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

Hussain J. Mohammed* Azhar Y. Muhi ** Fatema. Abbas**

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Abstract
A simple, accurate and sensitive spectrophotometric method has been developed for the determination of Cobalt(II) and Copper (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 $\varepsilon_{max}$ $0.531 \times 10^4$ and $0.12 \times 10^5$ 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, antipyryl azo -2-Naphthol.

Introduction:
Pyrazolone 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 photocromatic, redox responsive, stability low valent metal oxidation states due to the presence of a low –lying azo centered $\pi$ molecular or bital serves as a molecular switch is used as ametal ion indicator, dyes and pigments in industry [2]. Copper is an nutritionally 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’-antipyryl azo)-2-Naphthol has been used as a reagent for the spectrophotometric determination.
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 1.0 g, 0.004 mol 4-amino antipyrin in 25 ml of ethanol and 5 ml concentrated hydrochloric acid with 15 ml of distilled water, and adding sodium nitrite solution dropwise at 0-5°C. 2-Naphthol 0.0083 mol 1.2 g was dissolved in 50 ml of ethanol and 35 ml of (4N) NaOH were added at (0-5°C). The mixture was allowed to stand and added 20% HCl solution. The precipitate was filtered off and recrystallized from ethanol [10] scheme 1.

B- Preparation of complex
The complex was prepared by stoichiometric amount from ligand in 50 ml of ethanol then added dropwise with stirring to a stoichiometric amount 1:2 ions (copper, cobalt) 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. Copper (II) stock solution (100 μg.ml⁻¹)
Dissolve 0.0268 gm of CuCl₂·H₂O 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 (100 µg ml⁻¹)
Dissolve 0.02203 gm of CoCl₂ in 100 ml 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-Naphthol(1x10⁻³ M)
0.0358 gm of reagent (APAN) was dissolved in 100 ml of ethanol, working (APAN) (1x10⁻³ 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 10 µg.ml⁻¹ to cover the range of calibration curve, add 3.5 ml and 2.5 ml of 5x10⁻⁴ 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 513 nm, 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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Co(II)</th>
<th>Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maxime (nm)</td>
<td>513 nm</td>
<td>506 nm</td>
</tr>
<tr>
<td>Beer's law range (µg/ml)</td>
<td>0.2-2.4</td>
<td>0.2-2</td>
</tr>
<tr>
<td>pH range</td>
<td>5.5-9.5</td>
<td>2.5-4.5</td>
</tr>
<tr>
<td>Sandell’s S sensitivity (µg.cm⁻²)</td>
<td>0.005 µg.cm⁻²</td>
<td>0.0018 µg.cm⁻²</td>
</tr>
<tr>
<td>Molar absorptivity (L.mole⁻¹.cm⁻¹)</td>
<td>0.531x10⁴</td>
<td>0.12x10⁴</td>
</tr>
<tr>
<td>Stability constant (L.mol⁻¹)</td>
<td>2.91x10⁷</td>
<td>9.09x10⁸</td>
</tr>
<tr>
<td>K_f</td>
<td>0.14x10⁴</td>
<td>0.74x10⁴</td>
</tr>
<tr>
<td>ΔG KJ.mole⁻¹</td>
<td>-6673.3</td>
<td>-4953.8</td>
</tr>
</tbody>
</table>

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.

![Absorption spectra of (APAN-Cu)](image1)

**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.

![Absorption spectra of (APAN-Co)](image2)

**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′-antipyril 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.
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) . H₂O ] shows one broad in visible region at 60.70 cm⁻¹ refer to ⁴T₁g(F) → ²T₁g(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) CH₃COONa, 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 ] H₂O shows bands appearing in the range of 250 - 373 nm attributed to π → π* transition. The other bands observed in the region of 373 - 506 nm is attributed charge transfer to electronic transition Fig 4.

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).
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).

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 $1\times10^{-3}$M solution at 25°C 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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Conductivity measurements</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>S.mole$^{-1}$.cm$^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Co(APAN)$_2$.XH$_2$O</td>
<td>10.3</td>
<td>15.7</td>
</tr>
<tr>
<td>Cu(APAN)$_2$.XH$_2$O</td>
<td>9.2</td>
<td>12.5</td>
</tr>
</tbody>
</table>

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 = °C + 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 its Complexes

The I.R. bands of the (APAN) and its Co (II) and Cu(II) complexes with their probable assignment are given in Table . The IR Spectrum of the ligand shows a broad band at 3422 cm\(^{-1}\), which can be attributed to the \(\nu(\text{OH})\) group. However, the \(\nu\) (N=N) stretching band in the free ligand is observed at 1570 cm\(^{-1}\). This band is shifted to lower with low intensity 1565 cm\(^{-1}\) 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 \(\nu\) (C=N) of the N pyrozo 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 \(\nu\) (M-O)[17].

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu) (OH)</th>
<th>(\nu) (C=N)</th>
<th>(\nu) (N=N)</th>
<th>(\nu) (C=O)</th>
<th>(\nu) (M-O)</th>
<th>(\nu) (C-H) Aromt</th>
<th>(\nu) (M-N) azo</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>3422 m</td>
<td>1643 s</td>
<td>1570 m</td>
<td>1115 s</td>
<td>-</td>
<td>3045 m</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(HL)(_2)]XH(_2)O</td>
<td>3320 m</td>
<td>1530 s</td>
<td>1565 m</td>
<td>1110 s</td>
<td>520 w</td>
<td>3030 m</td>
<td>425 w</td>
</tr>
<tr>
<td>[Co(HL)(_2)]XH(_2)O</td>
<td>3316 m</td>
<td>1532 s</td>
<td>1563 m</td>
<td>1120 s</td>
<td>525 w</td>
<td>3030 m</td>
<td>430 w</td>
</tr>
</tbody>
</table>

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).

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

Application

The propose method were 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

<table>
<thead>
<tr>
<th>Composition of mixture µg.mL⁻¹</th>
<th>Found by present method µg.mL⁻¹</th>
<th>%R.SD of the Co(II) and Cu(II) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co⁺⁺(1),Cu⁺⁺(10),Fe⁺⁺⁺(10)</td>
<td>1.040</td>
<td>0.291</td>
</tr>
<tr>
<td>Co⁺⁺(0.8),Ni⁺⁺⁺(10),pd⁺⁺⁺(10)</td>
<td>0.896</td>
<td>0.336</td>
</tr>
<tr>
<td>Cu⁺⁺⁺(0.4Co⁺⁺⁺(10)Mn⁺⁺⁺(10)</td>
<td>0.472</td>
<td>0.332</td>
</tr>
<tr>
<td>Cu⁺⁺⁺(1),Cr⁺⁺⁺(10),Fe⁺⁺⁺(10)</td>
<td>0.623</td>
<td>0.985</td>
</tr>
</tbody>
</table>

Conclusion:
4-(4-antipyril 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.

References:
2. Y. Azhar ; J. Hussain, proceedings of The first Conference for pure and Applied sciences2008
تخليق ودراسة طيفية للمركب Antipyryl azo 2-Naphthol ككاشف جديد لتحديد ايونات Co(II) و Cu(II) و استخدامه

حسين جاسم محمد*، أزهر ياسين محي**، فاطمة عباس خزعل***

*كلية العلوم جامعة الكوفة
**كلية التربية للبنات/جامعة الكوفة
***كلية العلوم جامعة الكوفة

الخلاصة:

تم تطوير طريقة طيفية حساسة وسريعة ودقيقة في تقدير الكوبالت (II) والنحاس (II) . اعتمدت الطريقة على عملية التعقيد بين الايونات المذكورة والكاشف (4- بابروزولون ازو) -2-نفول في الوسط المائي. كانت قيمة الامتصاصية العظمى وثابت الامتصاصية المولارية للمعقدين المتكونة 999 و 995 لتر.مول -1 سم -1 للكوبالت والنحاس على التوالي . تم تحضير الكاشف ومعقديه من المحاليل الائثانولية المائية. أثبتت الدراسة استقرارية الدقة (1:2) . درست التداخلات الايونية من خلال استعمال الايونات السالبة والموجبة وكانت قيم ثوابت الاستقرار والانحراف القياسي 93979 لتر زمول -1 و 93999 لتر زمول -1 (0,291) و (0,332) على التوالي . تم تطبيق الطريقة ونجاح على نماذج مختبرية محضرة.