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Preparation of A New Azo-Reagent Derivative from 8-hydroxy Quinoline for Determination of Copper (II) ion Using Spectrophotometric Technique

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Abstract

A new, sensitive, and accurate spectrophotometric analytical technique is used to determine copper (II) ion in different samples using a new azo derivative reagent of 8-hydroxy quinoline;4-((8-Hydroxy quinolin5-yl) diazenyl) benzoic acid (HQDABA). To diagnose the reagent and Cu(II) complex, Infrared spectroscopy, Ultraviolet-Visual radiation, Elemental Analysis (CHN), and techniques such as nuclear magnetic resonance spectroscopy (1HNMR) and mass spectroscopy were used. The approach is based on the interaction of copper (II) with the HQDABA reagent in a neutral solution, which results in the formation of a yellow complex with a maximum absorbance at 420 nm. The optimal circumstances, such as medium pH, reagent volume, reagent concentration, and time effect, were also thoroughly examined. The limits of detection (LOD), limits of quantification (LOQ), and Sandell sensitivity were determined to be 0.22 mgL-1, 0.740 mgL-1, and 7.46210-2g.cm-2, respectively. The proposed approach complied with beer's low concentration range of 0.5-15 mgL-1, and the recovery percentage of the various samples ranged from 78.26% to 111.53%. The proposed spectrophotometric technique has been shown to be simple, quick, and sensitive for determining Cu (II) ions in various materials.

Keywords: *spectrophotometric, copper, different samples, determination, Azo derivative of 8-hydroxy quinoline.*

INTRODUCTION

Copper is a mineral that is present all over the body that aids in the production of red blood cells as well as the maintenance of nerve cells and the immune system. It also aids in the formation of collagen, which is an essential component of bone and connective tissue. Copper also functions as an antioxidant, decreasing free radicals that harm cells and DNA, and it aids the body's iron absorption. In general, copper is required by the human body for energy production.

Large amounts of copper are not required by the body. Many people may not get enough copper in their diets, although those who are severely copper deficient are rare. Copper deficiency symptoms include anemia, hypothermia, bone fractures and osteoporosis, low white blood cell counts, irregular heartbeat, loss of skin pigmentation, and thyroid disorders. Although copper is considered a highly hazardous mineral when discovered in high amounts in drinking water, it is nevertheless necessary for human life, and a deficiency can result in ischemic heart disease, anemia, improper wool development, and

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bone diseases. As a result, determining trace quantities of Cu(II) is becoming more crucial. 1 Because of its chemical and physical properties, copper and its compounds are widely used in industry, with many products containing copper metal in their chemical structures, Copper is utilized in electrical equipment such as wire and motors, for example. This is due to copper's strong conductivity in terms of heat and electricity, as well as its ease of drawing into electrical wires. It is also utilized in building (for example, roofing and plumbing) and industrial gear (for example, heat exchangers).

Copper concentrations in drinking water should not exceed 1300 ug/L, according to the United States Environmental Protection Agency (US EPA).2 Several standard methods are utilized to measure trace amounts of copper in various materials, including graphite furnace atomic absorption spectrometry3, atomic fluorescence, and chromatography.4 Spectrophotometric methods are superior to other methods in accuracy, simplicity, precision, and rapidity, making them common methods, especially in developing countries.5-8 A new approach based on the reattachment of copper(II) with 5-(4-nitrophenyl azo) salicylic acid (NPAS) and 2,2′-dipyridyl (Dp) in ethanol medium at room temperature resulted in maximum absorption at 520 nm and a molar absorbance of 2.60 x 104 L mol-1 cm-1. At pH=5, the chromogenic reagent (2,2[O-trilidine-4,4-bisazo]bis[4,5-diphenylimidazole]) (MBBAI) was utilized. The compound absorbed at 409 nm.9-10 A simple, low-cost, and environmentally friendly centrifuge-free cloud point extraction method was devised to preconcentrate tiny quantities of Cu(II) before spectrophotometric measurement of Cu(II). It is based on the complexation process with the hydrophobic azo reagent 6-hexyl-4-(2-thiazolyl azo) resorcinol (HTAR), which produces an absorbance maximum at 535 nm.11 This study used HQDABA reagents to estimate copper ions and select the ideal reaction conditions for best outcomes.

EXPERIMENTAL

APPARATUS

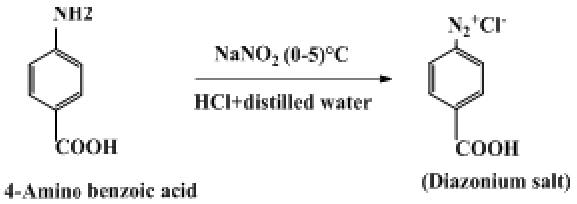
All absorbance measurements were tested using the Biochrom Libra S60 double beam spectrophotometer, and the pH value was measured using the Oakton 2100 Series pH/mV/Ion/0C/0F Meter. All samples were weighed using an Ohaus PA214 Pioneer Analytical Balance. The maximum wavelength was selected by using Shimadzu UV-1700 spectrophotometer. Flame atomic absorption spectrometry was used to calculate the real value of copper samples. The reagent and copper (II) combination was diagnosed by Infrared spectroscopy I.R, ultraviolet-visual radiation, element analysis (CHN), proton nuclear magnetic resonance spectroscopy (1HNMR), and mass spectroscopy (Shimadzu LCMS 2010 A).

MATERIALS

With the exception of the HQDABA reagent, all compounds were analytical grade and used without further purification. Distilled water was used to make the solutions in this investigation.

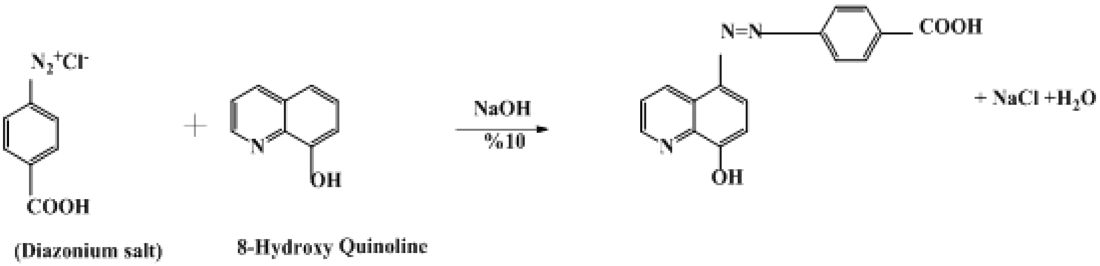
PREPARATION OF THE HQDABA

1.3714 g,0.01 mol of 4-amino benzoic acid was dissolved in 20 mL of water and 3 mL of rated HCl to make diazoinum chloride solution. The solution was dropwise treated with 5 mL of aqueous 0.69g,0.01mol sodium nitrite and agitated at 0°C for 30 minutes (the diazonium salt production stage is shown in Scheme (1).



Scheme (1): Formation stage of diazonium salt

With stirring, diazonium chloride solution was added dropwise to an alkaline solution of 8-hydroxy quoline1.4516g,0.01mol, the resultant mixture was then diluted in 150 mL of ethanol, and 5 mL of 10% sodium hydroxide was added. After stirring the mixture for 1 hour at 0-5°C. As illustrated in Scheme 2, the product was filtered, air dried, and recrystallized twice from hot ethanol before being dried in an oven at 50°C for two hours, m.p 190-195 °C.



Scheme (2): Formation stage of HQDABA

The STANDARD PREPARATION OF STOCK SOLUTIONS

100 mg L-1 Copper (II) ion Solution: A stock solution was generated by dissolving 0.0268 g of copper chloride in 100 mL of distilled water, and working solutions were obtained by further dilution.

- New organic reagent solution (HQDABA) 1 ×10-4 molL-1: 0.0293g of the organic reagent was dissolved in 100 mL of ethanol to make a stock solution. As needed, more dilute reagent solutions were produced.

- Interference solutions: All interference ions solutions are prepared in 100 mgL-1 concentration, by dissolving amounts(0.0404,0.0403,0.0231,0.0484,0.022,0.013,1.63,0.0137) gram of the substance NiCl2.6H2O, CoCl2.6H2O, Pb(CH3COO)2, FeCl3.6H2O, NaCl, NaF, CH3COONa and NaHCO3 respectively in distilled water (pH=7) and completing the volume to 100 mL. to get on Ni+2 , Co+2, Pb, Fe+3, , F-, CH3COO-, Cl-and HCO3-1 as interference ions. In two different concentrations, each foreign ion was tested. In contrast to the second test, which was conducted with an interference ion concentration of 50 mg L-1, the first test used an interference ion concentration of 10 mg L-1.

- Masking agent: All masking agents have been prepared in 100 mg L-1 concentration, by dissolving the right quantities of the chemical in distilled water and bringing the total volume to 100 mL. The masking Tartare sodium weight is 0.01 g. The masking agent for each interfering ion was added drop by drop until reached the appropriate amount needed to remove the interfering effect.

SAMPLES COLLECTION

The suggested method was applied to different samples. Samples were including foods (sesame), samples of tap water, metal wire, and medicine sample. In order to compare the concentration of copper in the samples to the indicated approach, all samples were processed using the wet digestion technique, and the concentration of copper on these samples was evaluated using the Flame Atomic Absorption Spectrometry (FAAS) standard method.

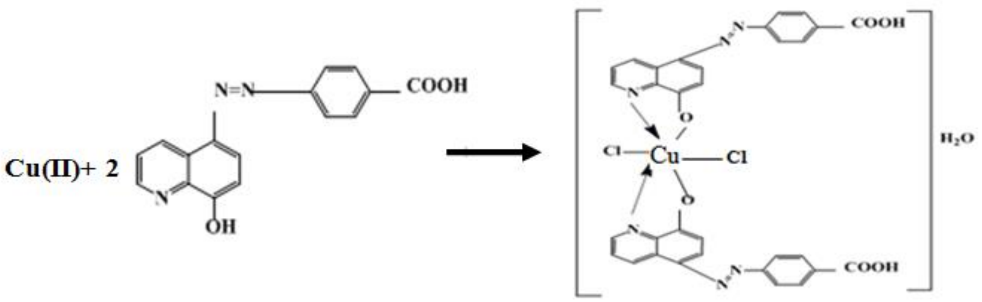
PREPARATION OF SAMPLES

The wet digestion method was used to prepare the samples in this study and the procedural show as follows12:

10g of sample was weighed and then transferred to a 200 ml beaker.20 mL of concentrated nitric acid HNO3 was added and the mixture was heated up by using a boiling water bath until the total remnant volume of the mixture became 2-3mL. The mixture cooled down.20mL from concentrated HNO3,10mL from concentrated H2SO4 and 8mL from H2O2 were added and the mixture was heated up for another time. After completing the digestion process, 20 mL of distilled water is added and the mixture is heated up to discard all extra acids. (Repeat this step as needed until remove all extra acids). Finally, the mixture cooled down, then filtered in a 100 mL volumetric flask, and the solution was diluted to the mark with distilled water.

RESULTS AND DISCUSSION

The proposed spectrophotometric method in this study was depending on the complexation of copper (II) ion with of HQDABA which gave the yellow complex an absorbance maximum at 420 nm. The laboratory-prepared HQDABA reagent and copper (II) complex were diagnosed by using many techniques including 1HNMR, mass spectroscopy, elemental analysis (CHN), infrared and ultraviolet-visual spectroscopy. The optimum conditions for this reaction were studied carefully to increase the accuracy of the results.



Scheme 3. Proposal mechanism between copper (II) and HQDABA reagent.

REAGENT AND COPPER (II) COMPLEX ELEMENTAL ANALYSIS (CHN)

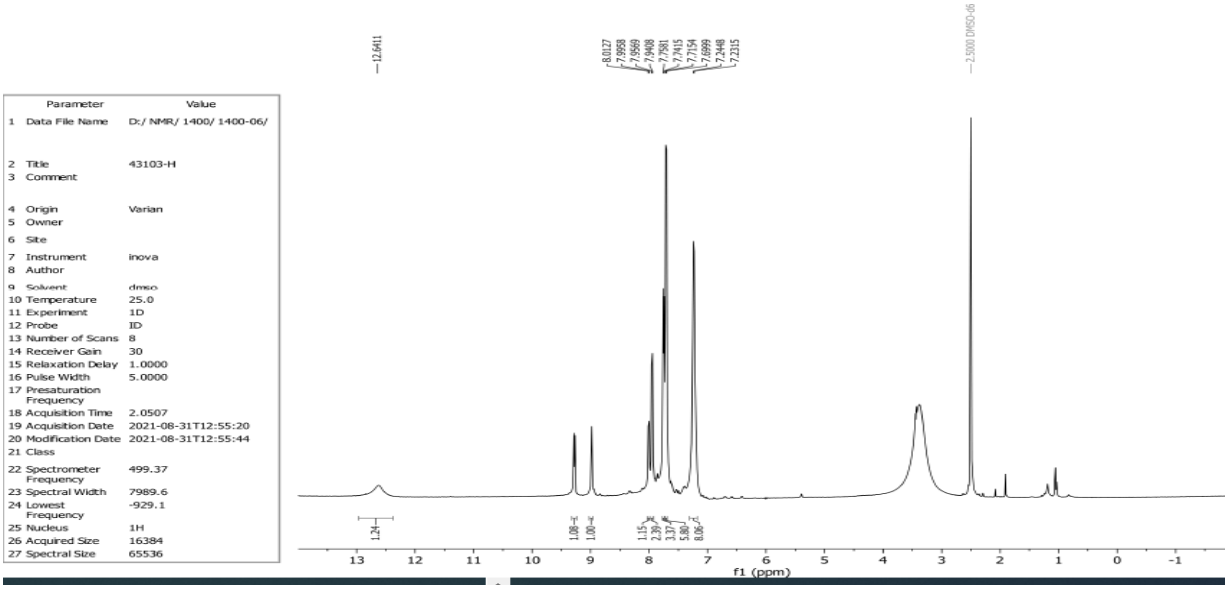
A significant degree of convergence is observed between the experimentally gathered data and the theoretically estimated data in Table I, confirming the accuracy of the composition of the HQDABA reagent and copper(II) complex.

Table 1. Reagent and its copper complex's physical and analytical characteristics

Compound	**Color**	**m.p ° C**	**Yield %**	**M.f (M.wt g/mol)**	**Found (Calc.)%**			
					C	**H**	**N**	**M**
Reagent $C_{16}H_{13}N_3O_3$	**Red**	**190-195**	**80**	**293.3**	**(61.71)** **65.41**	**(4.41)** **4.43**	**(14.08)** **14.31**	**___**
$[Cu(C_{16}H_{13}N_3O_3)_2 Cl_2].H_2O$	**Brown**	**224**	**78**	**739.146**	**(50.57)** **51.95**	**(3.22)** **3.36**	**(11.70)** **11.36**	**(7.67)** **8.59**

^{1}HNMR OF REAGENT

The reagent's 1HNMR spectrum in DMSO (Fig. 1) exhibits a number of aromatic proton-related signals at (=7.2315-8.0127 ppm). On the other hand, the proton of phenol is responsible for the signal at (=7.630 ppm). While the signal peak at (=2.500ppm) is referred to as DMSO-d6, the signal at (=12.6411 ppm) is attributed to the proton of the carboxylic group.



	Parameter	Value
1	Data File Name	D:/ NMR/ 1400/ 1400-06/
2	Title	43103-H
3	Comment	
4	Origin	Varian
5	Owner	
6	Site	
7	Instrument	inova
8	Author	
9	Solvent	dmso
10	Temperature	25.0
11	Experiment	1D
12	Probe	ID
13	Number of Scans	8
14	Receiver Gain	30
15	Relaxation Delay	1.0000
16	Pulse Width	5.0000
17	Presaturation Frequency	
18	Acquisition Time	2.0507
19	Acquisition Date	2021-08-31T12:55:20
20	Modification Date	2021-08-31T12:55:44
21	Class	
22	Spectrometer Frequency	499.37
23	Spectral Width	7989.6
24	Lowest Frequency	-929.1
25	Nucleus	1H
26	Acquired Size	16384
27	Spectral Size	65536

Figure 1. ^{1}HNMR spectrum of reagent

INFRARED SPECTRUM

To determine the mechanism of bonding and the impact of the metal ion on the reagent, the FTIR spectra of the reagent and copper complex were studied and assigned based on a thorough comparison of their spectra, as shown in Table 2. The stretching vibration of the carboxyl group's (OH) stretching vibration has been assigned to the FTIR spectrum of the reagent (Figs. 2 and 3), which displayed broadband at (3441 cm-1).13 The disappearance of this band in the spectra of the copper (II) complex indicated the deprotonation of the carboxyl group prior to and indicated the coordination with the copper (II) ion. The band at (3074 cm-1) in the reagent's spectra was identified as the (OH) group of phenol.14 The carboxyl group's (C=O) has been attributed to a strong band in the reagent spectra at (1687 cm-1).15 In complexation with copper(II) ions, a notable shift to a higher frequency has also been seen. On complexation with a metal ion, a notable change in intensity and location to a lower frequency was seen in the strong band at (1589 cm-1) caused by the (COO) asymmetric vibration. The band at (1506 cm-1) in the reagent's spectrum was identified as the (COO) symmetric band and underwent a significant frequency change during complexation with the copper(II) ion.16 On complex non-shifting without change in form, bands corresponding to the azo bridge vibration at (1463 cm-1) and (1402 cm-1) were found, showing that this group was not involved in the coordination with the copper(II) ion. The complex spectrum lacks a new band that appears in the reagent spectrum and is caused by metal nitrogen and oxygen at 526 and 441 cm-1, respectively.17

Table 2. The Main Frequencies of the Reagent and its copper(II) complex.

Compounds	**ν(OH)carboxyl + ν(OH)phenol**	**ν(C=O)**	**ν as(COO)**	**ν s(COO)**	**ν(-N=N-)**	**ν (M-O)**	**ν (M-N)**
Reagent =$C_{16}H_{13}N_3O_3$	**3433 br. 3074 br.**	**1687 s.**	**1589 sh.**	**1591sh.**	**1463 sh. 1402 sh.**	**-**	**-**
$[Cu(C_{16}H_{13}N_3O_3)_2Cl_2].H_2O$	**3441br.**	**1689 sh.**	**1591sho.**	**1506sh.**	**1463sh. 1398sh.**	**526w.**	**441w.**

br = broad, s= strong, , sh = sharp, sho = shoulder, w = weak , as= asymmetric, s= symmetric

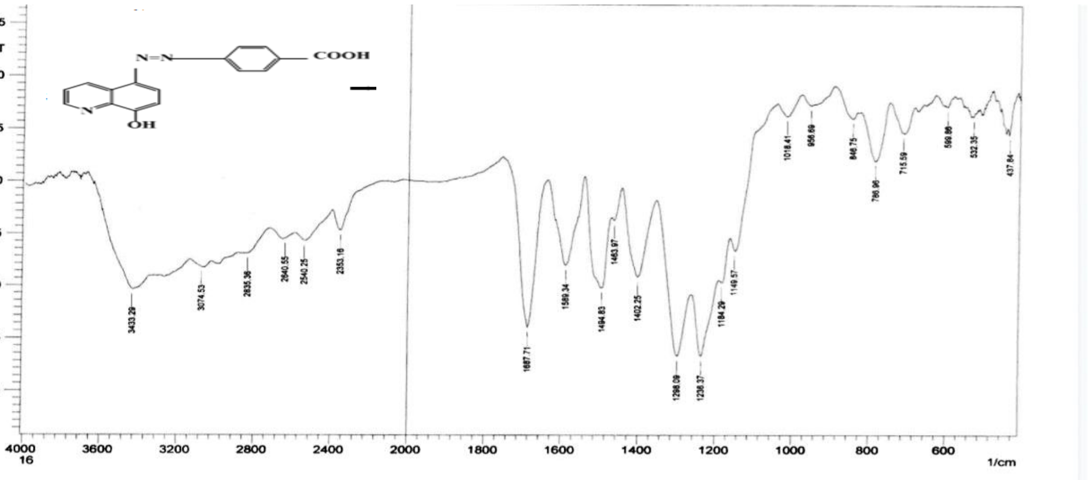


Figure 2. FTIR spectrum of Azo derivative of 8-hydroxy Quinoline reagent.

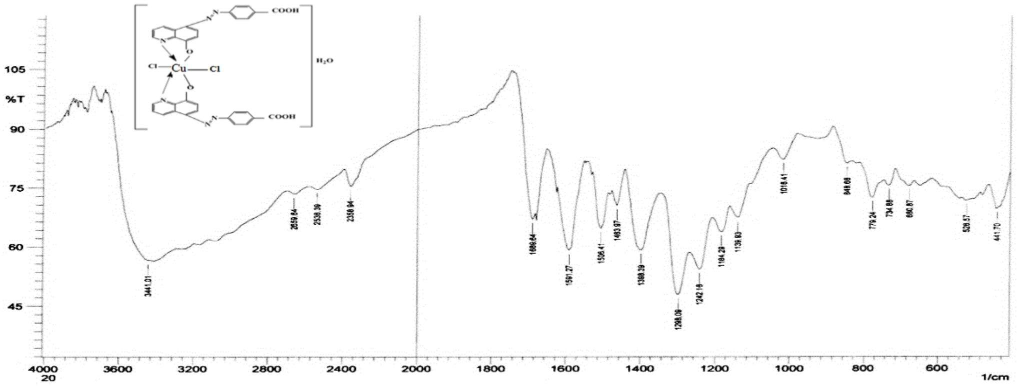


Figure 3. FTIR spectrum of copper (II) complex.

MASS SPECTROSCOPY FOR REAGENT

The mass spectrum of the HQDABA reagent is recorded at room temperature,(Fig 4) and showed a molecular ion peak M+ at m/z+ = 293.3 attributed to the main molecular weight of the reagent (293.3), and the spectrum showed several peaks assigned to the molecular ions at (m/z+), 293.3, 144.2, and248 were due to various fragments ions [C16H11N3O3]+, [C9H6N3]+, [C15H10N3O]+. respectively. This data is in good contrast with the corresponding molecular formula.

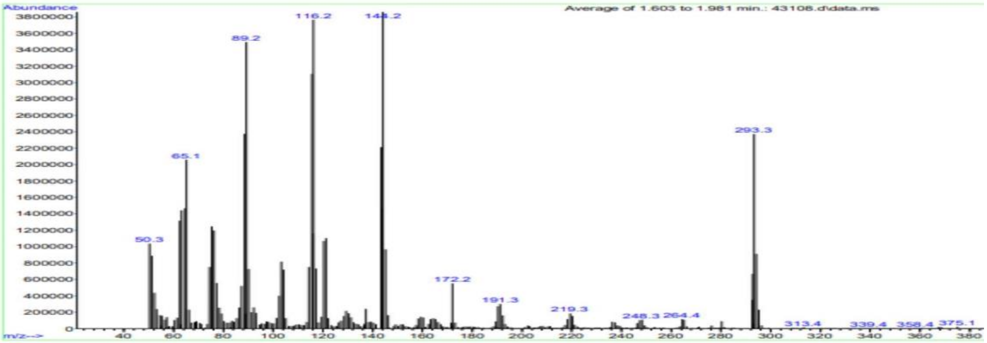


Figure 4. Mass spectroscopy for Azo derivative of 8-hydroxy Quinoline reagent

THE WAVELENGTH OF THE MAXIMUM ABSORBANCE OFAZO REAGENT AND IT'S COMPLEX

In order to attain the highest sensitivity, the maximum absorbance of HQDABA and its complex with copper (II) was examined in various media using a Shimadzu UV-1700 spectrophotometer. The results showed that the best spectra were in neutral medium. The reagent's maximum absorbance was detected at 499 nm, while the copper (II) complex's maximum absorbance was seen at 420 nm. According to Fig. 5. These findings led to the decision to use 420 nm as the study's maximum wavelength.

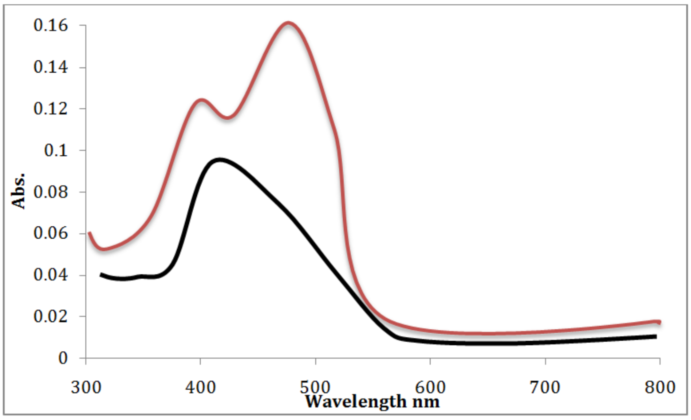


Figure 5. The absorption spectra of copper (II) complex (Red line) and the reagent (Black line) in neutral medium And ethanol (98%) as solvent of reagent.

CALCULATION OF THE SUITABLE SOLVENT FOR (HQDABA) REAGENT.

There has been extensive research on how solvent affects reagent solubility. Due to the high solubility of regent in ethanol 98% compared to the other solvents, it is evident that it is the best solvent out of all those that have been tested. This test used ethanol 98% as one of the solvents.

OPTIMAL PARAMETERS OF COPPER(II) COMPLEX FORMATION.

The effects of an acidic environment on the signal of a metal complex were examined over the pH range of 3 to 10, and the results revealed that the natural environment (pH=7) produced the best complex formation (see Fig. 6 a). This pH was chosen as the appropriate one for the test. The study examined the impact of reagent concentration on the creation of Cu (II) complexes across the range of 310-6 to 110-4mol L-1. The results were shown that the absorbance increased rapidly without any precipitate in solution until 8×10-5 mol L-1 then the precipitate started to appear. As shown in Fig.6 b. To determine the optimal volume of reagent and ion was investigated of complexity as shown in Fig. .6 c .and Fig.6 d and varying volumes (0.25–2.0 mL). The optimum absorption was obtained with 1.5 ml and 1 ml respectively.. Hence, these volumes were used in the subsequent experiments. The Influence of the buffer solution on the absorbance value was investigated in Fig. 6 -e-, the results showed that the citric solution was the best. The complex formation reaction was stable in 60 min. Fig. 6 -f- and it was achieved at room temperature (25 ± 5 °C). To obtain the optimum results, Fig. 6 -g-. The results showed that increasing the water bath temperature was found to produce a decrease in absorbance, room temperature was chosen as the optimum temperature for this study.

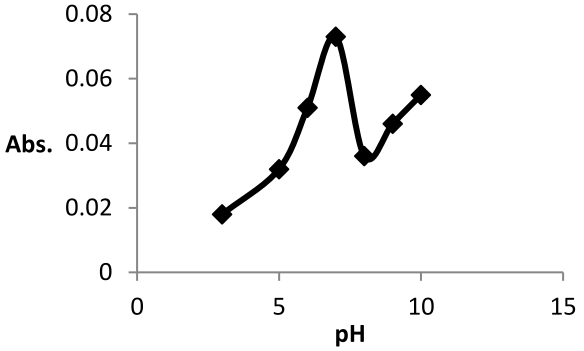


FIGURE 6 a: pH medium influence on the Abs. value for Cu(II) complex.

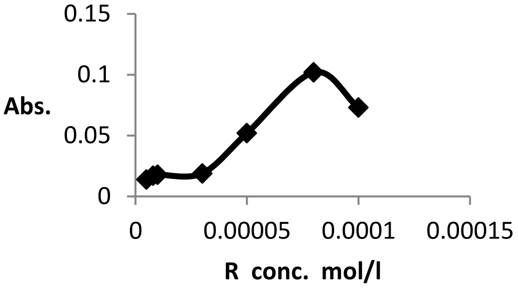


FIGURE 6 b: Reagent conc. effected on the Abs. value for Cu(II) complex.

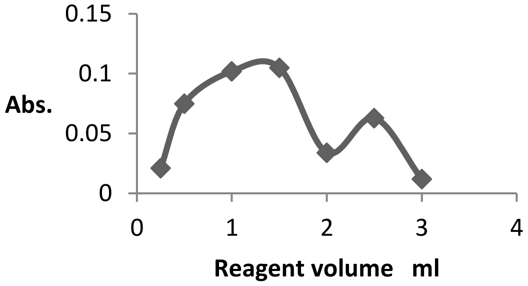


FIGURE 6 c: Reagent volume affected on the Abs. value for Cu(II) complex.

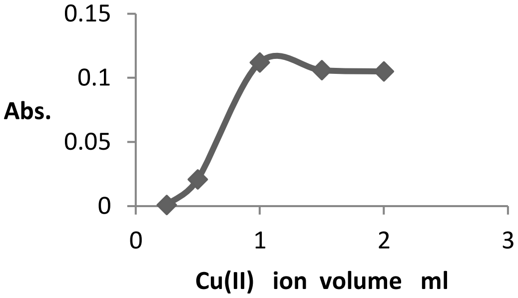


FIGURE 6 d: Effect of ion volume on the Abs. value for Cu(II) complex.

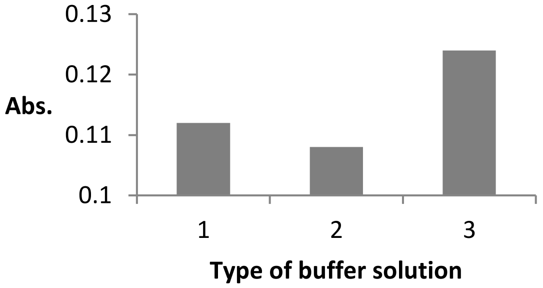


FIGURE 6 e: Effect of buffer solution on the Abs. value for Cu(II) complex.

1. solved in H_2O
2. solved in $NaH_2PO_4+Na_2H_2PO_4$
3. solved in $Na_2HPO_4+C_6H_8O_7$

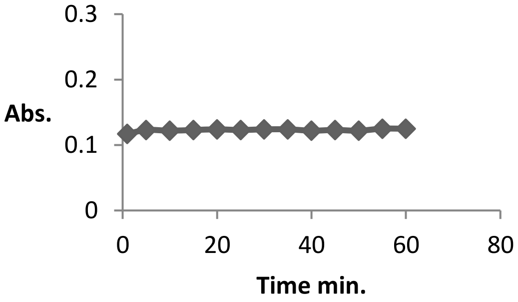


FIGURE 6 f: Influence of Time on the Abs. value for Cu(II) complex

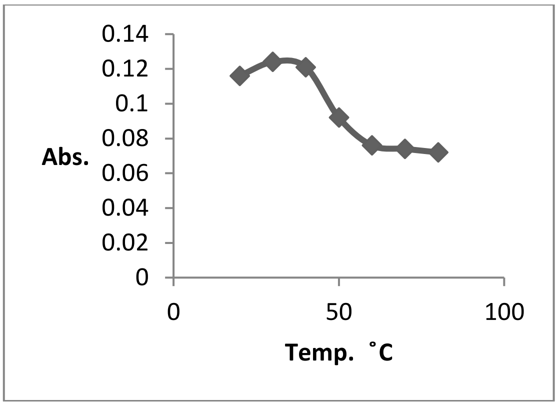


FIGURE 6 g: Influence of Temperature on the Abs. value for Cu(II) complex.

Figure 6: Effect of optimal conditions on the Absorbance value of the complex.

Calibration curve for Cu (II) complex

Cu(II) was identified at the ideal circumstances for the procedure, and the calibration curve at 420 nm was established by inspecting a number of Cu(II) standard solutions. The Cu(II) concentration can be determined using the proposed approach between 0.5 and 15 mg L1Fig.7. The obtained calibration equation for linear regression was y = 0.0134x - 0.001, with an R2 value of 0.995. The limits of detection (LOD), limits of quantification (LOQ), and Sandell's sensitivity for the suggested methods were calculated to be 0.22 mgL-1, 0.740 mgL-1, and 7.46210-2g.cm-2, respectively.

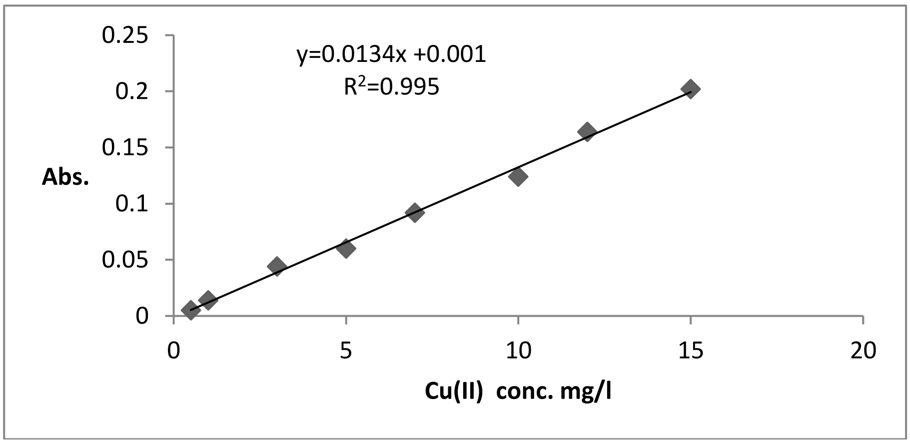


Figure 7. Calibration curve of Cu (II) complex using HQDABA as a new reagent.

A comparison of the values of LOD, LOQ, and molar absorptivity for the suggested method with other research using the same technique but a different reagent for cu+2 ion determination. As compared to another study that used 4-(furan2-ylmethylene) amino)-5-methyl-4 H-1,2,4-triazole-3-thiol (FAMT) as a reagent in the determination of cu+2 in various environmental samples, the results for the proposed method were 0.22 mg L-1, 0.740 mg L-1, and 8.502 102L. mol-1.cm-1, respectively.9 Additionally, a study that used a brand-new fluorescent nano-sensor to detect nitrofurantoin (NFT) for the first time in order to detect the ion of Cu+2 obtained . A deeper investigation could result in a (LOD) of 0.73 M.18 The greatest absorption was observed at 520 nm with a molar absorptivity of 2.60104 L mol-1 cm-1 in a highly stable ternary complex of copper (II) with 5-(4-nitrophenyl azo) salicylic acid (NPAS) and 2,2′-Dipyridyl (Dp) in ethanol medium at ambient temperature. 6.8 ng mL-1 was discovered to be the detection limit.19 Finally, in this study, a new chromogenic reagent called N, N′-bissalicylidene-2,3-diaminopyridine (H2IF) was used to establish a unique, selective, and highly sensitive spectrophotometric approach for the measurement of copper (II). Max = 414 nm was used to measure the absorbance. After the experimental setup was perfected, the copper concentration range of 6.35-318 g L1 was found to exhibit Beer's law. It was computed that the complex's molar absorptivity was 1.46 105 L mol1 cm1. Calculations revealed that the detection and quantification limits were 6.38 g L-1 and 21.27 g L-1, respectively.20

- Stoichiometry of Cu(II) complex with HQDABA

- The volume of the HQDABA reagent was consistently changed from 0.5 to 3 mL (8 x 10-5mol L-1) while the cu (II) ion concentration was maintained at 1.00 mL (1 x 10-3 molL-1) in a series of solutions. In all ideal circumstances, the absorbance of these solutions was measured at 420 nm. The metal-reagent mole ratio was confirmed to be 1:2 as shown in Fig. 8. The suggested structure shown in Fig.9 depends on the mole ratio and all advance analysis.

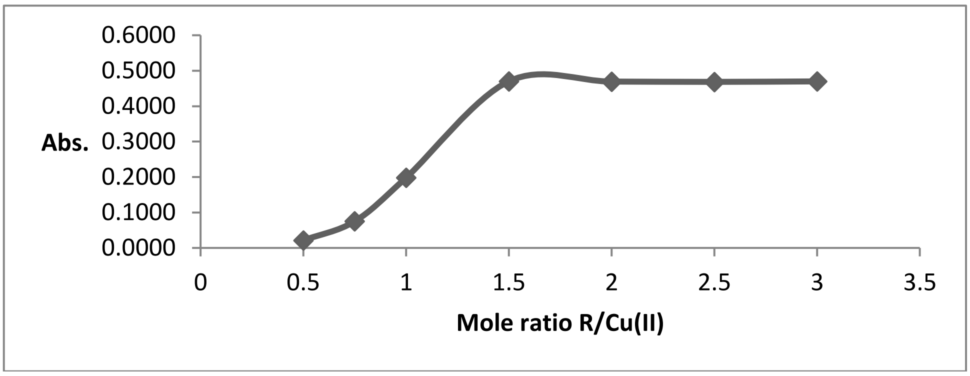


Figure 8. Mole ratio method to study stoichiometric for Cu (II) complex.

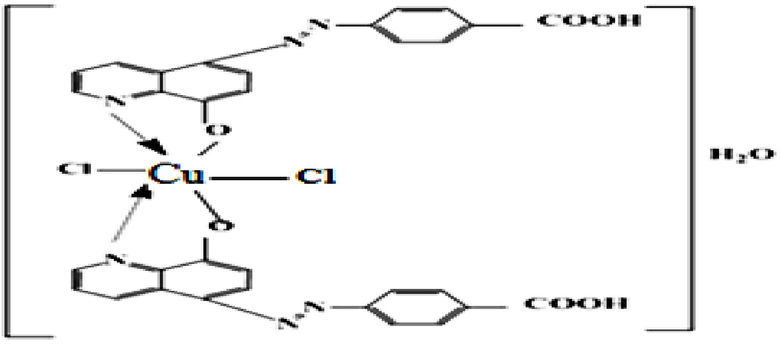


Figure 9. The suggested structure for copper (II) complex

- The effect of interference ions

In both low and high quantities of foreign ions, the impact of various cations and anions on the detection of Cu (II) ions was thoroughly investigated. While the concentration of Cu (II) ions remained constant throughout the experiment at 10 mgL-1, the taken amounts of foreign ions varied from 10 mg L-1 at low concentration to 50 mg L-1 at high concentration. All cations (Pb+2, Fe+3) interfered at both concentrations, according to the results, with the exception of Co+2 and Ni+2, which interfered at both high and low concentrations. At the same time, the results confirmed that all anions examined (CH3COO-, Cl-, F-) showed no interference in high and low concentrations. Thus masking agents (as shown in Table 3 were needed to reduce interfering effects to increase the accuracy of Cu+2 evaluation.

Table 3. The interference ions and their masking agent at both concentrations

Interference Ions	Conc. of Interference (mg L^{-1})	The change in absorbance	Masking agent (100 mg L^{-1})
Ni^{+2}	10	0.026	No need
	50	0.037	No need
Co^{+2}	10	0;036	NO need
	50	0.045	NO need
Fe^{+3}	10	0.1	5 ml $KNaC_4H_4O_6.4H_2O$
	50	0.09	5 ml $KNaC_4H_4O_6.4H_2O$
Pb^{+2}	10	0.073	5 ml $KNaC_4H_4O_6.4H_2O$
	50	0.068	5 ml $KNaC_4H_4O_6.4H_2O$

- Applications

The proposed technique was applied to determine Cu (II) ions in different samples. Depending on FAAS as a standard method. The comparison between the suggested method and the FAAS method gave good accuracy with a recovery percentage between (78.26 - 111.53 %) as shown in Table 4.

Table 4. Comparison of the suggested method's accuracy to the FAAS method for determining the presence of the Cu(II) ion in various samples

Sample	The concentration of copper found by FAAS (mg L^{-1})	The concentration of copper found by the proposed method (mg L^{-1})	Error %	Recovery %
sesame	2.3	1.8	-21.73	78.26
Copper wire	2.6	2.9	+11.53	111.53
Aqueous solution	1.8	2.0	+11.11	111.11
Medicine FOOD SUPPLEMENT CU 1mg of 100%	1.02	1.08	+5.88	105.88

CONCLUSION

A novel reagent, HQDABA, for the determination of copper (II) ions in various samples using spectrophotometry has been accomplished. For the detection of Cu (II) ions in various materials, the suggested spectrophotometric approach has proven to be straightforward, quick, and accurate. The suggested approach complied with beer's low over a broad concentration range, 0.5-15 mgL-1, making it appropriate for quantifying Cu (II) ions in both samples with trace amounts and those with significant amounts. By employing a sufficient amount of tartrate sodium masking, the interference from Fe+3, and Pb+2 has been lessened. Comparatively to a study that employed the same methodology but a different reagent, the proposed approach was more sensitive. According to calculations, the relative limits of detection (LOD), quantification (LOQ), Sandell's sensitivity, and molar absorptivity were 0.22 mg L-1, 0.740 mg L-1, and 7.46210-2 g.cm-28.502102. The proposed approach was successful in recovering 78.26% to 111.53% of the various samples.

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