Sys Rev Pharm 2020;11(10):171-181
A multifaceted review journal in the field of pharmacy

Spectrophotometric Determination of Micro Amount of Copper (II) Using a New of (Azo) Derivative, Study of Thermodynamic Functions and Their Analytical Application

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ABSTRACT

The study involved the preparation and diagnosis of new Ligand is 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole) (BMTI), one of the azo compounds. And that of the traditional method of azoth. The study also considered the use of this reagent to express spectroscopy for copper(II) ion in the binary solution of water , where it was noted that the reagent be complicated The color purple with the ion and shows the greatest absorption at λ max= (573) nm (pH = 8). Was found to be a complex copper duo Reagent with a stable of more than (24hours) when the pH best with compliance to Beer's law in the range of concentrations ranging between (0.1 – 6.0 µg/mL). The effect of several factors including the value of the absorption effect of reagent concentration , reaction time, masking agent , sequences of addition and the effect of different parameters such as effect cations and anions ,and the effect of ionic strength and temperature effect . the stoichiometry of complex was investigated by ratio of the reagent - metal molar ratios, Jobs (the constant changes) mollard methods showed that the proportion of the metal regent is (1:2) , with molar absorptivity ($1.11x10^4$ L mol^{-1} cm^{-1}). Limit of detection (LOD) and Limit of quantification were (0.0114 µg/mL) and (0.0376µg/mL), respectively. . As has been the preparation of complex solid was studying some of his physical characteristics such as solubility and molar conductivity and the melting point of the complex. All compound has been characterized by spectroscopic methods [FT.IR.,UV-Vis].(UV-Vis) absorption spectra show bathochromic shift) compared with that of free reagent) the results of the accuracy and precision of the method used to estimate the value of the element copper percentile relative deviation (RSD%) ranged between(0.534% -2.903%) while the values of the relative error(E%) between (-7.943- 4.033). The thermodynamic functions () were also calculated by studying the effect of temperature. The method was applied to some environmental and industrial models, and the results were of high accuracy and precision.

Keywords: Azo dye (BMTI), Copper (II), Dental filling and Spectrophotometry

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INTRODUCTION

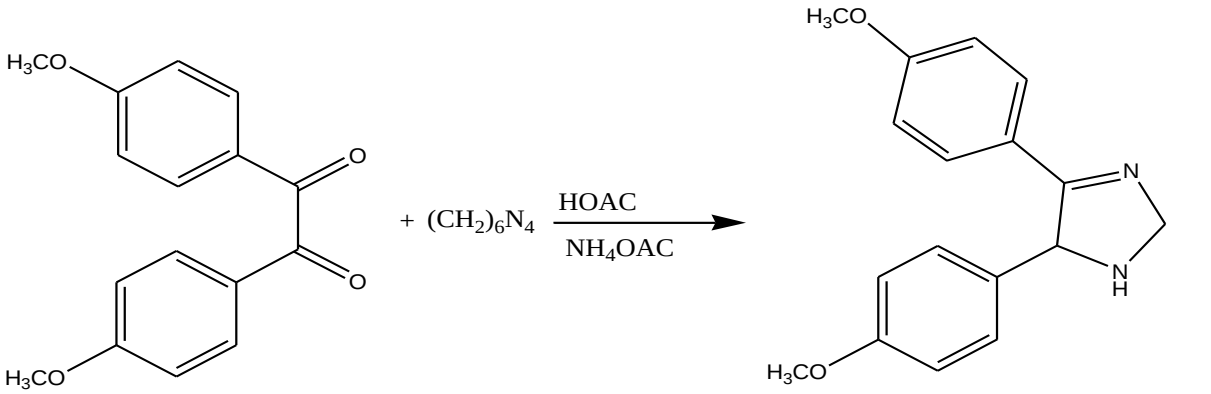
Azo dyes represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future They play a crucial role in the governance of the dye and printing market.These dyes are synthesized from a simple method of diazotization and coupling. Different routes and modifications are made to obtain the desired color properties, yield and particle size of the dye for improved dispensability [1,2]. Rhodanine derivatives, a class of heterocyclic compounds, are used in colorimetric sensors, fluorescent dyes, and pharmacological studies [3]. These compounds are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals [4][5]. The chemistry of hetero cyclic compounds is studied extensively because of its high synthesis [6] and are used to design medicinal compounds. Many of hetero cyclic compounds are synthesized, hundreds of them which have been tested to find new prospective leads for different pharmacy, therapeutic areas [7,8]. Copper and its compounds have been used as disinfectant agents for many centuries Since the nineteenth century, the discovery of a causal link between diseases and pathogens has revolutionized modern medicine. Research turned to the development of antimicrobial agents, especially antibacterial ones and many studies have been carried out on the antibacterial effects of metals such as copper (II) [9,10]. Copper (II) is a heavy metal which can pollute the environments widely when released from industry and agriculture for this reason, there has been an interest by the researcher in studying quantitative estimation methods of copper (II) [11]. Many techniques are used to determine copper including atomic absorption spectrometry [12,13]. inductive coupled plasma-emission spectrometry [14]. Potentiometric [15-17]. and flow injection catalytic photometric method [18]. inductive coupled plasma-mass spectrometry [19]. Aim of the study :The current study aims at the possibility of developing a new method for quantifying the copper ion using the new reagent (), knowing the best conditions for working measures, estimating the accuracy and presicion of the proposed method and comparing it with other methods. And applying the method to some environmental models.

EXPERIMENTAL

Preparation of the compound 4,5-dimer (4-methoxyphenyl) imidazole

In a 500ml round flask, (2.70g, 0.01mol) of the benzyl derivative and (0.256g, 0.005mol) of hexamethylene tetraamine were mixed with (6.0g, 0.23mol) of ammonium acetate followed by adding (40ml) of acid. Ice acetic, and the solution was sublimated for a period of (90min) and after cooling the reaction product, (400g) of ice grits were added, then the ammonium hydroxide solution was added drop by drop to modify the acid function and obtain the imidazole derivative in the form of a white precipitate. The precipitate

was filtered, and washed with water for several times to get rid of The remnants of the base and salts, and the product was dried and recrystallized from ethanol to obtain white crystals, dried and the melting point was measured (73-74C0), while the product was (84%).

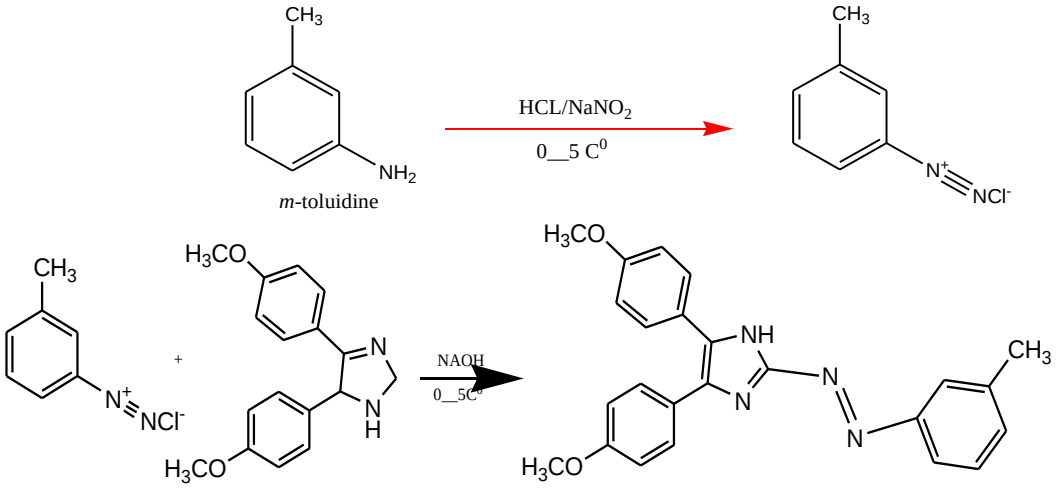


1,2-bis(4-methoxyphenyl)ethane-1,2-dione
Exact Mass: 270.09

2,5-dihydro-4,5-bis(4-methoxyphenyl)-1*H*-imidazole
Exact Mass: 282.14

Scheme 1: Preparation of the compound 4,5-dimer (4-methoxyphenyl) imidazole
A/Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI).

Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (B The new isoamidazole liquor was prepared from the diazonium salt pairs of the tlodine derivative with the derivative.Imidazole in an alcoholic medium by dissolving (1.08 ml, 0.01 mol) of methaldodine in a solution obtained by mixing (3 ml) hydrochloric acid with (50 ml) distilled water. 0.7 gm, 0.01 mol) of sodium nitrite dissolved in (10 ml) of distilled water drop by drop, taking into account stirring and maintaining the temperature below 5 C°, after which the solution was left to settle for a period of (30 minutes) to complete the nitrogenation process and obtain a solution Diazanium chloride. This salt solution was added gradually with continuous stirring to a solution (2.80 g, 0.01 mol) from the base pairs 5,4-dimethyl (methoxyphenyl) amidazole dissolved in a mixture of (150 ml) of ethyl alcohol and (15 ml). The sodium hydroxide solution (1 M) was observed to discolor the solution in an orange color. The solution was left for the next day, and the acidic function was modified down to (pH = 6) to obtain a reddish orange precipitate. The precipitate was filtered and washed with distilled water to get rid of the sodium chloride resulting from the pairs and neutralization process, and it was dried and recrystallized from ethanol to obtain the lycand in its pure form. The two equations below explain how to obtain the aforementioned licand iso.MTI).



m-toluidine

4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole

Scheme 2*:* Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI)

B- Instrumentals used

a/ Single Beam UV-visible Spectrophotometer Sp -300(Japan).
b/ pH – meter – WTW-720.
c/UV-Visible Spectrophotometer -1800, Shimadzu (Japan)
d/FT-IR 8400, Shimadzu (Japan).
e/ Water bath type BS-11 JEIO TECH (Korea)

Materials and Methods:

In this paper. All analytical reagents and solutions used in preparation are in high purity.

D/Preparation of Standard Solutions.

1-Copper (II) solution (1000µg/mL): - was prepared by dissolving (0.380 g) from [Cu $(NO_3)_2$].$3H_2O$ in 100 mL distilled water.

2-Sodium hydroxide solution (0.1M): - was prepared by addition of 100 mL distilled water to 0.4 g of sodium hydroxide.

3-Nitric acid solution (0.1M): - was prepared by diluting (0.18 mL) concentrated nitric acid (65%,1.41 g/cm3) in 50 ml distilled water.

4-Reagent solution (BMTI) (1000µg/ml): -was prepared by dissolving appropriate weight (0.1g) in absolute ethanol and complete the volume to (100mL) with ethanol.

5-INTERFERENCES

Cations solution of (Cd^{+2} , Ni^{+2} , Fe^{+3} , Ba^{+2} , pb^{+2},Cr^{+3},Co^{+2}) ions (0.1mg/mL) were prepared by dissolving (0.274g) of $Cd(NO_3)_2.4H_2O$, (0.495g) of $Ni(NO_3)_2.6H_2O$, (0.635g) of $Fe(NO_3)_3.9H_2O$, (0.190g) of $Ba(NO_3)_2$,(0.159g) of $pb(NO_3)_2$,(0.493g) of $Co(NO_3).6H_2O$, (0.677g) of $Cr(NO_3).9H_2O$ respectively, in 100 mL distilled water for each.

PRELIMINARY STUDY

1ml of a solution of prepared copper (II) (100 µg /ml) was placed in a test tube, then 1ml of a solution prepared from a ligand (BMTI) (1000 µg / ml) was added to the test tube drop wise with shaking noting the color formation Or a precipitate, and then drops of nitric acid (0.1 M) were added to one part of this mixture and drops of NaOH (0.1 M) or HNO_3(0.1M) were added to the other part to study the effect of the acidic function. It was found that the color formed clearly in the basic medium while in the acidic medium there was a weak fading of the color

RESULTS AND DISCUSSION

The spectra absorption

The absorption spectra of (reagent and copper (I) complex shown in Figures 2,3) ,The reagent solution spectra is given the absorption maximum at (λ_{max}=498),While the mercury (II) complex formed at (pH= 8) is given the absorption maximum at (λ_{max}= 573nm), So that the formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately (75nm) optimization of variables.

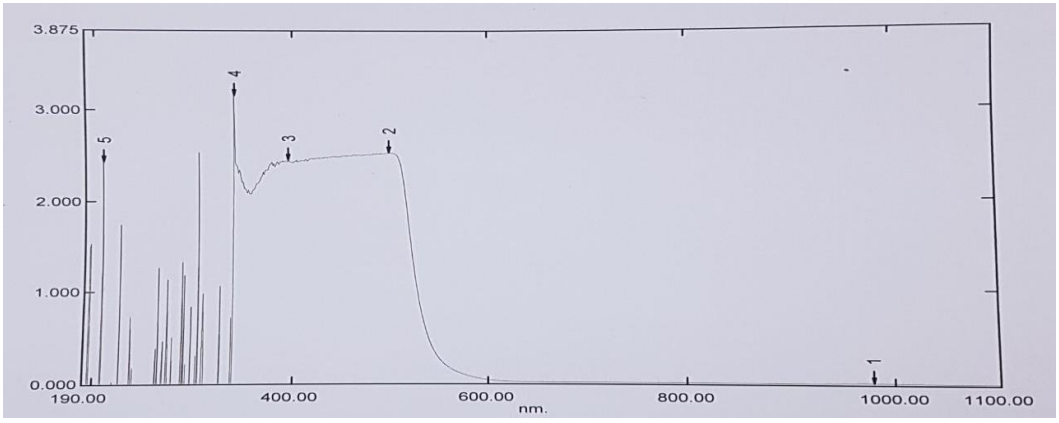


Figure 1: - The spectrum of reagent (BMTI)

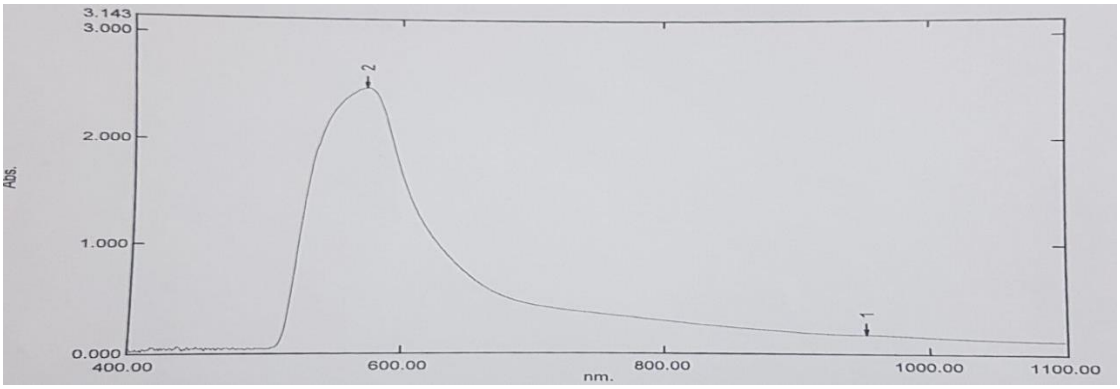


Figure 2: - The spectrum of Cu (II) complex with (MBBAI) reagent.

Optimization of Reaction Conditions.

The pH effects Standard amount of copper (I) and reagent(BMTI) were buffered at different pH- range from(1 to 10) using HNO_3(0.1M)/ NaOH (0.1M) , the final pH of each solution was measured with a pH-meter and the absorbance measured at (573nm) at $20C^0$

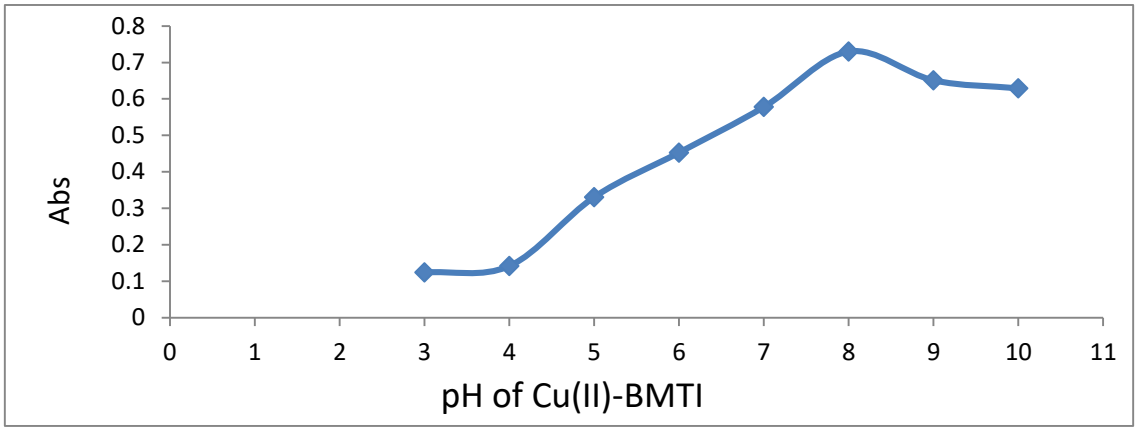


Figure 1. Effect of pH value

The result in Figure (1) showed that the absorbance was increased gradually as the pH increased from (3.0 – 8.0) , but decreased rapidly(above pH 8.0) , The increased in the copper complex solution absorbance under these conditions may be explained by an increasing the sensitivity of the reagent at this value of pH [20]

Effect of Time on stability of the complex

The results of table (1) show the follow-up reaction of the reagent with the ion using the best conditions, and these results indicate the composition of the Copper(II) complex and remains stable (in terms of absorption values) 90 minutes from the start of the experiment.

The results of this study promote the use of this reagent as one of the reagents used to quantify the element Copper parasitically

Table 1: The effect of time

Time/Min.	Abs.
1	0.710
10	0.694
20	0.688
30	0.688
40	0.688
50	0.681
70	0.677
100	0.667
24h	0.633
48 h	0.633

Effect size of reagent

The result in table (2) showed the effected of reagent concentration on the absorbance of the copper complex at (pH=8), From the result was explained that the absorbance was increased with increasing of the reagent concentration.

Table 2: - The effect of reagent conc.

Volume Conc. of L. × 10^{-3}	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Abs.	0.451	0.491	0.554	0.649	0.711	0.670	0.666	0.656

Effect of Sequence

To study the sequence of the reaction content in a complex absorbance, the three arrangement of addition was depending, and the result given in a table (3)

Table 3: - The effect of sequence

Sequence of Number	Sequence of Addition	Abs. of Cu Complex
1	M+L+PH	0.711
2	L+PH+M	0.633
3	M+PH+L	0.433

M = copper ion, L = ligand, pH= function of hydrogen ion
The result showed in table (3)that the first arrangement is the best one while the other sequence give decrease in absorbance of complex that may be return to effect of acid , base inions with a metal , so the first sequences addition was depend to determine the copper ion complex in this method.

Effect of Temperature

The effect of temperature change on complex formation was studied. Figure (2) includes the results obtained through this study, from which it can be seen that the absorption values of the complex reach their peak and give the best color intensity, at the temperature of (15-20 C^0), then the absorption values decrease, and the reason may be due to the decrease in the stability of the complex. Preparing the complex at a temperature not exceeding 20 C^0

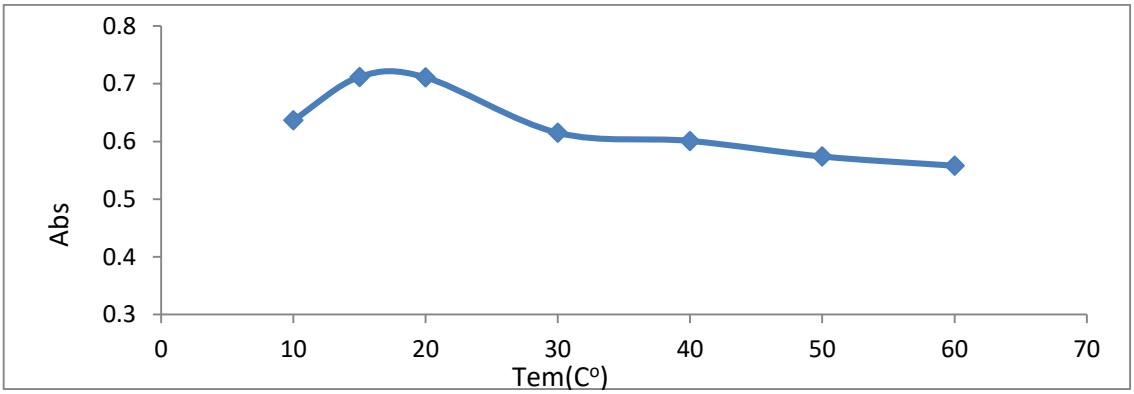


Figure (2). Effect of temperature

Calibration Curve

The absorbance of copper ion complex was found to be linear depending on the concentration of metal , Beer s low obeyed in the concentration range (0.1 – 6.0 µg /mL) with molar absorbtivity of ($1.11x10^4 Lmol^{-1} cm^{-1}$), Fig. (3) shown the calibration curve of copper ion ion and table (4) shown the analytical data to determine copper ion by using reagent (BMTI).

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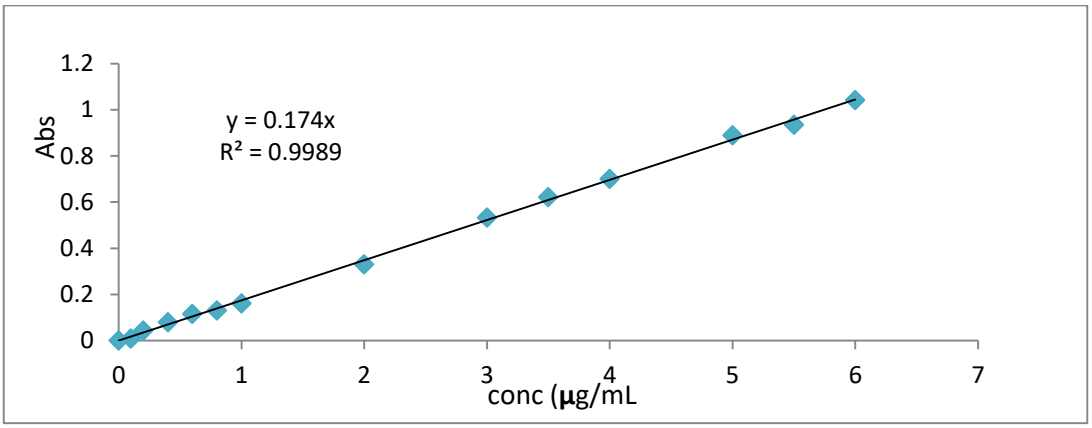

Figure 3. Calibration curve for Spectrophotometric determination of copper (II).

Table 4. Analytical data to determine copper (II)

Analytical Data	Value
linear equation	Y=174x
Linear range [µg/mL]	0.1-6.0
Detection limit(µg/mL) [a]	0.0114
Limit of quantificationb (µg/mL) [b]	0.0376
Molar Absorpitivity ($Lmol^{-1}cm^{-1}$)	1.11×10^4
Correlation coefficient	0.9989
λ_{max}	573nm
Temp.	20^0C
Time	90 min
Color of product	purple

[a] Limit of detection (LOD)= (SD/S) *3.3
[b] (Limit of quantification) LOQ= (SD/S) *10
where SD is standard deviation, S is the slope of calibration curve

Determination of Stoichiometry and Formation Constant

Mole ratio method and addition of Job`s method of continuous variations were chosen to study the composition of the complex formed, results illustrated in Figs 7 and 8. Both methods indicated that the ratio of metal ion to reagent molecules (M:L) was (1:2) at pH=8.

1- Mole Ratio method

by using a known and constant concentration from copper(II) ion (3.988 x 10^{-5} M) with increasing concentration from reagent (BNTI) ($1.994x10^{-5}$ - $13.958x10^{-5}$M) ,The method shows that copper ion forms a (1:2) complex (metal -L) with reagent .

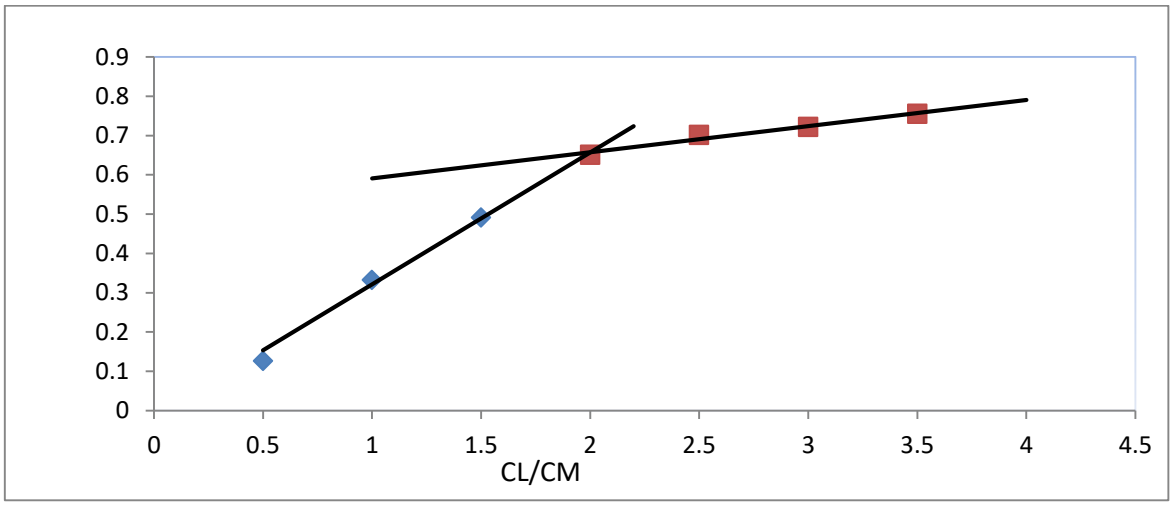

Figure 4. Mole ratio method

Mole ratio method was used to determine the stability constant of the colored complex depending on the equilibrium reaction for the complex. Calculations illustrated in Table (5).

$$M^{+n} + nL^{-} \longrightarrow MLn \text{-----1}$$

$$\text{----2 } K_{\text{stability constant}} = [ML^{+n}]/[M^{+n}]\,[L^{-}]^{n}$$

$$\alpha = \frac{A_m - A_s}{A_m} \qquad \text{.....(3)}$$

Where (Am) is the maximum absorption and (As) is Absorption at the stoichiometry

Table 5. The stability constant value of complex

Complex	Am Value	Value As	α	K ×10^{10}
[Cu $(BMTI)_2$]	0.755	0.651	0.1377	2.650

The results in Table (5) explain that the complex has high stability, for that it is possible to use the ligand (BMTI) in the spectral estimation of copper ion.

2- Job`s method

In this method mixture of different volumes of the solution in equal concentration
(1x10^{-5} M) from both ion (Cu^{+2}) and ligand were mixed.

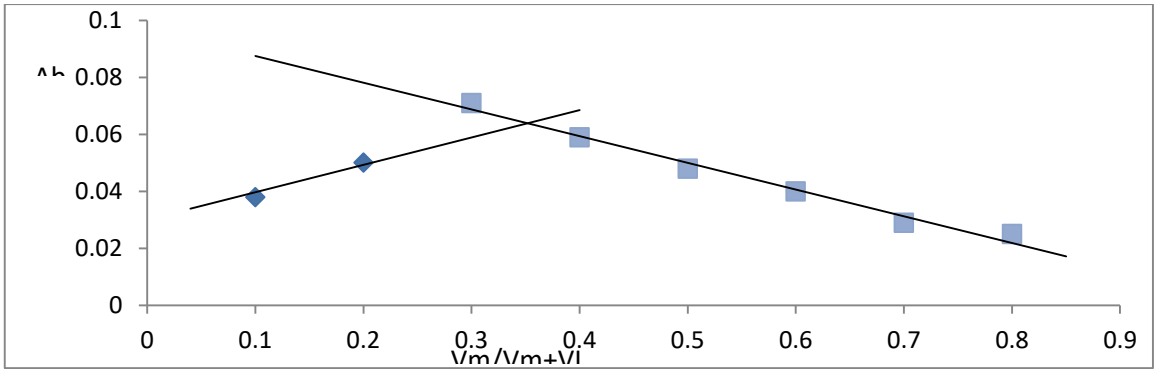

Figure 5. Job`s method of continuous variations.

The effect of adding buffer solutions.
To study the effect of the type of buffer solution on the absorbance of the copper (II) complex, three types of buffer solutions were tested and to note the difference in the absorption values of the copper(II)ion complex with the reagent (BMTI)) using optimal conditions and the results are shown in Table (6).

Table 6. The effect of adding buffer solutions.

No. N	Buffer Solution	Abs. A
1 11	Ascorbic	0.350
2 2	Citric acid	0.192
3	Acetate	0.682
Absorption before adding to the copper (II) complex 0.711		

From the results, we find that the absorption of the copper (II) complex and the presence of the buffer solution is less than the absorption obtained with the use of nitric acid and dilute sodium hydroxide, so the amendment of the acidic function was limited by using an acid or base only to obtain a high sensitivity and accuracy for the determination of the copper II ion

Effect of ionic strength-
The effect of adding different concentrations of constant volumes of Na_2SO_4 and $NaNO_3$ to the complex solution was studied to find out the extent of their effects on the complex as the results are shown in Table (7).

Table 7. The effect of ionic strength solutions

Salt Added	. of add. saltCon	Abs.	Added salt	On.of addsaltC	.
$_2SO_4Na$	0.5 0.05 0.005 0.0005 00	0.833 0.631 0.621 0.629	$NaNO_3$	0.5 0.05 0.005 0.0005 o	0.579 0.619 0.641 0.629
Absorption before adding to the copper (II) complex 0.71					

Effect of Foreign Ions
The definite concentration of some cation and anion solutions used as foreign ions were added with iron solution to study the interference effect,
A-The cation effect: -
B- The inions effect

Table 8. The effect of Cation

Foreign ions	Formula structure of ions	20µg/mL Absorption after addition of ions	E%	40µg/mL Absorbance after addition of ions	E%
	Cations				
	Absorbance without interferences	0.711			
Fe^{+3}	$Fe(NO_3)_3.9H_2O$	0.527	25.88	1.322	-85.93
Cr^{+3}	$Cr(NO_3)_3.9H_2O$	0.545	23.34	0.939	-32.06
Co^{+2}	$Co(NO_3)_2.6H_2O$	1.466	-106.1	1.503	-111.3
Ni^{+2}	$Ni(NO_3)_2.6H_2O$	0.758	-6.610	0.854	-20.11
Cd^{+2}	$Cd(NO_3)_2.4H_2O$	1.086	-52.74	1.379	-93.95
Ba^{+2}	$Ba(NO_3)_2$	0.611	14.06	1.242	-74.68
Pb^{+2}	$Pb(NO_3)_2$	0.599	15.75	1.413	-98.73

Table 9. The inions effect

Foreign ions	Formula structure of ions	20µg/mL Absorption after addition of ions	E%	40µg/mL Absorbance after addition of ions	E%
	Anions				
	Absorbance without interferences	0.711			
$Cr_2O_7^{+2}$	$K_2Cr_2O_7$	0.638	10.26	0.864	-21.51
$SO4^{-2}$	K_2SO_4	0.629	11.53	0.930	-30.80
$CO3^{-2}$	K_2CO_3	0.691	2.812	0.906	-27.42
SCN^{-1}	KSCN	0.771	-8.438	0.853	-19.97
CN^{-1}	KCN	0.272	61.74	0.173	75.66
Br^{-1}	KBr	0.642	9.704	0.833	-17.15
Cl	KCl	0.779	-9.563	1.005	-41.35
F^{-1}	KF	0.672	5.485	0.836	-17.58

Some ions were selected to study the effect of the interferences with Cu(II) ion (Table 6) , it was found that some of the ions increased the absorbance while the others decreased the absorbance ,this was due to the competition of this ions with Cu(II) to form the complex with the ligand which decreased the competition and increased the sensitivity of this method towards Cu(II) ion. The reaction was specific and sensitive for Cu (II). Selectivity of reaction can be confirmed by using suitable masking agents.

Accuracy and Precision of the Described Method.

Accuracy and precision were determined for the applied method in term of recovery and relative standard deviation (RSD%), respectively. Results of recovery and RSD% were illustrated in table (10).

Table 10. Accuracy and precision studies.

Conc.of Cu^{+2} present[M]	Conc.of Cu^{+2} found[M]	RSD%	Recovery%	Error%
1.574×10^{-5}	1.635×10^{-5}	1.827	103.93	-3.93
4.724×10^{-5}	4.527×10^{-5}	0.72	95.83	4.17
9.44×10^{-5}	9.188×10^{-5}	2.11	97.33	2.44

Results in Table (10) explain that the developed method was precise as the value of relative standard deviation was <0.4%.

The effect of temperature on the stability constant for the Cu-BMTI complex.

The values of stability constant of Cu (II) with the reagent (BMTI) were studied at various temperatures ranged from (10-35) ^oC. The results are illustrated in Table (11)

Table 11. The effect of temperatures on the stability constant for Cu (II)complex.

T(C^0)	T(K)	Am	As	α	K*10^9
10	283	0.211	0.249	0.1526	8.175
15	288	0.210	0.247	0.1495	8.147
20	293	0.203	0.238	0.1470	8.123
25	298	0.201	0.235	0.1447	8.102
30	303	0.199	0.232	0.1422	8.078
35	308	0.197	0.229	0.1397	8.053

Results obtained in Table 8 explained that there is a limited effect of temperatures on the stability of complex.

Thermodynamic Function of the Complex.

Thermodynamic function ΔH, ΔG and ΔS were calculated, results were illustrated in Fig (6) and Table (12).

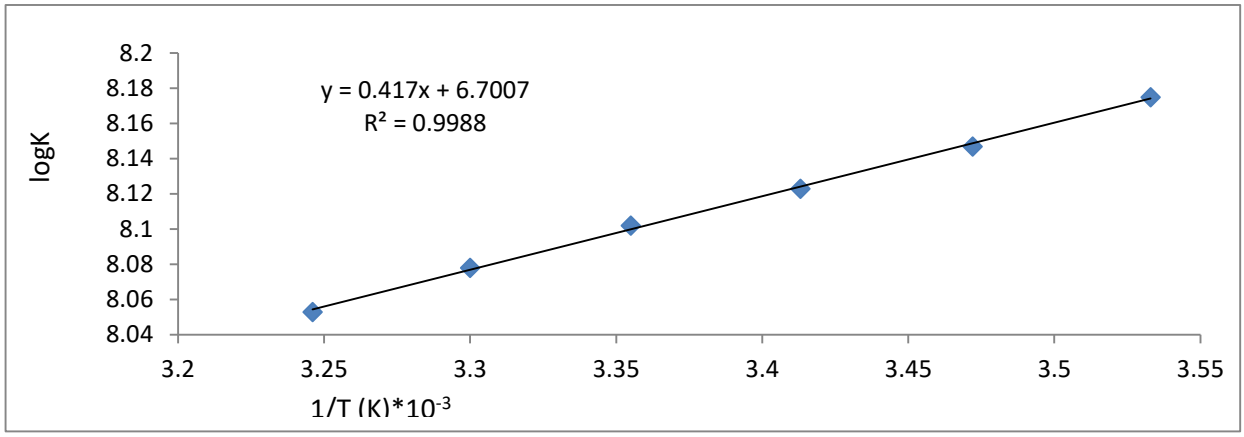

Figure 6. Relation between Log K and 1/T values for copper (II) complex.

Table 12. The effect of temperature on thermodynamic function for Copper (II) complex.

T(K)	$1/T*10^{-3}$ (K^{-1})	log K	ΔH	ΔG (K.J/mole)	ΔS (K.J/mole.K)
283	3.533	8.175	-7.984	-44.297	0.12831
288	3.472	8.147		-44.399	0.12644
293	3.413	8.123		-45.570	0.12827
298	3.355	8.102		-46.228	0.12833
303	3.3	8.078		-46.865	0.12832
308	3.053	8.053		-47.491	0.12826

Negative value of enthalpy explained that the reaction was exothermic for that, it can be noted by decreasing the temperature the possibility of. complex formation will be increased, in addition to that the reaction was spontaneous according to the negative sign of free energy. The stability of the complex was confirmed due to the value of entropy which approach to zero (less random and spontaneous).

Study of FT-IR Spectra for Ligand and Complex

Figs 7, 8 and Table 10 explain the FT-IR study and the absorption frequencies for reagent and the reagent-BMTI.

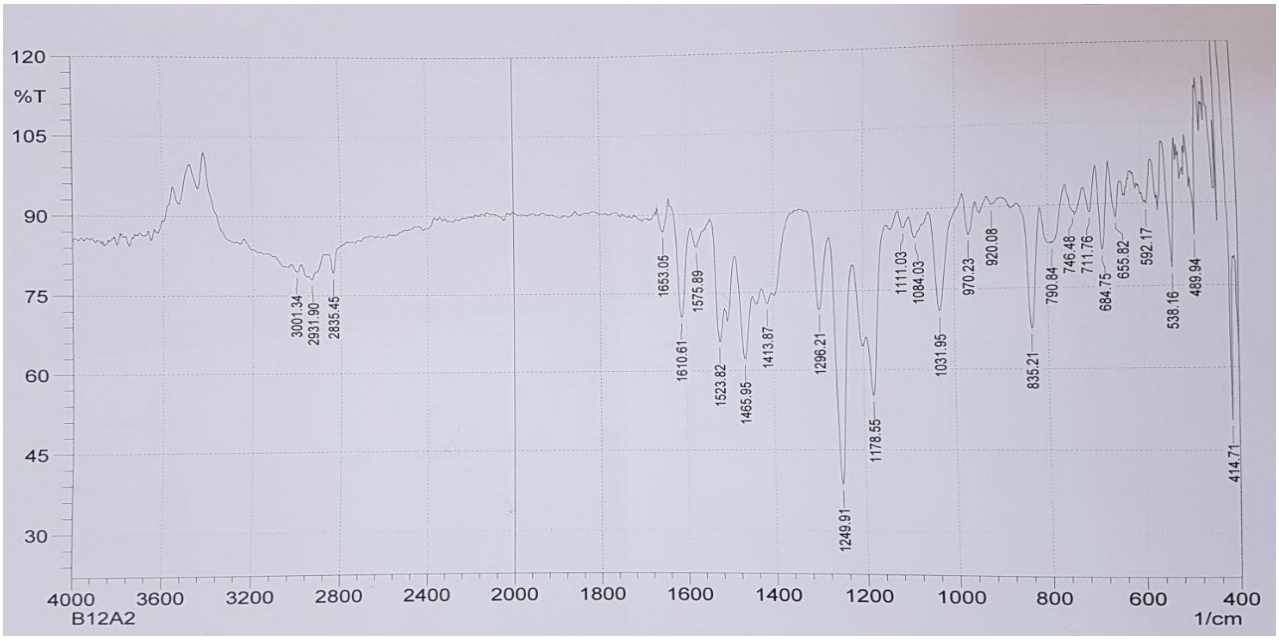

Figure 7. FT-IR spectrum of ligand.

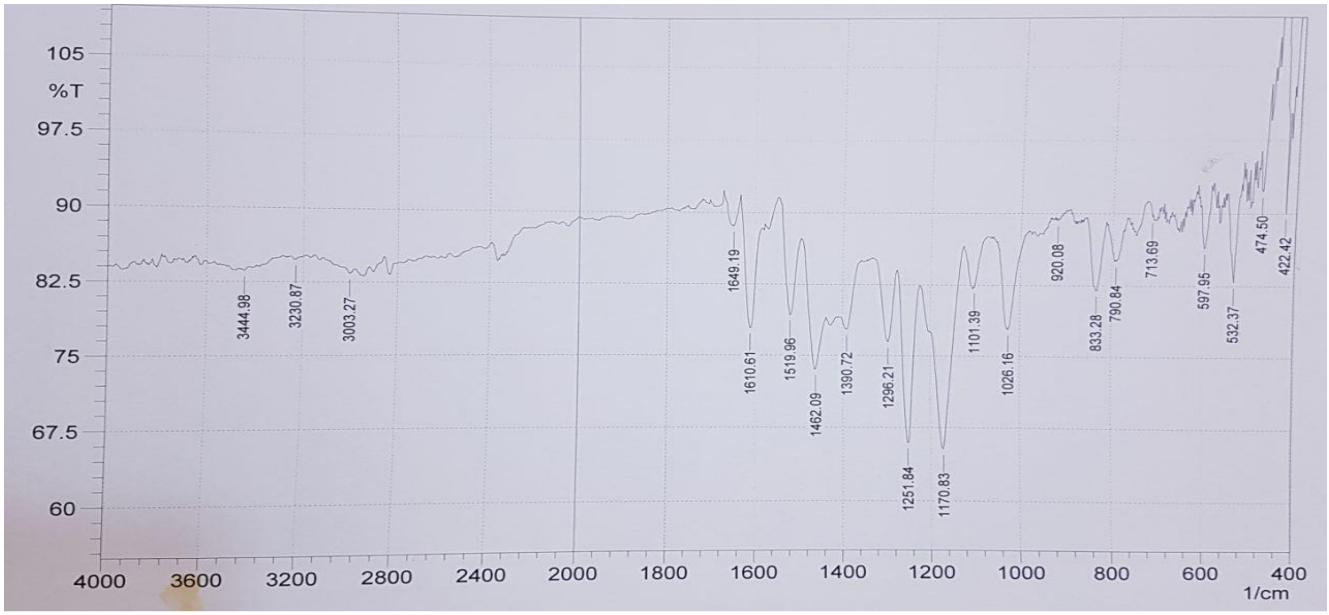

Figure 8. FT-IR spectrum of complex.

Table 13. FT-IR absorption frequencies for reagent and the reagent-BMTI.

Compound	BMTI	Cu [BMTI]
(N-H)	3400 w	3444 w
(C-H) Ar	2931 m	3003 w
(N=N)	1649 m	1653 m
(C=N)	1610 m	1610 w
(C=C)	1575 w	1580 m
(C-O)	1200 m	1251 s
(M-O)	.....	474 w
(M-N)	.....	532 w

S=strong, M=medium, W=weak

The Suggested Figure for the Complex.
Suggestion of the complex structure as shown in figure (9) is due to FT-IR spectra and the stoichiometry obtained from Job and Mole ratio methods.

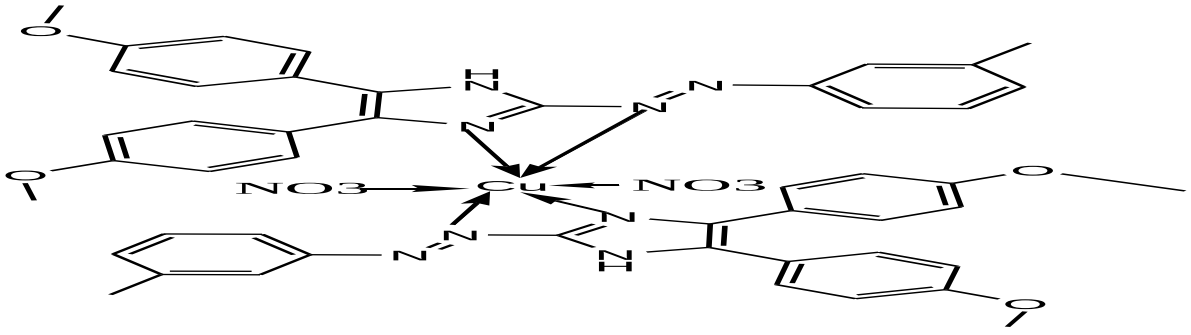

Figure 9. The suggested structure for the complex.

Application.
Samples were prepared from tap water and tea leaves and then added to Ligand (BMTI) to detect copper concentration in these samples and the results are shown in Table (14).

Table 14. Result of the application for copper (II) in samples.

Sample	Spectrophotometric method µg/mL	Flam atomic absorption µg/mL
Tap water	3.965×10^{-6}	
Tea leaves	6.867×10^{-6}	

CONCLUSION

A very sensitive method for quantifying copper in multiple samples has been developed and is also inexpensive for quantifying Cu (II). Verification and application studies demonstrated that Cu (II) can be quantified using this developed method. The results obtained showed that the reagent is able to quantify copper (II) in many samples. Analytical parameters such as identification, detection limit, accuracy, and recovery indicate that this method can be successfully applied to determine Cu (II).

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