

The azo dyes of heterocyclic compounds play a vital role in analytical chemistry due to highly sensitive colour reaction, stability and selectivity towards several metal ions[1–3].

Cobalt is an essential element required for metabolic processes in human body. It is the core of vitamin B_{12} and Cobalt is used to treat anemia with pregnant women, because it stimulates the production of red blood cells. Nowadays the interest to the analytical chemistry of cobalt is rather great. It is used as an alloying component of special alloys with high hardness. Radioactive isotopes of cobalt are widely used in medical applications[4]. Due to these properties, the determination of cobalt in biological and environmental samples is of great significance from the public health environmental point of view[5-8]. In this study we wish to report this reagent as a selective reagent in spectrophotometric determination of cobalt (II).

Experimental

I/ Preparation of the reagent (1-APANDOL)

The reagent prepared as in previous study by coupling 2,7-naphthalendiol with diazotate 4-amino antipyrine in alkaline alcoholic solution. A diazonium solution was prepared by taking 1.1 g of 4-amino antipyrine in 30 mL of ethanol and concentrated hydrochloric acid with 10mL of distilled water and adding sodium nitrite solution drop wise at (0-5 C^0). 1.3 g of 2,7-naphthalendiol was dissolved in 20 mL of ethanol and 30 mL of 0.1 M from sodium hydroxide were added at (0-5 C^0) .The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol[9].

II/Preparation of Cobalt (II) complex

The complex was prepared by stoichiometric amount from ligand in 200 mL of ethanol then added drop wise with stirring to a stoichiometric amount 2:1 for cobalt salt in 100 ml distilled water. The mixture was stirred at room temperature for 5 min. The pH of solution was adjusted to 8.0 then left for 24 hr. The solid product thus formed off, washed with distilled water, and recrystallized from ethanol.

Apparatus:

Spectrophotometric measurement were made with **Shimadzu UV–visible – 1700 double beam spectrophotometer** using 1.00 cm glass cells. Vibrational spectra were recorded on **Test scan Shimadzu FT.IR 8000 series**. Measurements of pH were made using an **Hanna, HI9811-5 pH–meter** equipped with a glass – saturated calomel combined electrode Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus. Conductivity was measured in DMSO (10^{-3}) solution with an Alpha digital conductivity model -800. Elemantal analysis (C.H.N) were carried out with a **EuroEA Elemental Analyser.**

Reagents

All chemicals used were of analytical grades

Cobalt (II) stock solution (100 µg. mL^{-1})

prepared by dissolving 0.4037g of cobalt chloride hexahydrate in 1000mL of distilled water in a volumetric flask ,other working standard of Co (II) solutions were prepared by simple dilution of the appropriate volume of the standard Co (II) solution (100 µg. mL^{-1}) with distilled water.

1–(4'- Antipyryl azo) 2,7-naphthalendiol (1 mM)

0.1872 g of reagent was dissolved in 500 mL of ethanol.

Foreign ion solutions (10 µg . mL^{-1})

The solutions for all foreign ions were prepared by dissolving an

appropriate amount of the foreign ion compounds in distilled water in a volumetric flask.

General Procedure

In to a series of 10 mL calibrated flask, transfer increasing volumes of Co(II) working solution 10 ppm to cover the range of calibration curve, add 2.5 mL 0f 1mM of (1-APANDOL) solution and pH was adjusted to 8. The complexes formed were solubilized in water and diluted up to 10 mL in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition but containing no cobalt ion. The color of the complex is stable for 24 hrs.

Results and Discussion

Properties of (1-APANDOL) and its metal chelate

1-APANDOL is a tridentate reagent contain three position for coordination, which is nitrogen of azo group, hydroxyl group and carbonyl group and it has the following suggested structure:

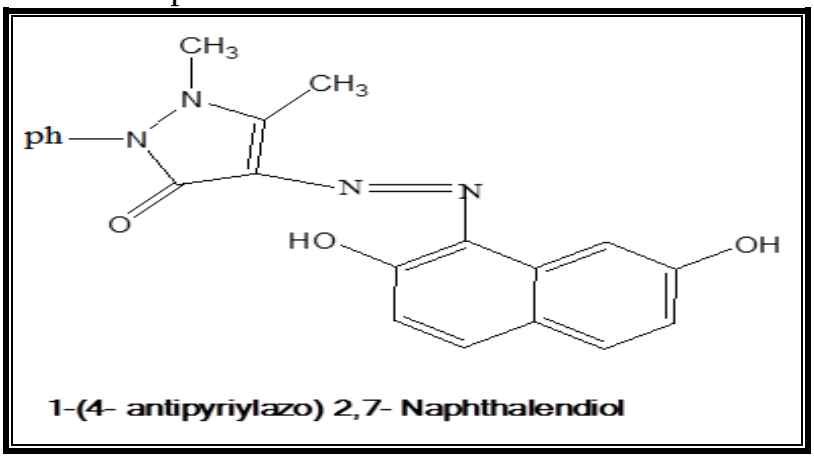


Fig.1 structure of 1-APANDOL

Spectra:

The absorption spectra of complex was studied and shown in figures 2.. The spectra of metal complex was recorded within wavelength 542 nm.

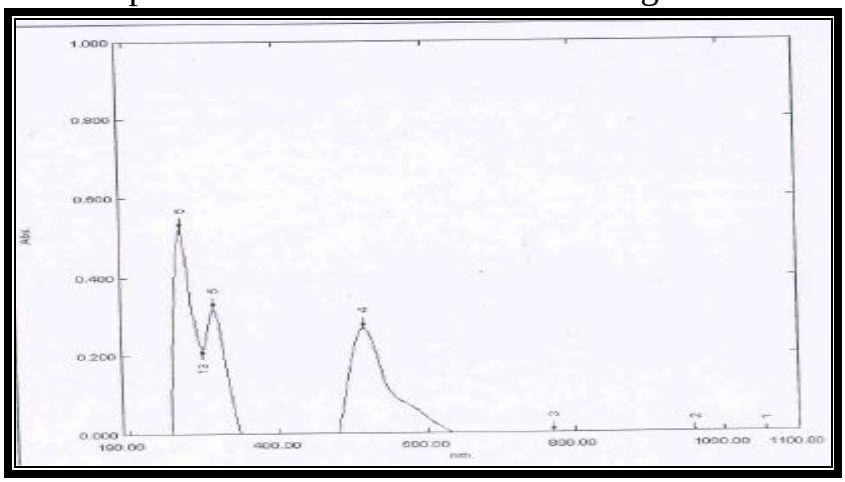


Fig.2 :- Absorption spectra of [Co (II) + 1-APANDOL] treated as described

under procedure and against reagent solution as blank .

The spectrum of complex showed a red shift for ($\pi - \pi^*$) electronic transition band. [Co (L)] shows one broad in visible region at (15000-20000) cm^{-1} refer to ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) that is in accordance with octahedral geometry of Cobalt metal ion[10,11].

Effect of pH:

The pH of metal complex solutions was adjusted using dilute solutions (0.05M) NaOH and (0.05 M) HCl, and the effect on absorbance was studied Fig. 3. The absorbance of the complex was maximum and constant in the pH range given in Table 1.

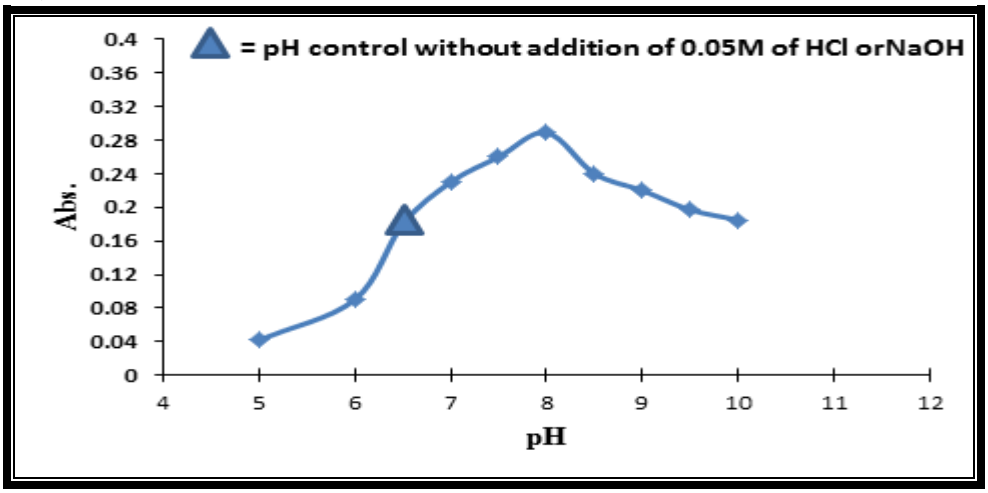


Fig.3: Effect of PH

Table.1 :- Analytical characteristics of Co (II) – complex.

Characteristic	Co (II) – complex
Maximum Absorption peak	542 nm
Beer's law validity range (ppm)	(0.1– 2.5)
pH range	(7 – 9)
Sandell's sensitivity µg . cm^{-2}	0.0051
Molar absorptivity (L. mol^{-1}. cm^{-1})	1.15×10^4
Stability constant (L. mol^{-1})	1.6×10^8
Melting point for reagent	(232 - 234) C^0
Melting point for Co (II) – complex	(310 - 312) C^0

Effect of (1-APANDOL) concentration

Various concentrations of 1 –(4'-antipyriyl azo) 2,7-naphthalendiol were added to fixed concentration of Co (II), 2.5 ml of 1 mM (1-APANDOL) solution was sufficient and gave minimium blank value was increased causing a decrease in the absorbance of the sample. Therefore 2.5 mL of 1 mM of 1-APANDOL was used in all subsequent experiment Fig. 4.

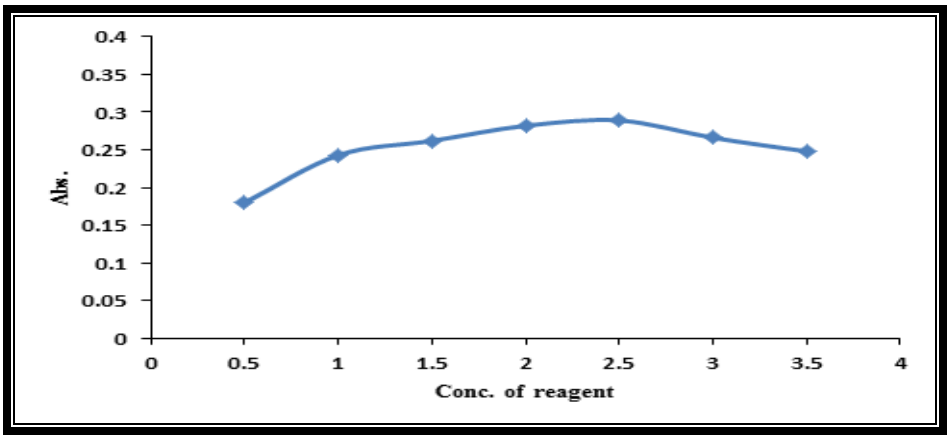


Fig.4 :- Effect of (1-APANDOL) concentration

Effect of reaction time:

The colour intensity reached a maximum after the Co (II) has been reached immediately with 1-APANDOL and became stable after one minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least 24 hours Fig 5.

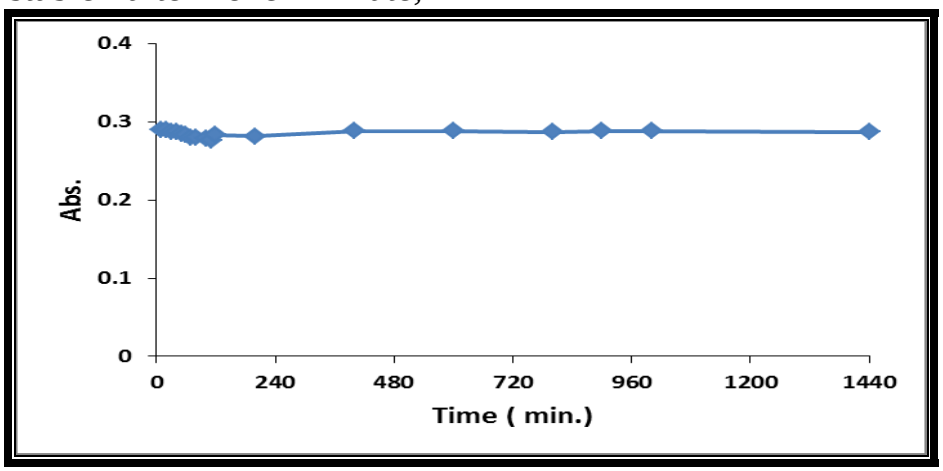


Fig.5:-Effect of time on complex of Co[1-APANDOL]$_2$ *Calibration graph*

The calibration equation for (0.1 – 2.5 µg mL^{-1}) Co (II) is:
Y = 0.1955X + 0.1008 (R^2 = 0.9984).
Since the coloured complex is stable for 24 hrs , the method can be applied to large series of samples . The molar absorptivity and sandell' sensitivity are given in Table.1 .

Composition of the complex:

The composition of complex was studied in the excess of reagent solution by the mole-ratio and Job s` methods Fig 6,7. A break at a 1:2 (M:L) mole ratio suggested the formation of complex where M= Co(II) and L=1-APANDOL under the given condition.

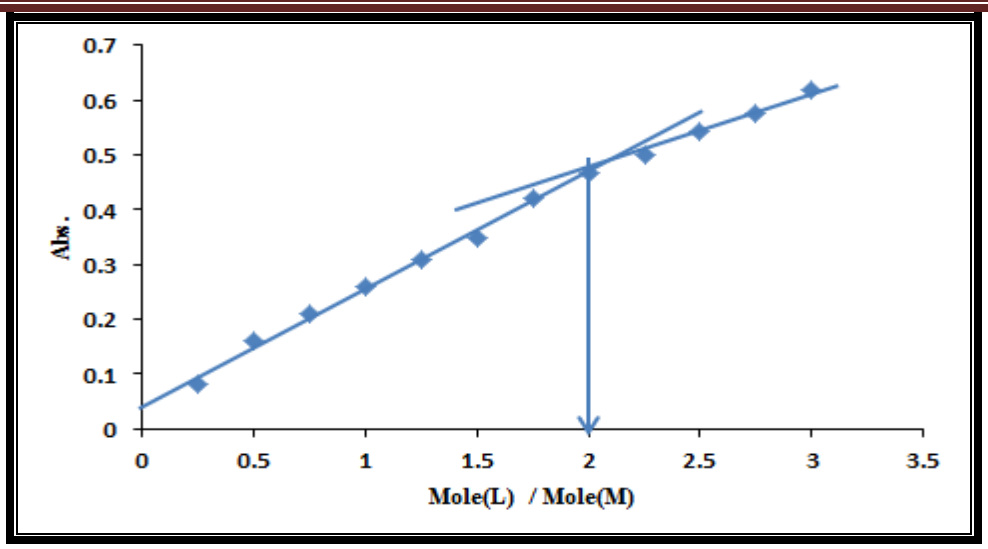


Fig 6:- mole-ratio method for Co[1-APANDOL]$_2$ complex

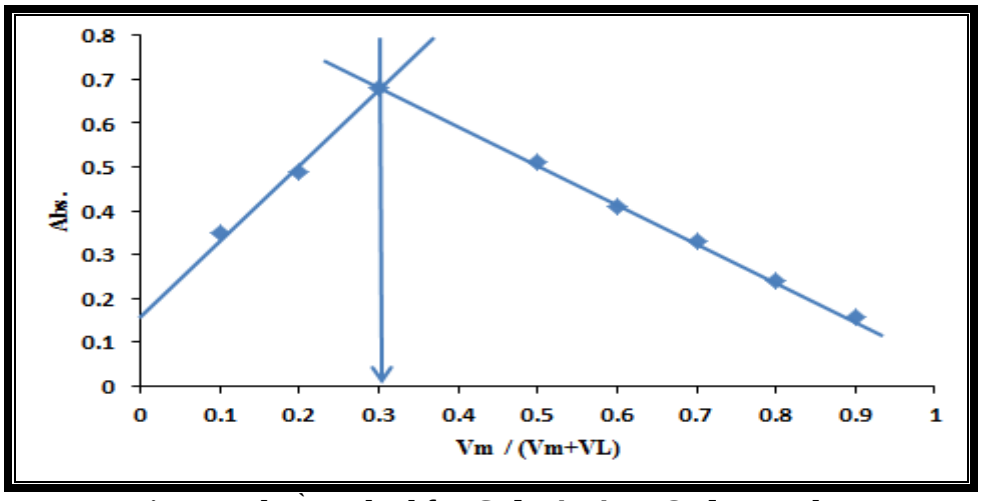


Fig 7:- Job s` method for Co[1-APANDOL]$_2$ complex

Conductivity measurements

The solubility of the complex in dimethyl sulfoxide and ethanol permitted of the molarconductivity of 1 x10^{-3} M solution at 25 °C and by comparison, the electrolytic nature for complex. The low values of the molar conductance data listed in Table 2 indicate that the complex is non electrolyte.

Table2. Conductivity values of complex

Complex	Molar conductivity, S. mole^{-1} .cm^2 DMSO	Molar conductivity, S mole^{-1}. cm^2 Ethanol
Co (1-APANDOL)	13.46	9.23

FT.IR of reagent and it's complex

The FT. IR of the free ligand and it's metal chelate were carried out in the (400-4000) cm^{-1} Range. The IR bands of the (1-APANDOL) and its Co (II) complex with their probable assignment are given in Table.3. The IR spectrum of ligand shows a broad band at 3414 cm^{-1}, which can be attributed to the naphtholic OH

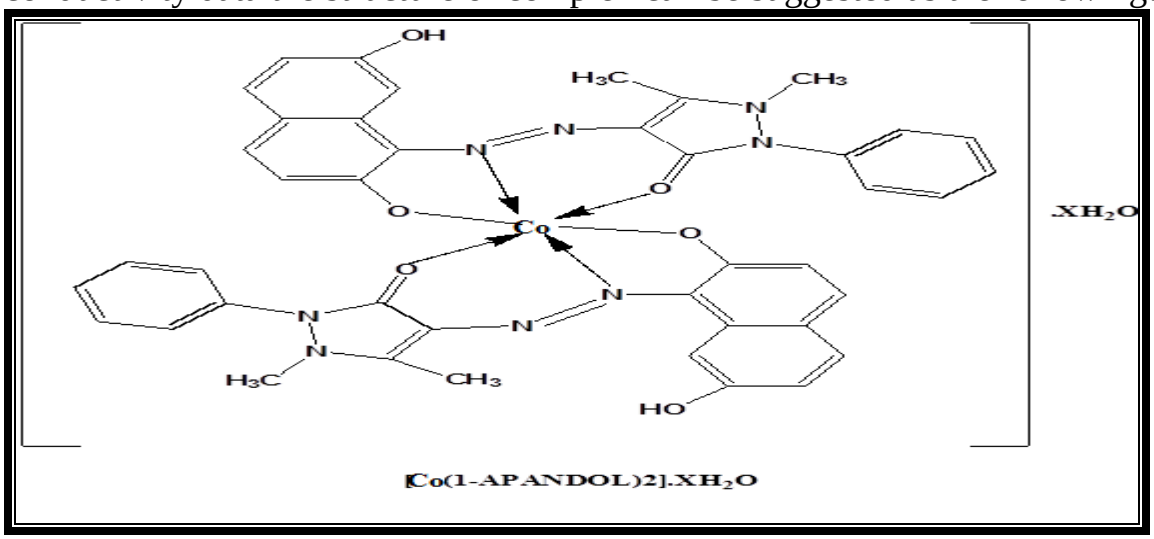
group. However, the υ(N=N) stretching band in the free ligand is observed at 1494 cm^{-1}. This band is shifted to lower with low intensity at 1448 cm^{-1} frequency value upon complexation suggesting chelation via the (M-N) [9,12]. The IR spectrum of the ligand revealed a sharp band at 1637 cm^{-1} due to υ(C=O) of pyrazole azo. This band is shifted to lower with low intensity at 1588 cm^{-1} frequency value upon complexation [13]. The bonding of oxygen to the metal ion is provided by the occurrence of band at 476 cm^{-1} as the result of υ(M-O) [14,15].

Table.3:Selected FT.IR data of (1-APANDOL) and it's complex with Co (II)

Compound	υ (OH)	υ (C-H) arom.	υ (N=N)	υ (C=O)	υ (M-O)	υ (M-N)
HL	3414 m	3069 w	1494 m	1637 s	-	-
[Co (L)]	3372 m	3069 w	1448m	1588 m	476 w	451 w

S: sharp ; m: medium ; w: weak

On the basis of the FT.IR, stoichiometric, and elemental analysis molar conductivity data the structure of complex can be suggested as the following:-



Scheme.1 structure of Complex

Conclusion:

The proposed method is highly sensitive and selective than the other reported methods for the spectrophotometric determination of micro amounts of Cobalt. It offers advantages like reliability and reproducibility in addition to its simplicity.

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الخلاصة:

تم تطوير طريقة طيفية جديدة وسريعة وحساسة في تقدير الكميات الضئيلة للكوبلت الثنائي، إعتمدت الطريقة على أساس تكوين معقد 2:1 (فلز– كاشف) مع الكاشف 1- (4′-انتي بايرايل آزو)-2،7- ثنائي هيدروكسي نفثول (1- APANDOL)، يمتلك المعقد أعلى قمة إمتصاص عند الطول الموجي (542) نانوميتر ومعامل إمتصاص مولاري 1.15×10^{4} لتر. مول$^{-1}$. سم$^{-1}$. كانت العلاقة الخطية بين الإمتصاص عند الطول الموجي الأعظم والتراكيز تتراوح بين (0.1– 2.5) جزء في المليون أما الدقة والضبط للطريقة فقد أعطت نتائج تراوحت ما بين 0.44% بالنسبة إلى 0.35RSD % بالنسبة إلى الخطأ النسبي. كان ثابت الإستقرار للمعقد تحت الظروف الفضلى ودرجة حرارة الغرفة 1.6×10^{8} لتر.مول$^{-1}$.