Novel cyclic voltammetry behavior of 3-((benzothiazol-2-diazenyl)naphthalene-2,7-diol) and use it for spectrophotometric determination of copper (II) in honey sample

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Abstract:
The azo reagent 3-((benzothiazol-2-diazenyl)naphthalene-2,7-diol) was synthesized and characterized by FT-IR, 1H-NMR and 13C-NMR spectral techniques. The electrochemical behavior of the azo reagent and its complex with Cu (II) has been studied at glassy carbon disk GCE electrode in different supporting electrolyte at concentration (1M) and scan rate (100mv.s-1). Spectrophotometric determination of copper (II) is based on the formation of a 2:1 complex with above reagent. The complex has Amx at(588) nm and Emax of 1.436x104L.mol⁻¹.cm⁻¹.

A linear correlation (0.1 – 3.0 μg. ml⁻¹) was found between absorbance at λmax and concentration. The effect of diverse ions on the determination of copper (II) to investigate the selectivity of the method were also studied. The stability constant of the product was (1.1x105). The proposed method was successfully applied to the analysis of honey sample.

Key Words: Cyclic voltammetry, 3( benzothiazol-2-diazenyl)naphthalene-2,7-diol), copper (II), spectroscopy.

Introduction:
Azo compounds have been the most extensively used class of dyes owing to their versatile application in several fields, such as advanced application in organic synthesis, dyeing cloth fiber biomedical studies, azo dyes are also used in coloring agents in Pharmaceuticals and foods. Azo dyes have wide interest of applications in complexometric titration and in analytical chemistry. These compounds are also used in oils, plastics, waxes and polishes. In addition, azo compounds and their bio conjugates have attracted clinical interest related to photo therapy and photo diagnosis of tumors and their lesions [1-5]. The determination of metal ion at trace amount have been shown important in the fields of biological and environmental studies literature date indication that azo compound have been broadly used in the spectrophotometric determination of metal ions [6-13]. Several instruments method are present in the literature used to determine copper ion, and these method inductively coupled plasma atomic emissions spectrometry [14,15], flame and electro thermal atomic absorption spectrometry [16,17], flow injection [18-19]. 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 study, we wish to report the electrochemical behavior of this reagent and as a selective reagent in spectrophotometric determination of micro amounts of copper (II).BTHN is a tridentate via azo group, hydroxyl group and nitrogen atom of thiazol group: it has the following structure:

![Structure of the (BTHN)](image)

Experimental: All chemicals used in this work were of analytical grade.

In this study the FT-IR spectra of azo compound was recorded on Schimadzu FT-IR spectrophotometer model in KBr wafer and the NMR spectra was obtained on BRUKER AV 400 AvanceII 400MHz instrument using DMSO as solvent and reported relative to TMS as internal standard. CE440CHN/O/S Elemental Analyser was made by EAI while voltammetric experimentas were carried out using a computer – controlled electroanalysis system using a (EZ-State by NuVant) system. A three- electrode combination system was an Ag /AgCl reference electrode, a Pt wire auxiliary electrode and glassy carbon electrode as working electrode, the potential range selected was in the Range(1-1.25) mV. All measurements were carried out at room temperature.

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Synthesis of thiazol derivative:

2- amino Benzothiazole(0.0066mole) 1.0000g was diazotized by dissolving it in (5ml) ethanol then (15ml) of HCl(4M) was added keeping the temperature at (0-5°C) then adding NaNO₂ solution gradually and left it about (15min) to cool well. The coupling material (2,7-dihydroxy naphthalen)(0.0066mole)(1.0650g) was dissolved in 15ml of NaOH(4M) and leave to cool well, then this solution was added to diazonium salt solution slowly drop by drop to maintain temperature (0-5°C). The mixture was allowed to precipitate was filtered off and washed several times with (1:1) (alcohol:water) mixture then recrystallized from boiling ethanol and left to dry.

Scheme (1).

Reagents

Copper stock solution (100 µg.ml⁻¹): The solution was prepared by dissolving (0.00536 g) of copper chloride in (200 ml) of deionized water.

3(benzothiazol-2-diazenyl naphthalen-2,7diol(1X10⁻³M): This solution was prepared by using (0.0321 g) of reagent in (100 ml) of ethanol.

Other ions (foreign) solution: All of ions were prepared by using a suitable amount of the compound in deionized water in a calibrated flask.

Results and Discussion:

Absorption Spectra:

The reagent (BTHN) nm possess a maximum absorption at 440 nm (Fig.1) reacts with (CuCl₂.2H₂O) at room temperature to give a (BTHN-Cu(II)) colored complex at pH 7. The absorption spectrum shows a maximum at 588 nm, whereas the reagent blank give no absorption at this wavelength (Figure. 2)
The effect of various parameters on the absorption intensity of the formed products was studied and the reactions conditions were optimized. The reaction of (BTHN) with Cu(II) was studied at different pH by using HCl or NaOH (0.05N) in the range (2-10). It was found that the chelating complex was formed at pH 7. (Fig. 3). It was found that absorbance rises with increasing reagent concentration and got its maximum value on using (1.5 ml of 1×10⁻³ M) in subsequent experiment.

**Quantification:**

In order to study the range in which the colored complex adhere to Beer’s law the absorbance of the complex was measured at λmax for sequence of solutions containing increasing amounts of Cu(II) at optimum conditions. The validity of Beer’s law, molar absorptivity and Sandell’s sensitivity values were estimated and are given in Table 1, shown that the method is sensitive. The proposed method showed a good linearity for the determination of Cu(II) with a good correlation coefficient (0.9588). The relative standard deviation % (RSD) for the analysis of six replicates of Cu(II) is equal to (0.464) showed that the method is precise and accurate, while detection limit is equal to (0.0139). The stoichiometric ratio of (BTHN) and Cu(II) was studied applying the continuous variation (Job’s) and mole ratio methods [20,21] using equimolar solutions of the new ligand and Cu(II) (1×10⁻⁴). It was found that (BTHN) forms a dye coupled product with Cu(II) in the ratio 2:1 as in (Figure 4).

**Table (1) characteristics data of Cu(II)-BTHN complex**

| parameter                  | Values of method |
|----------------------------|------------------|
| Beers law limits (µg.ml⁻¹) | (0.1-3.0)        |
| Molar absorptivity (L.mol⁻¹.cm⁻¹) | 1.436×10⁴     |
| LOD(µg/ml)                 | 0.0139           |
| R.S.D %                    | 0.464%           |
| Correlation coefficient    | 0.9588           |
| Sandell’s sensitivity µg .cm⁻² | 0.0044       |
FTIR Analysis:

The FT-IR spectra of the free ligand have a broad band about (3421-3176) cm\(^{-1}\) which could be attributed to (OH) stretching vibration. The shape and intensity of band were changed that led to expect coordination was accurate in complex (Cu-BTHN). Likewise, the stretching frequency of (N=N) at (1561) cm\(^{-1}\) was shifted to a lower frequency (1531) cm\(^{-1}\) in complexes. The bands at frequency (1651-1593) cm\(^{-1}\) also was changed as well as the band at (1305-1201) cm\(^{-1}\) which corresponding with (C-N=N-C) and (C=N-N=C) were shifted towards lower frequency [22-24]. The FT-IR spectra of copper complex also shows additional bands in (495) cm\(^{-1}\) which is due to the formation of (M-O) and (449) cm\(^{-1}\) for (M-N). (Fig. 5.6)

Fig(4) continuous variation plot of the Cu-BTHN

Fig (5) The FT-IR Spectrum of the dye (BTHN)

Fig(6) The FT-IR Spectrum of (Cu-BTHN) complex

\(^1\)H-NMR data of BTHN and it complex with Copper(II):

The \(^1\)H-NMR and \(^{13}\)C-NMR spectra of the prepared azocompound was made ligand in DMSO solution with tetra methylsaline as an internal standard indications the following signals as in Table. 2 and Table.3. (Fig.7-10)
Table (2) $^1$H-NMR data of BTHN and its complex with Copper(II)

| compound     | C-OH Ar | CH-     | Ar-H naphthalene | CH benzothaizol | CH$_3$ of DMSO |
|--------------|---------|---------|------------------|-----------------|--------------|
| BTHN         | 10.3    | -----   | 6.93-6.184       | 7.84            | 2.5          |
| Cu-BTHN      | 10.2    | 3.387   | 7.120-6.8        | 7.32-7.75       | 2.5          |

Table (3) $^{13}$C-NMR data of BTHN and Cu-BTHN complex

| compound       | C-N benzothaizol | C-OH naphthalene | C-H benzothaizol | C-H naphthalene | C-N naphthalene |
|----------------|------------------|------------------|------------------|-----------------|-----------------|
| BTHN and Cu-BTHN | 160              | 156.3            | 136.76-122.34    | 122.34-115.7    | 107.7           |

Fig (7): The $^1$H NMR spectrum of azo compound (BTHN)

Fig (8): The $^1$H NMR spectrum of (Cu-BTHN) complex
Fig (9): The $^{13}$C NMR spectrum of compound (BTHN)

Figure (10): The $^{13}$C NMR spectrum of complex Cu-(BTHN)

According to the results of the FT-IR, $^1$H-NMR, $^{13}$C-NMR, stoichiometric and elemental analysis the structure of complex can be suggested as the following:

Interferences

The effect of different ions in the determination of copper (II) was studied. Cu(II) can be determined in presence of 10 or more fold excess of cation and the interference via the various ions were removed by using suitable masking agent Table(4)
Table (4): Interference of ions and removed them by masking agent

| No | Foreign ions | Conc. ppm | Error% | Masking agent | Error% |
|----|--------------|----------|--------|---------------|--------|
| 1  | Co\(^{2+}\)  | 10       | 48.08  | Thiourea(1ml) | 0.52   |
| 2  | Cd\(^{2+}\)  | 10       | 1.21   | ----          | ----   |
| 3  | Sr\(^{2+}\)  | 10       | -3.11  | ----          | ----   |
| 4  | Ni\(^{2+}\)  | 10       | -35.88 | Formaldehyde(0.5ml) | 0.36   |
| 5  | Sn\(^{2+}\)  | 10       | 2.7    | ----          | ----   |
| 6  | Cs\(^{+}\)   | 10       | 1.52   | ----          | ----   |
| 7  | Zn\(^{2+}\)  | 10       | 0.8    | ----          | ----   |
| 8  | Pb\(^{2+}\)  | 10       | -2.39  | ----          | ----   |
| 9  | Mn\(^{2+}\)  | 10       | 12     | Formaldehyde(1ml) | 0.28   |
| 10 | Hg\(^{2+}\)  | 10       | -1.913 | ----          | ----   |
| 11 | Ag\(^{+}\)   | 10       | 2.8    | ----          | ----   |
| 12 | Fe\(^{3+}\)  | 10       | 51.3   | Na\(_2\)HPO\(_4\)(1ml) | 0.45   |

Determination of Copper(II) in honeysample

0.1g of honey digested in microwave with 5ml of concentrated HNO\(_3\) and 3ml of 30% H\(_2\)O\(_2\). The result of digested solution was diluted to 100ml with deionized water, from this solution transfer 2ml in centerfuge tube for 10 min and analysis with UV-Vis proposed method and atomic absorption [25]. The results are shown in Table 5, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table (5): Cu(II) levels in Honey Sample

| Table of Honey                | Amount found by our spectrophotometric method(µg.ml\(^{-1}\)) | Amount found by Atomic Absorbtion(µg.ml\(^{-1}\)) |
|-------------------------------|---------------------------------------------------------------|-----------------------------------------------|
| Granja San Francisco          | 0.33                                                          | 0.29                                          |

Electrochemical behavior of azo dye(BTHN) and redox mechanism in aqueous solution:

The cyclic voltammograms of investigated azo dyes shown one to three irreversible cathodic peaks [26,27]. The number of peaks depends on pH and nature of compounds. The peaks observed are due to the reduction of azo -N=N- center. The reduction mechanism includes the formation of hydrazo derivatives followed by the cleavage of the -N=N- bond and the final formation of amines [28,29] according to the following equations:

\[-N=N- +2H^+ +2e^- \rightarrow \text{NH}_2\text{NH}^- \quad \text{(1)}\]

\[-\text{NH}_2\text{NH}^- +2H^+ +2e^- \rightarrow 2(-\text{NH}_2\text{H}) \quad \text{(2)}\]
Different supporting electrolyte was be used with the reagent (BTHN) at GCE with scan rate (0.1Vs⁻¹) for all cyclic voltammogrames. All voltammogrames are shows reduction peak of azo group (-N=N-) at potential ranged (-500mv –750mv). The choice of the better supporting electrolyte depends on the higher current for oxidation peak and clarity of peak (Fig.12-14) Table .6.

For reagent (BTHN) was proposed that the best supporting electrolyte is (KCl) (Fig. 11,12), current was highest between other electrolytes, cyclic voltammogram shows irreversible electrochemical system in which the electron transfer rates are significantly less than the rate of mass transport and the reduction in two steps, the first reduction attributed to azo group giving a hydrazo derivative, second reduction peak to breaks N-N linkage to form two primary amine molecules (scheme .2). All current peak ratio shows irreversibility of electrochemical system at different electrolyte due to the Ipc/Ipa≠1 Table .7, the deviation from number one due to the chemical reaction that arises subsequent transmission electron, such interactions can be complex, involving dissociation and isomerization [30].

**Table(6) Current –Potential data of(BTHN) in several supporting electrolyte Solution (1M) with scan rate (0.1Vs⁻¹)**

| R3  | Supporting Electrolyte | Ia₁ µA | Ea₁ mv | Ia₂ µA | Ea₂ mv | Ia₃ µA | Ea₃ mv | -lc₁ µA | Ec₁ mv | lc₂ µA | Ec₂ mv | lc₃ µA | Ec₃ mv |
|-----|------------------------|--------|--------|--------|--------|--------|--------|---------|--------|--------|--------|--------|--------|--------|
| 1   | KCl                    | 14.5   | 461    | 5.38   | 246    | ---    | ---    | 22.6    | 510    | 27.3   | 701    |        |        |
| 2   | KClO₃                  | 5.31   | -250   | 11.8   | 679    | ---    | ---    | 23.0    | 497    | ---    | ---    |        |        |
| 3   | K2HPO₄                 | 7.95   | 266    | 3.64   | 113    | ---    | ---    | 21.4    | 701    | ---    | ---    |        |        |
| 4   | KNO₃                   | 7.50   | 66.5   | 3.41   | 276    | ---    | ---    | 6.59    | 159    | 24.1   | 688    |        |        |
| 5   | K2SO₄                  | 8.41   | 465    | 5.45   | 220    | -6.59  | 677    | 5.68    | 192    | 23.9   | 599    |        |        |
| 6   | NaCl                   | 9.76   | 497    | 6.19   | 132    | 3.88   | 335    | 5.77    | 146    | 21.3   | 580    |        |        |
| 7   | NaH₂PO₄                | 9.62   | 699    | 6.15   | 89.6   | ---    | ---    | 5.19    | 163    | 23.5   | 675    |        |        |
| 8   | Na₂HPO₄                | 9.72   | 78.9   | ---    | ---    | ---    | ---    | 23.1    | 596    | ---    | ---    |        |        |
| 9   | TBABr                  | No res.|        |        |        |        |        |         |        |        |        |        |        |
| 10  | B.R                    | No res.|        |        |        |        |        |         |        |        |        |        |        |

**Enhancement in current of peak follows the following sequence:**

KCl > NaCL > Na₂HPO₄ > NaH₂PO₄ > K₂SO₄ > K₂HPO₄ > KNO₃ > KClO₃

**Fig(11 ) Effects of supporting electrolyte on the anodic peak current of reagent (BTHN)**
Table (7) Current–Potential data for (BTHN) at different supporting electrolyte (1M) and scan rate (0.1 Vs⁻¹)

| Supporting electrolyte | $E_a$ | $E_c$ | $I_a$ | $I_c$ | $\Delta E$ | $E_{1/2}$ | $I_a/I_c$ |
|------------------------|-------|-------|-------|-------|-----------|-----------|----------|
| 1 KCl                   | 461   | 14.5  | 510   | 22.6  | 49        | -24.5     | 0.641    |
| 2 KClO₃                | -250  | 497   | 5.31  | 23.0  | 248       | 373.5     | 0.230    |
| 3 KNO₃                 | 66.5  | 159   | 7.50  | 6.59  | 225.5     | -46.25    | 1.138    |
| 4 K₂HPO₄              | 266   | 701   | 7.95  | 21.4  | 435       | -217.5    | 0.371    |
| 5 NaCl                 | 497   | 146   | 9.76  | 5.77  | 643       | 175.5     | 1.691    |
| 6 Na₂HPO₄             | 78.9  | 596   | 596   | 23.1  | 674.9     | -258.55   | 0.420    |
| 7 NaH₂PO₄            | 699   | 163   | 9.62  | 5.19  | 862       | 268       | 1.85     |

Fig (12) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of KCl at scan rate 0.1Vs⁻¹

Fig (13) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of KClO₃ at scan rate 0.1Vs⁻¹
Fig (14) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of \(K_2HPO_4\) at scan rate 0.1 V s\(^{-1}\)

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\text{Scheme(2) Proposed mechanism of voltammetric reduction of reagent(BTHN)}
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Redox behavior of(Cu-BTHN) complex

Cyclic voltammograms of copper complex was recorded in different supporting electrolyte ,the results are summarized in Table.8 (Fig . 15-18), \(NaH_2PO_4\) 1M as supporting electrolyte was proposed the best electrolyte depending on the clarity of redox peaks (Fig . 23) .It clearly reveals that the redox process of the copper (II) complex at the scan rate (0.1Vs\(^{-1}\)) involves one reduction cathodic peak (Epc=48.6 mv) . In the anodic side the direct oxidation of complex is observed with a strong peak at( Epa= 90.2 mv) .It is observed that \(\Delta E_p\) values was found equal to (138.8 mv) and the ratio of anodic to cathodic peak currents(Ipa/Ipc\(\neq\)1) corresponds to more than one electron transfer process. The difference in the value of (Epc-Epa is \(\Delta E_p\)) which is smaller than the value required for a reversible process ( 59 mv) indicating that , reduction of copper complex at silver electrode is irreversible Table .9 [31,332].

Fig( 15)cyclic voltammograms for( Cu-BTHN)complex in(\(NaH_2PO_4\)) (1M) at scan rate 0.1Vs\(^{-1}\)
Fig(16)cyclic voltammograms for (Cu-BTHN)complex in(KNO₃) (1M) at scan rate 0.1Vs⁻¹

Fig(17)cyclic voltammograms for (Cu-BTHN)complex in(NaCl) (1M) at scan rate 0.1Vs⁻¹

Fig(18)cyclic voltammograms for (Cu-BTHN)complex in(K₂HPO₄) (1M) at scan rate 0.1Vs⁻¹

Table (8)Current –Potential data for(Cu-BTHN)complex at different supporting electrolyte (1M) at scan rate (0.1 Vs⁻¹)

| Supporting Electrolyte | Ia₁ (µA) | Ea₁ (mV) | Ia₂ (µA) | Ea₂ (mV) | Ia₃ (µA) | Ea₃ (mV) | -Ic₁ (µA) | Ec₁ (mV) | Ic₂ (µA) | Ec₂ (mV) | Ic₃ (µA) | Ec₃ (mV) |
|------------------------|---------|---------|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1 KCl                   | 9.41    | 626     | 4.37     | 181     | --      | --      | 5.14    | 129     | 12.0    | 471     | --      | --      |
| 2 KClO₃                | 12.2    | 645     | 6.29     | +92.1   | 1.89    | 289     | 29.4    | 535     | --      | --      | --      | --      |
| 3 K₂HPO₄               | 7.31    | 166     | 3.81     | 80.9    | 385     | 432     | 4.58    | 53.5    | 6.50    | 211     | 13.0    | 632     |
| 4 KNO₃                | 7.88    | 31.8    | 4.74     | 250     | --      | --      | 6.12    | 59.2    | 14.3    | 549     | --      | --      |
| 5 K₂SO₄               | 8.08    | 539     | 5.87     | 150     | --      | --      | 5.14    | 133     | 14.7    | 514     | --      | --      |
| 6 NaCl                | 4.51    | 132     | --       | --      | --      | 11.3    | 460     | --      | --      | --      | --      | --      |
| 7 NaH₂PO₄            | 7.55    | 90.2    | --       | --      | --      | --      | 5.0     | 48.6    | 11.4    | 701     | --      | --      |
Table (9) Current –Potential data for(Cu-BTHN)) at (NaH₂PO₄)(1M) as supporting electrolyte at scan rate (0.1 Vs⁻¹)

| compound  | $E_a$, mV | $E_c$, mV | $I_a$, µA | $-I_c$, µA | $\Delta E_p$ | (Ipa/Ipc) | $E_{1/2}$, mV |
|-----------|-----------|-----------|-----------|------------|--------------|-----------|-------------|
| Cu-BTHN   | 90.2      | 48.6      | 7.55      | 5.0        | 138.8        | 1.5       | 20.8        |

Conclusion:
This work azo employing 3-((benzothiazol-2-diazenylnaphthalene-2,7-diol(BTHN) was successfully applied for the estimation of copper(II) ion. Due to of the sensitivity, rapidly and selectivity of the method, its application can be estimation of this ion in biological sample.

The cyclic voltammetric system of (BTHN) led to the formation of same hydrazine derivative which remains at the electrode surface according to equations:

The cyclic voltammetric system of complex (Cu-BTHN) led to the formation of two reagent molecule and copper (II) ion according to equation below:

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