Synthesis ,spectroscopic study of Antipyryl azo 2-Naphthol and use it as new reagent for determination of Co(II) and Cu(II)

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Abstract

A simple ,accurate and sensitive spectrophotometric method has been developed the determination of Cobalt(II) and Cupper (II) .The method is based on the chelation of Co(II) and Cu(II) ions with 4-(4´-pyrazolon azo) -2-Naphthol(APAN) in aqueous medium . The complexes have a maximum absorption at (513) and (506) nm and ε_{max} 0.531×10^{4} and 0.12×10^{5} L.mol $^{-1}$.cm $^{-1}$ for Co(II) and Cu(II) respectively .The reagent and two complexes have been prepared in ethanolic solution.The stoichiometry of both complexes were found to be 1:2 (metal :legend) .The effects of various cations and anions on Co(II) and Cu(II) determination have been investigated .The stability constants and standard deviations for Co(II) and Cu(II) $0.291\ x10^{7}$,$0.909X10^{8}$ L.mol $^{-1}$,(0.291) and (0.332) respectively .The optimum condition for full color development for described methods were applied satisfactorily to synthetic samples.

Key Word:- Copper (II) , Cobalt (II) , determination , spectrophotometry , antipyriyl azo -2-Naphthol.

Introduction:

Pyrazolne moiety (a five- membered lactam ring alternatively a derivative of pyrazole possessing an additional carbonyl /hydroxyl group)[1].Metal complexes of azo compounds containing hetero aryl ring systems find various applications .These type of molecules have several advantages ,for example the azo group is photo cromic ,redox responsive,stability low valent metal oxidation states due to the presence of a low –lying azo centered π^{*}molecular or bital serves as a molecular switch is used as ametal ion indicator ,dyes and pigments in industry [2].Copper is anutitionally essential metal and is widely distributed in nature ,Cobalt is an important essential micronutrient for all living systems [3]. As well as these two ions were studied by many researchers [4],estimated by these two ions in the samples biologic and environmental[5].At present ,a lot of analytical methods have been proposed for the determination copper (II) and cobalt (II) ,inductively coupled plasma mass spectrometry (ICP-Mass)[6,7],and atomic absorption spectrometry (AAS)[8,9] ,Show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis .According to the best of our knowledge ,this reagent has not been reported in the literature as being used for any cation determination. In this method 4-(4□-antipyriyl azo)-2-Naphthol has been used as a reagent for the spectrophotometric determination

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Cu(II) and Co(II) ,The present method has been found to be simple ,rapid and sensitive for the determination of these metal ions .

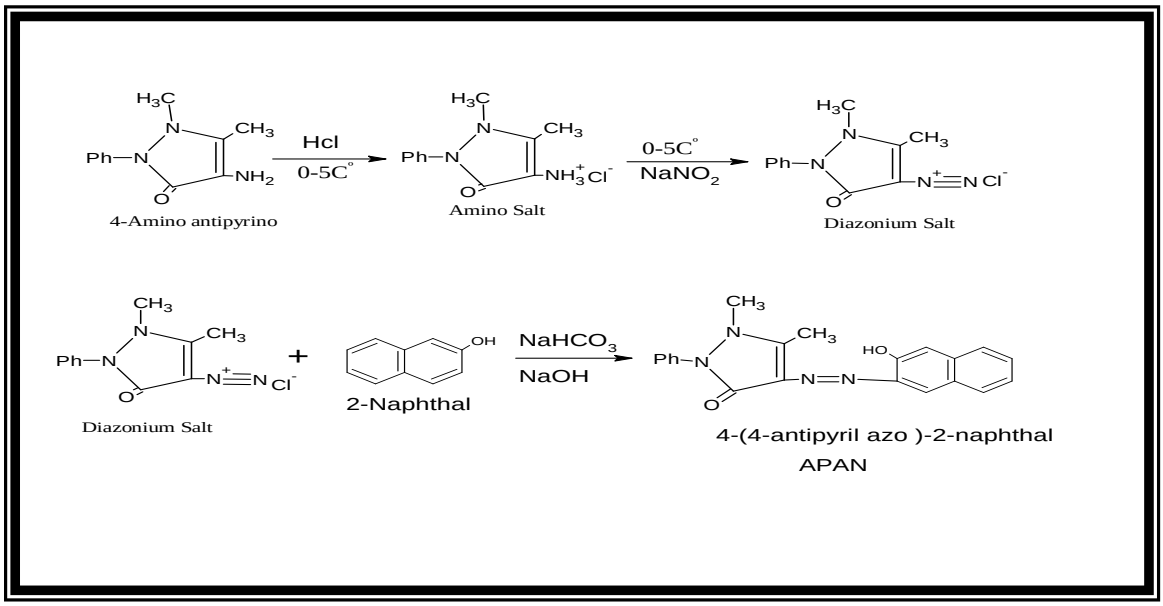
Experimental Part

All chemical used were of analytical grade

A- **Preparation of reagent (APAN)**

The reagent was prepared by coupling 2-naphthol with 4-amino antipyrin diazotate in alkaline alcoholic solution. A diazonium solution was prepared by taking 1.0g , 0.004 mol 4-amino antipyrin in 25 ml of ethanol and 5ml concentrated hydrochloric acid with 15 ml of distilled water ,and adding sodium nitrite solution dropwise at 0-5°C ,2-Napthol 0.0083 mol 1.2 g was dissolved in 50 ml of ethanol and 35 ml of (4N) NaOH were added at (0-5C°) .The mixture was allowed to stand and added 20%HCl solution .The precipitate was filtered off and recrystallized from ethanol [10] scheme 1.

Scheme 1. Preparation of reagent APAN



B- preparation of complex

The complex was prepared by stoichiometric amount from ligand in 50 ml of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 ions(cupper,coblet) in (25) ml hot distilled water. The solid product thus formed off , washed with ethanol and dried .

Apparatus

Spectrophotometric measurements were made with shimadzu UV-Visible -1700 double beam spectrophotometer using (1.0) cm glass cell .The pH measurements were performed with AWTW pH –meter 720 . Electric molar conductivity measurements were carried out at room temperature using an Alpha digital conductivity model -800 .Vibration spectra were recorded in Testscan Shimadzu FT.IR 8000 series .

Reagents

All chemicals used were of analytical reagent grade

1.Cupper (II) stock solution (100 µg.ml^{-1})

Dissolve 0.0268 gm of $CuCl_2.H_2O$ in 100 ml of distilled water ,working standard Cu(II) solution were prepared by dilution of the appropriate volume of standard Cu (II) solution (10 µg/ml) with distilled water .

2. Cobalt (II) stock solution (100µg ml $^{-1}$)

Dissolve 0.02203 gm of $CoCl_2$ in 100ml of distilled water ,working standard Co (II) solution were prepared by dilution of the appropriate volume of standard Co(II) solution (10 µg/ml) with distilled water .

3. 4-(4- antipyriyl azo) -2-Naphtol(1x10^{-3}M)

0.0358 gm of regent (APAN) was dissolved in100ml of ethanol working(APAN) (1×10^{-3}M) solution was prepared by simple dilution of appropriate volume of the reagent solution with ethanol.

Foreign ion solutions (100 µg ml^{-1})

These solutions were prepared by dissolving an amount of the compound in distilled water completing the volume in a volumetric flask.

General procedure

In to a series of 10 ml calibrated flask, transfer increasing volumes of Co(II) and Cu(II) working solution 10µg.ml^{-1} to cover the range of calibration curve ,add 3.5 ml and 2.5 ml of 5×10^{-4} M of(APAN) solution and PH was adjusted to 3 and 9 by buffer solution from ammonium acetate (0.01) for Cu(II) and Co(II) respectively .Measure the absorbance at 513nm ,for Co(II) and at 506 nm for Cu(II) for against blank prepared in the same way but containing no Co(II) or Cu(II) respectively .The color of the complexes is stable for 24 hrs.

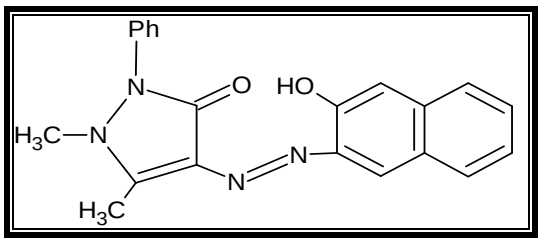
Table (1): The characteristics of two complexes with APAN reagent

Characteristic	**Co(II)**	**Cu(II)**
Absorption maxime (nm)	513 nm	506 nm
Beer's law range (µg/ml)	0.2-2.4	0.2-2
pH range	5.5-9.5	2.5-4.5
Sandell 's sensitivity µg.cm^{-2}	0.005µg.cm^{-2}	0.0018µg.cm^{-2}
Molar absorptivity (L.mole^{-1}.cm^{-1})	0.531×10^4	0.12×10^5
Stability constant (L.mol^{-1})	0.291×10^7	9.09×10^8
K_f	0.14×10^2	0.74×10^2
ΔG KJ.mole^{-1}	-6673.3	-4953.8

Results and Discussion:

Properties of (APAN) and its metal chelate

APAN is a tridentate with coordination of azo group nitrogen , hydroxyl group
and carbonyl group ; it has the following structure



Structure of APAN

Owing to the large conjugated system , the compound showed excellent chelating ability to form metal chelates . APAN and their metals chelates can be easily solubilized in an aqueous solutions

Spectra

The results of this work indicated that the reactions of Co (II) and Cu(II) with APAR at pH 9 and 3 yield highly soluble products which can be utilized as a suitable assay procedures for Co (II) and Cu(II) respectively . These products have a maximum absorption at 513 nm and at 506 nm at which the blank at these wave lengths shows zero absorbance Fig. 1,2 .The effect of various parameters on the absorbance intensity of the formed products were studied and the reactions conditions were optimized .

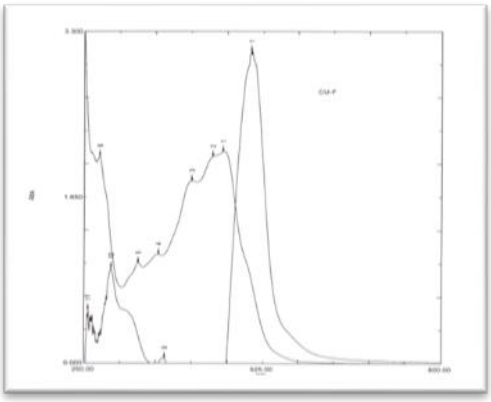


Fig (1). Absorption spectra of (APAN-Cu) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol

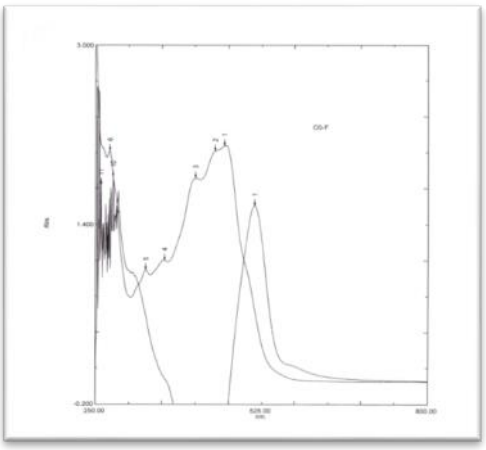
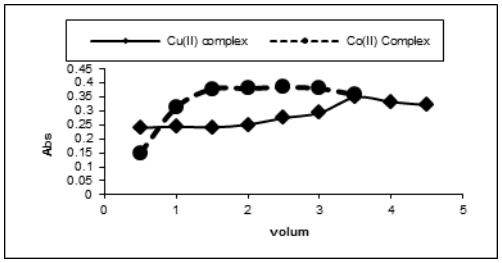


Fig (2).Absorption spectra of (APAN-Co) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol.

Effect of (APAN) concentration

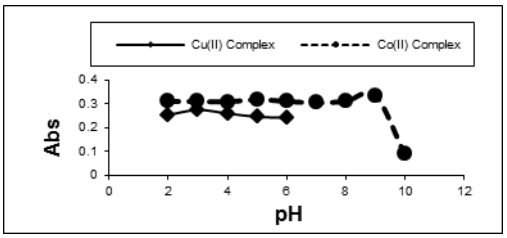
Various concentrations of 4 –(4'-antipyriyl azo)-2- Naphtol were added to fixed concentration of Co (II) and Cu(II): 3.5 ml and 2.5 ml of 1×10^{-4} M (APAN) solution was sufficient and gave minimum blank value and were consider to be optimum for the concentrating range . Therefore 3.5 ml and 2.5 of 1×10^{-4} M of(APAN) were used in all subsequent experiment Fig 3.



Fig(3). Effect of concentration

Effect of pH

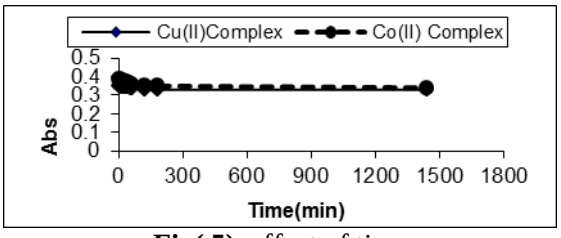
The electronic absorption of APAN and their complexes in ethanol have been recorded in the wavelength range (200 – 465) nm Fig. 1.2 . The electronic absorption of complex Co(II) showed a red shift for) electronic transition band charge transfer . [Co(L) . H_2O] shows one broad in visible region at 60.70 cm^{-1} refer to $^4T_{1g}$ (F) $\longrightarrow$ $^2T_{1g}$ (F) that is in accordance with tetrahedral geometry of cobalt metal ion[11] . The pH of metal complex solutions was adjusted using dilute solutions (0.01 M) CH_3COONa, and the effect on absorbance was studied Fig.4 . The absorbance of the complex was maximum and constant in the pH range given in Table. 1 whereas , The complex of $[Cu(L)_2]$ H_2O shows bands appearing in the rang of 250 - 373 nm attributed to $\pi \longrightarrow \pi^*$ transition .The other bands observed in the region of 373 -506 nm is attributed charge transfer to electronic transition Fig 4.



Fig(4). Effect of pH

Effect of reaction time

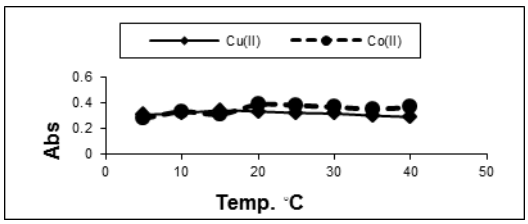
The color intensity reached a maximum after the Co(II) and Cu(II) has been reacted immediately with APAN therefore one minute development time was selected as optimum in the general procedure . The color obtained were stable for a least 24hr for both complexes Fig(5).



Fig(5). effect of time

Effect of temperature

The effect of temperature on the colour intensity of the products was studied . In practice , the same absorbance were obtained when the colour was developed at room temperature (20 – 30)C° complexes , but when the volumetric flask were placed in a water – bath for both at (30 – 40) C° a loss in colour intensity and stability were observed , therefore it is recommended that the colour reactions should be carried out at room temperature for complexes Fig(6).



Fig(6.) Effect of temperature

Calibration graph

The calibration equations for (2 – 22 µg per 10 ml 0.2 – 2.2 ppm) Co (II) and for (2-24 µg per 10 ml ,0.2 -2.4 ppm) Cu (II) are Y = 0.2482×+0.0002 (r = 0.9791) y = 0.2122× +0.1153 (r = 0.9777) respectively . Since the coloured complexes are stable for 24 hrs , the method can be applied to large series of samples . The molar absorptivity and sandell sensitivity given in Table.1

Conductivity measurements

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

Table (2) *:- Effect of Conductivity measurement*

Complexes	**Conductivity measurements S.mole^{-1}.cm^{-2}**	
	DMSO	**Ethanol**
$Co(APAN)_2.XH_2O$	10.3	15.7
$Cu(APAN)_2.XH_2O$	9.2	12.5

Composition of the complexes and free energy

The composition of complexes were studied in the excess of reagent solution by the mole-ratio method . A break at a 1:2 (M:L) mole ratio suggested the formation of complexes where M= Co(II),Cu(II) and L= APAN under the given condition . The formation constant of the reaction products was calculated according to the equation[12].Also the free energy changes (ΔG) were calculated according to the following equation; ΔG = -2.303RT log Kf Where R=gas constant=8.3 J/degree. mole, T= absolute temperature = ºC + 273.Using the above equation ΔG were found to be -4953.8 KJ.mole^{-1} and -6673.3 respectively. The negative value of ΔG indicates that the reactions are spontaneously.

IR Spectra of reagent and it`s Complexes

The I.R. bands of the (APAN) and its Co (II) and Cu(II) complexes with their probable assignment are give in Table .The IR Spectrum of the ligand shows abroad band at 3422 cm^{-1} ,which can be attributed to the *v*(OH) group. However, the *v* (N=N) stretching band in the free ligand is observed at 1570cm^{-1} .This band is shifted to lower with low intensity 1565cm^{-1} and 1560 cm^{-1}frequency values upon complexation suggesting chelation via the (M-N) [13-15] .The IR Spectrum of the ligand revealed a sharp band at 1643 cm^{-1} due to *v* (C=N)of the N pyrozol azo nitrogen. The band of (C=O) is shifted to lower frequencies in the complexes indication to that it has been affected upon chelation to the metal ion[16] .The bonding of oxygen to the metal ion is provided by the occurrence of bands at 520-525 cm^{-1} as the result of *v* (M-O)[17].

Table(3):- ***Selected IR data of (APAN) and its complexes with Co ,Cu(II) .***

compound	*v* (OH)	*v* (C=N)	*v* (N=N)	*v* (C-O)	*v* (M-O)	*v* (C-H) Aromt	*v* (M-N) azo
HL	3422 m	1643 s	1570 m	1115 s	-	3045 m	-
$[Cu(HL)_2]xH_2O$	3320 m	1530 s	1565 m	1110 s	520 w	3030 m	425 w
$[Co(HL)_2]\ xH_2O$	3316m	1532 s	1563 m	1120 s	525 w	3030 m	430 w

S: sharp, m: medium ,w: weak

On the basis of the IR , and a stoichiometric data the structure of complexes can be suggested as follows Fig(7)

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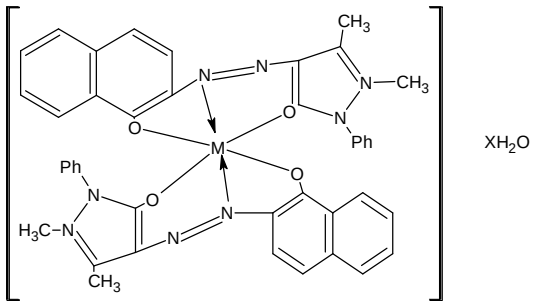

M =Cu(II) ,Co(II)

Fig (7):- The proposed structural formula of Co(II) & Cu(II)complexes with APAN.

Application

The propose method ware applied to the determination of Co(II) and Cu(II) in synthetic mixture were analyzed by the procedures described above and results displayed in Table .3.

Table (4):- Determination of Co(II) and Cu(II) in synthetic mixtures

Composition of mixture µg.ml^{-1}	*Found by present method µg.m^{-1}*	*%R.SD of the Co(II) and Cu(II) complexes*
Co^{++}(1) ,Cu^{++}(10) ,Fe^{+++}(10)	1.040	0.291
Co^{++}(0.8),Ni^{++}(10),pd^{++}(10)	0.896	0.336
Cu^{++}(0.4Co^{++}(10) Mn^{++}(10)	0.472	0.332
Cu^{++}(1) ,Cr^{++}(10),Fe^{+++}(10)	0.623	0.985

Conclusion:

4-(4-antipyriyl azo) -2-Naphthal react with Cu(II) and Co(II) ,which from complexes which can be easily dissolved in ethanolic solution .The present method has been found to be simple ,rapid and applicable for the determination of Cu(II) and Co(II) metals in the presence of each other ,which makes it an alternative to the existing methods for the determination of these metals.

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تخليق ودراسة طيفية للمركبAntipyryl azo 2-Naphthol واستخدامه ككاشف جديد لتحديد ايونات Cu(II) و Co(II)

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الخلاصة:
تم تطوير طريقة طيفية حساسة وسريعة ودقيقة في تقدير الكوبلت (II) والنحاس (II) . اعتمدت الطريقة على عملية التعقيد بين الايونات المذكورة والكاشف 4(4- بايروزولون ازو|)-2-نفثول في الوسط المائي. كانت قيمة الامتصاصية العظمى وثابت الامتصاصية المولارية للمعقدات المتكونة 513 و 506 ، 104x0,531 و 105x0,12 لتر .مول-1 .سم-1 للكوبلت والنحاس على التوالي . تم تحضير الكاشف ومعقديه من المحاليل الايثانولية المائية. اثبتت الدراسة الستكيومترية ان نسبة الفلز الى الكاشف هي (2:1) . درست التداخلات الايونية من خلال استعمال الايونات السالبة والموجبة وكانت قيم ثوابت الاستقرار والانحراف القياسي 107x0,291 و 108x0,909 لتر زمول-1 ، (0,291) و (0,332) على التوالي. تم تطبيق الطريقة وبنجاح على نماذج مختبرية محضرة .