



Spectrophotometric Determination of Cu (II) by Complexation with 2-(4-biphenyl) Imidazo[1,2-]Pyrimidine-3-Hydrazone and Studying Characteristics of Prepared Complex



Suhair Mohammed Yaseen^{*1}, Bushra Basheer Qassim², Naeemah Owayed Al-lami²

¹ Electrical Engineering Technical College, Middle Technical University, Iraq

² Chemistry Department, Faculty of Science, Bagdad University, Iraq

Abstract

2-(4-biphenyl)imidazo[1,2-]pyrimidine-3-hydrazone (BIPH) is synthesized and used as a new complexation analytical reagent in quantitative determination of copper ions, a yellowish green complex is resulted from this reaction. At the beginning, the reaction conditions were optimized at 430 nm which is the maximum wave length (λ_{max}) of the complex. The linear concentration range is 0.05-500ppm and the limit of detection is 0.122 ppm.

To test validity of this determination method, it was applied on samples with different matrix, and copper ion concentrations such as life samples of urine, tap water, wastewater and industrial samples of 4% copper alloy and 99% copper alloy. Standard addition method is also used to avoid matrix effect on analytical results. In application of suggested method, the values of relative error were (-4.536)–2.071% and values of recoveries were 95.46-102.07%.

The high stability constant of resulted complex ($K=0.25 \times 10^8$), and the simplicity in procedure of complex preparation, both provided us a motivation to prepare complex, and to study some of its characteristics by performing the identified analyses such as FTIR, UV-Visible spectroscopy, SEM+EDX, conductance measurement, reflectance percent R% to enrich the proposed structure of complex.

KEYWORDS: Schiff base, spectrophotometric analysis, copper complex, hydrozone derivatives, Schiff base complex.

INTRODUCTION

The compounds of Schiff base and their derivatives have wide range of applications in different domains [1]. But their complexes which are resulted from the reaction between Schiff base compounds and metal ions make their applications more and more active because these complexes:

- Have high stability in comparison with original parents as a result of Lewis basicity of imine (azomethine) group in metal complex [2].
- Are color products which can be used in quantitative and qualitative determination of metal ions at broad range of concentration by photometric techniques [3, 4].
- Are final compounds which are formed when pre-concentration or separation steps of metal ions by extraction [5] are required.
- Act as catalysts in many chemical reactions [6].
- Possess better biological activities than original Schiff bases [7].

- Have vital roles especially with life ions (Cu(II), Fe(II), Zn(II),) in lived cells [8].
- Are improved various industrial applications of schiff bases especially as coloring agent in paint [9] and anticorrosion compounds [10].

Copper ions are important ions as a main content of an erythrocytes and hemoglobin beside ferrous ions [11]. Also Copper ion has essential participation in both metabolism and growth of living organisms, therefore cupric ions should involve in cell nutrition [8]. In spite of its importance, cupric ions at high concentration (in comparison with allowed concentrations) are considered as a dangerous problem because of its toxicity on lived organisms [12]. As a result of above copper ion advantages (at low concentration) and disadvantages (at high concentration), it is necessary for suitable quantification methods of Cupric determination to be available. Many methods were reported in determination of copper ions in different samples as shown in table (1).

*Corresponding author e-mail: suhairyaseen@yahoo.com ; (Suhair Mohammed Yaseen).

Receive Date: 22 June 2019, Revise Date: 13 October 2019, Accept Date: 05 October 2020

DOI: 10.21608/EJCHEM.2019.13907.1861

©2021 National Information and Documentation Center (NIDOC)

Table 1: Some of recent spectrophotometric methods for cupric ions determination.

Reagent name	λ_{max} nm	linearity	comment	Reference number
N,N'-bissalicyliden-2,3-diimino pyridine	414	6.35-318 $\frac{\mu g}{L}$	This method was applied to determine cupric ions in water samples only.	13
Rubeanic acid	380	0.65-2.65ppm	This method was used to quantify cupric ions in mono or multi-component system with Co(II) and Ni(II)	14
2,7-di(2-benzothiazolyl)-fluorescein	559	1.92-127 $\frac{\mu g}{L}$	Preconcentration and dissolving in micellar (Triton X-114) steps were needed in this determination method.	15
4-(2'-benzothiazolylazo)-Salicylic acid	485	0.63-5.04 $\frac{mg}{L}$	This method is applied on Drugs and water samples	16

In the present work, light is focused on using of 2-(4-biphenyl)imidazo[1,2-a] pyrimidine-3-hydrazone as a new complexation analytical reagent in cupric ion quantification at 430nm and acidic medium of pH=4. This method of copper determination is performed easily with high sensitivity on different samples.

To omit all expected interferences in sample matrix, standard addition method was used in determination process of copper ion in different samples.

Because the formation reaction of complex is spontaneous, so it was prepared to study some its characteristics.

2-Experimental

2.1- Instruments:

- 1) FTIR-8400 (Fourier Transform Infrared) spectrophotometer from Shimadzu company with potassium chloride disk (in region 4000-400) was used to identify the prepared compounds, while cesium iodide disk (in region 4000-250 cm^{-1}) was used to identify resulted complex.
- 2) Double beam spectrophotometer UV-1800 from Shimadzu Corporation Company.
- 3) Single beam spectrophotometer of V-5000(320-1000 nm) from Metash company.
- 4) SEM (Scanning Electron Microscope) of Inspect S50 from FEI_ Company Netherland.
- 5) EDX (Energy Dispersive X-Ray Spectroscopy) of XFlash_6110 from Bruker Company/ Germany.
- 6) Electronic balance, Heater with magnetic stirrer.

- 7) Diffused Reflectance UV-VIS Spectrometer of AvaSpectro-2048 from Avantes.
- 8) Spectro max- Germany for elemental analysis of mild steel.
- 9) Linseis Platinum Evaluation V1.0.89 gravimetry to do thermal gravimetric analysis.
- 10) Magnetic Susceptibility Balance (JM) Johnson Matthey.

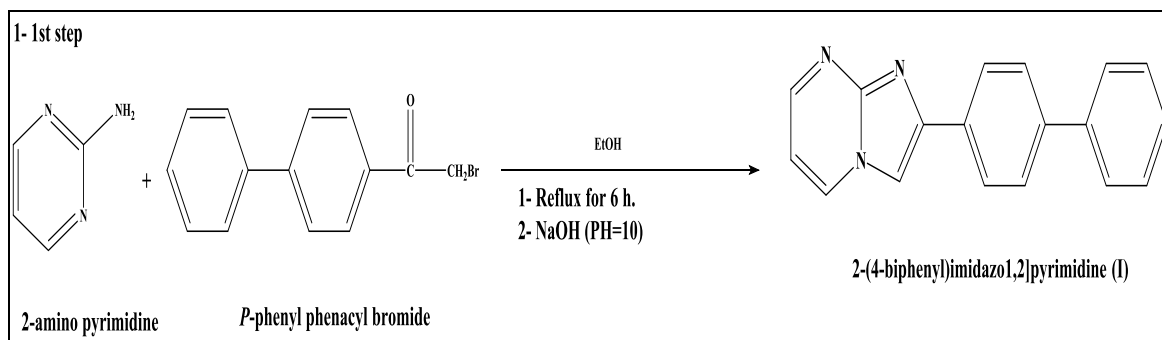
2.2- Chemicals: The chemicals with high purities from Fluka, BDH, Riedel de-Haen, Alpha Chemika, Alpha Aesar and Merck were used.

2.3 - Synthesis processes:

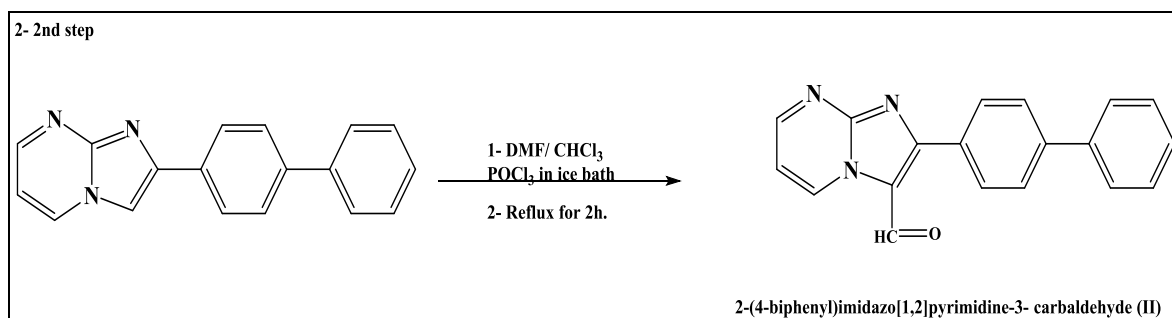
a. Synthesis ligand of 2-(4-biphenyl)imidazo[1,2-pyrimidine-3-hydrazone

The compound above was prepared by three sequence steps [17] with some modifications as follow:

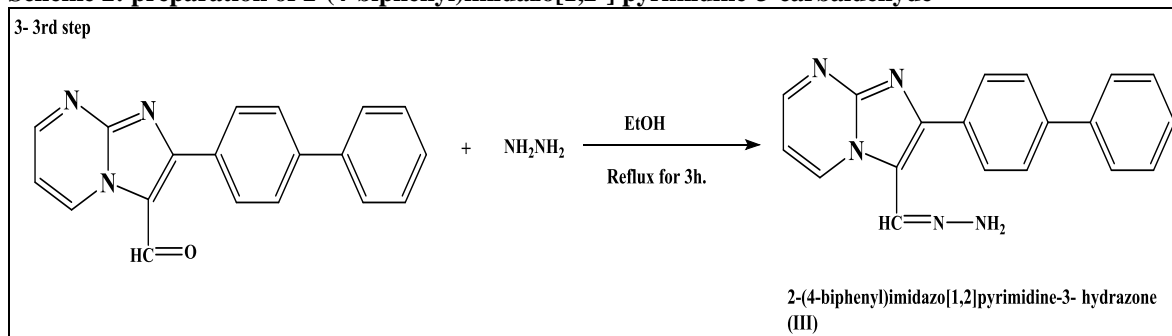
First step of Cyclization: To prepare (1mmol) of 2-(4-biphenyl)imidazo[1,2-pyrimidine, 2.77gm (1mmol) of p-phenyl phenacyl bromide (as limiting reactant) was mixed with 0.95gm (1mmol) of 2- amino pyrimidine. 10-12 ml of ethanol was added to the resulted mixture and refluxed with magnetic stirring for 6hours. The resulted solution was cooled and basified to pH=10 by adding 2-3ml of 5% Sodium Hydroxide. Solid crystals was formed, filtered, washed with water, and dried well in oven. The product yield was 95%.



Scheme 1: preparation of 2-(4-biphenyl)imidazo[1,2-]pyrimidine



Scheme 2: preparation of 2-(4-biphenyl)imidazo[1,2-] pyrimidine-3-carbaldehyde



Scheme 3: preparation of 2-(4-biphenyl)imidazo[1,2-]pyrimidine-3-hydrazone

Second step of aldehyde derivative preparation: In ice bath 5ml of chloroform was mixed with 1ml of dimethyl formamide. To this mixture, 2ml of POCl_3 was added drop by drop to maintain reaction temperature under 10C° because reaction is exothermic. Then 2.71 gm (1mmol) of solid 2-(4-biphenyl)imidazo[1,2-]pyrimidine with 5-7ml chloroform were added alternatively to cold mixture with stirring. The resulted mixture was refluxed with magnetic stirring for 2hours. The resulted solution was cooled with ice bath, filtered, washed with ethanol, and dried in oven. The product of 2-(4-biphenyl)imidazo[1,2-] pyrimidine-3- carbaldehyde yield was 91.3 % .

Third step of hydrazone derivative preparation: 3gm (1mmol) of 2-(4-biphenyl) imidazo[1,2-]pyrimidine-3-carbaldehyde was dissolved in 10-12 ml of ethanol, and 1-2ml of 99.5% hydrated hydrazine was added.

The resulted solution was stirred and refluxed for 3hours, then cooled and filtered to get 82.23% of 2-(4-biphenyl)imidazo[1,2-]pyrimidine-3-hydrazone which was recrystallized with ethanol.

b-Complex Synthesis:

Complex preparation process is spontaneous, so complex can be obtained by mixing equal volumes of (1000ppm) aqueous metal solution and (2000ppm) ligand solution (it is prepared by dissolving 0.2gm in small volume (5-10)ml of DMF or DMSO and completed volume with ethanol which has less boiling point and easily to evaporate). The mixture was left for few days to complete reaction, excess solvent to evaporate, and complex crystals to settle.

Solid precipitate was washed with water, filtered, and treated with ether to remove residual solvent. In this procedure, the yielded product is poor 25-30%.

Complex yield product can be increased to 60-70% by refluxing mixture of 2mmole (0.626gm) 2-(4-biphenyl)imidazo[1,2-*b*]pyrimidine-3-hydrazone which dissolved in hot ethanol with 1mmole(0.25gm) of copper sulfate penta hydrate($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) or (0.24gm) of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) or (0.17gm) of copper chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). The mixture was magnetic stirred with reflux for 2-3hours. The yielded product was filtered, washed with distilled water, acetone to remove unreacted substances, and with ether to remove any residual solvents. Then the precipitate was dried in oven.

2.4- Preparation of chemical solutions and samples:

1) Buffer solutions:

By diluting 82.2ml of 37% Hydrochloric acid (1.2gm/ml) to 1L with water, stock solution of 1N of hydrochloric acid is prepared. 0.2N of hydrochloric acid (HCl) was prepared by proper diluting of stock solution above. 0.2N of potassium chloride (KCl) was prepared by dissolving (1.5)gm in water. Buffer solutions with pH=1 and 2 were prepared by mixing various volumes of both of them and reaching the required volume by adding distilled water. 0.1N of sodium acetate (NaOAc) and 0.1N of acetic acid (HOAc) were prepared. By weighing (0.82 and 0.6)gm respectively and dissolving in water to 1L. Mixing various volumes of both of them and reaching the required volume by adding distilled water, buffer solutions with pH=3, 4, and 5 were prepared. 0.1N of sodium dihydrogen phosphate NaH_2PO_4 (1.2gm in 1L water) and 0.1 N of sodium hydroxide NaOH (0.4gm in 1L) were prepared. By mixing various volumes of both of them and reaching the required volume by adding distilled water, buffer solutions with pH=6, 7, and 8 were prepared. All buffers were tested by indicator strips.

2) Ligand solution: 0.01M (3130ppm) of prepared ligand was prepared by dissolving calculated 0.313gm of ligand 2-(4-biphenyl)imidazo[1,2-*b*]pyrimidine-3-hydrazone in 100 ml of DMF or DMSO as good solvents. By suitable dilution 2000ppm of BIPH was prepared and used in determination method.

3) Interference ions:

500ppm of cations salts as nitrate of (aluminum $\text{Al}(\text{NO}_3)_3$, copper $\text{Co}(\text{NO}_3)_2$, cadmium $\text{Cd}(\text{NO}_3)_2$, barium ($\text{Ba}(\text{NO}_3)_2$, ferric ($\text{Fe}(\text{NO}_3)_3$, Nickel $\text{Ni}(\text{NO}_3)_2$), lanthanum chloride LaCl_3 , ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, and of anions sodium chloride (NaCl), sodium bromide (NaBr), sodium

thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), potassium sulfate (K_2SO_4), sodium acetate (CH_3COONa), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), sodium dihydrogen phosphate (NaH_2PO_4), potassium iodide (KI) were prepared by weighing 2.5mg and dissolved in 5ml

4) Samples preparation:

a- Wastewater sample was taken from influent of waste water treatment plant (Al-Karkh project), collected in glass bottle (1L) with 1-2drops of concentrated nitric acid to stop any further action of microorganisms. Then the sample was filtered, neutralized with few drops of conc. sodium hydroxide to be ready to analyze. 1ml of this sample is added to each of four volumetric (5ml), 1ml of standard copper sulfate of 0.5, 1.25, 2.5 ppm were added to 2nd, 3rd, and 4th volumetric flasks respectively with 2 ml of BIPH ligand (2000ppm in DMF)+0.5 ml of buffer and finally completed volume to 5ml.

b- Tap water sample: 1ml of fresh tap water (Al-Resafa side) was added to each of four volumetric flasks which contained 2ml of BIPH (2000 ppm)+ 1ml of: deionized water, standard solutions of copper sulfate of 0.1, 0.3, 0.5 ppm were added to 1st, 2nd, 3rd, and 4th volumetric flasks respectively, then the volume was completed to 5ml with deionized water. It was noticed that the addition of buffer solution reduces sensitivity by decreasing solution color intensity; therefore determination process was done without buffer addition.

c- 99% Copper alloy: 0.17gm of 99% copper alloy was weighed, 12ml of mixture of 2ml concentrated hydrochloric acid + 10ml of concentrated nitric acid was added to dissolve solid alloy with stirring. The resulted solution was heated gently near dryness, and then 5ml sulfuric acid (diluted with water in 1:1 ratio) was added to convert white solid to blue solution because of the formation of hydrated copper sulfate. The solution was filtered and the volume is completed to 100ml with distilled water [18]. 1 ml of this stock solution was transferred volumetric flask of 50ml, diluted with deionized and by adding slowly and carefully few drops (approximately 0.5ml) of concentrated sodium hydroxide to prevent precipitation of blue copper hydroxide (at suitable hydroxide concentration) and to neutralize strong acidic medium (pH=1) which reduces color intensity of complex, the volume is completed to 50ml. It is important to test pH after each addition indicator strips to make sure that sample solutions had moderate to neutralized pH and the solution was tested by indicator strips. 1ml of the last solution is suitable for copper

determination by standard addition with 1ml of standard solutions of (25, 50, and 100) ppm of copper sulfate, then added to 2ml of BIPH ligand and completed volume with deionized water to 5 ml.

- d- 4% Copper alloy: 0.7gm of 4% copper alloy was treated as former alloy and 100 ml of its solution was prepared. 1ml of above solution was diluted to 25ml and its acidity organized to 5-7 pH by careful added of sodium hydroxide to prevent precipitation of aluminum hydroxide which is led to make solution turbid and absorbance readings to be variable. 2ml of above alloy solution+ 1ml of standard copper sulfate (0, 25, 50, 100) were added to 2ml of BIPH. As another procedure, 1ml of 4% copper alloy (100ml) was diluted to 5ml, then 1ml of this solution was added to each of four (10 ml) volumetric flasks and 0, 3, 6, 8.5 ml of 100ppm standard copper sulfate added to 1st, 2nd, 3rd, and the 4th volumetric flasks respectively with organization acidity of each one by 1 drop of concentrated sodium hydroxide.
- e- Urine sample: 5ml of concentrated nitric acid was added to 50 ml of urine sample and heated gently for 3-5 then cooled, 1ml of concentrated Sulfuric acid and 1ml of 60% perchloric acid were added to cooled solution. The mixture was reheated for 20-25 minutes. The content was cooled, filtered and neutralized with ammonium hydroxide in presence 1.5ml of 0.01% sodium tartrate, then the content was poured into 10ml volumetric flasks and diluted with water [18]. Equal volumes (1ml) of urine solution and standard solution of copper sulfate (5, 10, 20) ppm were added to 2ml of 2000ppm BIPH, and volume was completed to 5ml with deionized water.

5) Solutions of anticorrosion measurement:

0.1M of Hydrochloric acid (HCl) was prepared by diluting solution of 1 M of HCl. The solution of 1M was prepared from original HCl bottle with purity =36%, and density =1.98 g/ml. The required concentration was standardized by titration with 0.1 M of sodium carbonate Na_2CO_3 and methyl orange as indicator. 0.01 M of complex was prepared by dissolving 0.4gm in small volume of DMF and complete volume with 0.1M of hydrochloric acid solution. Other dilutions were done to prepare , 0.001, 0.0001, and 0.00001 M of complex solutions

6) Solutions of antibacterial activity:

500 ppm of complex was prepared by dissolving 2.5mg of complex in 5ml of dimethylsulfoxide (DMSO). By using the same solvent above, sample

solution of complex was prepared for conductivity measurement.

Results and Discussion

As in image 1, formation of yellowish green product as a result of mixing copper ion and ligand solutions for different concentrations of both of them is an evidence of reaction happening.



Image 1: from left to right, solution of copper sulfate, complex, and BIPH ligand.

Because of the considerable difference between maximum wave lengths (λ_{max}) 360nm of ligand and 430 nm of complex, it is suitable to use colored complex in spectrophotometric determination of copper ions in its samples.

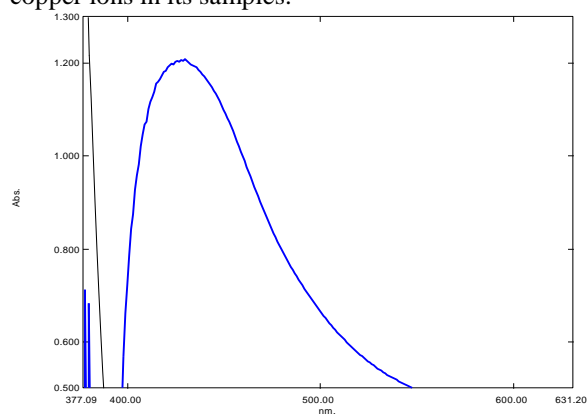


Figure 1: absorption spectrum of ligand (its solvent DMF as blank) in black line, and absorption spectrum of resulted complex (ligand as blank) in blue line.

3.1- Optimization conditions for spectrophotometric quantitative determination of cupric ion:

I. Effect of ligand solvent

Ligand has good solubility in DMSO and DMF but slightly soluble in ethanol (40%). According to solubility sequence above, intensity of color complex is increased in direction of increasing ligand solubility

as in figure 2. This effect was studied on sample solution which was contained 1ml of 200ppm of cupric ion + 1ml of 2000ppm of BIPH solution and complete volume to 5ml.

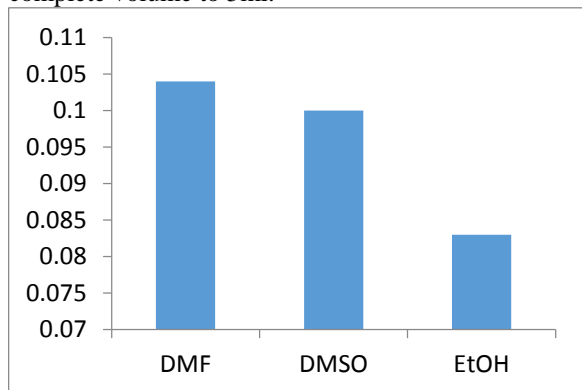


Figure 2: Effect of ligand solvent on complex color intensity.

II. Effect of metal salt

Effect of metal source (its salt) on complex color intensity was studied for sample mixture of 1ml 200ppm cupric ion + 1ml of 2000ppm of BIPH solution and complete volume to 5ml. there is no considerable influence for metal salt as in table 2 :

Table 2: metal salt effect on complex color intensity

Metal ion salt	Absorbance
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.106
$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.101
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.109

III. Effect of pH

By mixing equal volumes (1ml) of each of 1250ppm ligand, 1250ppm metal ion solutions, and 0.5ml of buffers with different pH, and complete volume to 5ml. After waiting period for 10 minutes to complete reaction, absorbance of complex solutions was recorded. It was found that the best medium acidity to perfume complex formation and to get a maximum light response (at 430 nm) was at pH = 4 as in figure 3. In the strong acidic medium, complex's absorbance is low and this is may be due to ligand (Schiff base) instability which leads to ligand dissociation and retardation complex formation. While in basic pH, absorbance also is reduced [19] because of salt formation between metal ions and basic ions of medium and turbid appearance of solution is a proof of this reaction. In figure 3, pH=0 refers to sample solution without buffer addition.

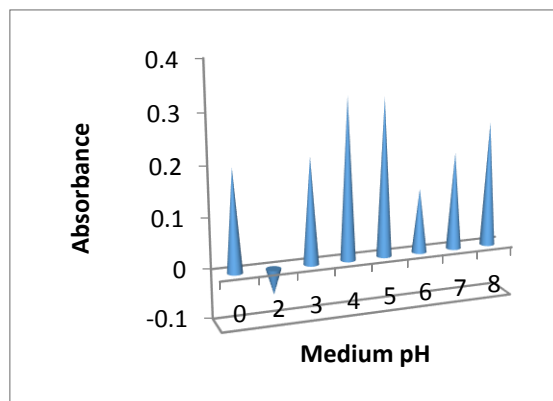


Figure 3: effect of pH medium on complex formation. Zero pH refers to solution without buffer addition.

IV. Effect of M:L fold:

Light absorption of yellowish green complex is increased with increasing mole ratio of M:L , in another words that means increasing sensitivity of analytical method. The absorption of complex is not only maximum (at M:L = 1:75) but also is constant for more than 80-100 minutes because of high complex stability at these conditions. Despite of the excess amount of ligand at M:L = 1:75 , there is no absorbance error because samples absorbance was measured against blanks which were prepared according to samples content to omit the effect of excess ligand. The effect of M: L folds from 1:1 to 1:75 on complex color intensity at metal ion conc. (0.0001 N), buffer's pH=4 and 8-10 minutes was studied as in figure 5. To cover the influence of M:L folds in increasing method's sensitivity at low metal ions concentration(0.0001N=25ppm) ,wide range of M:L from 1:1 to 1:250 was used in copper spectrophotometric determination at pH=4 and 8-10 minutes as reaction time as in figure 4.

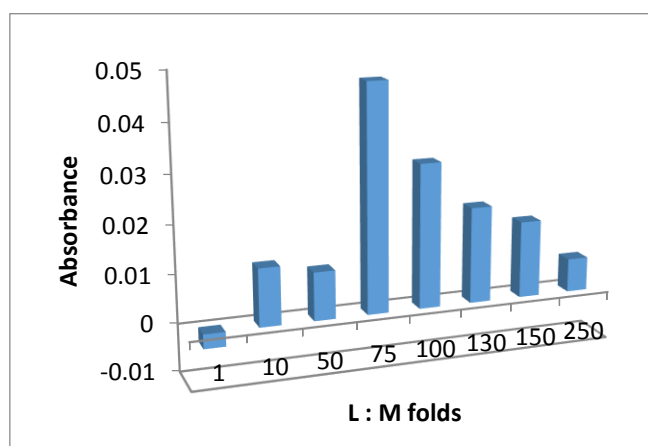


Figure 4: effect of BIPH ligand folds.

V. Effect of sequence addition

As shown in table 3, the best sequence of solutions addition (in complex formation) to deserve maximum absorbance is Ligand(L)+buffer(B)+metal(M)+water (W). This result is expected because buffered ligand solution is a suitable medium to form complex with better color intensity. The reaction involved addition solutions of 0.5 ml buffer, 2ml of 1500 ppm ligand, 2ml of 1500ppm cupric ion solution, and distilled water to 5ml.

Table 3: effect of sequence addition on complex color intensity

Sequence of addition	absorbance
M+B+ L	0.450
B+M +L	0.420
L+B+M	0.572
B+L +M	0.531

VI. Effect of reaction time:

Particularly at high cupric ion concentration (1250ppm), the reaction of complex formation approximately requires to 40 minutes to complete and absorbance to reach it's maximum value as in figure (5). But even at low cupric ion conc., the formation reaction did no need more than 10 minutes to complete when M:L folds was 1:75, linear relationship (between color intensity and time required to complete reaction) was recorded as in figure (6). This waiting time is considered as a first strong proof on complex formation after mixing solutions of both of them (metal ion and ligand) at very low concentrations (colorless solutions), and distinguished yellowish green color of complex is appeared after passing period of time.

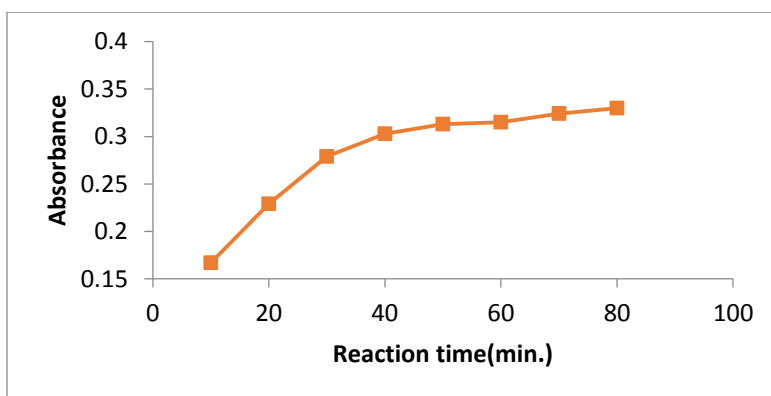


Figure 5: The dependence of complex color intensity on reaction time at 1:1 (M:L) folds.

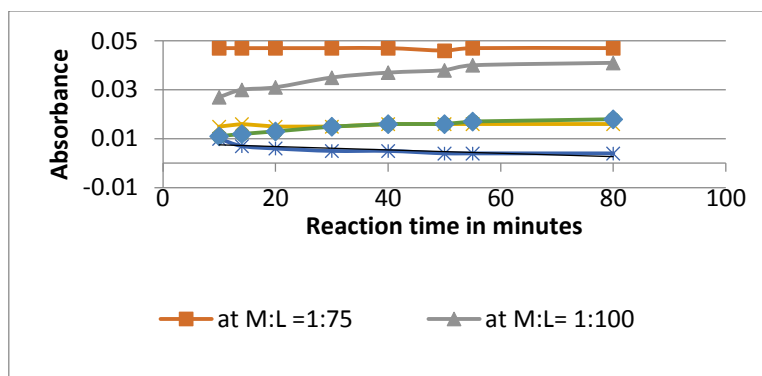


Figure 6: The decreasing influence of reaction time on color of complex at different folds of M:L

VII Effect of temperature

Because reaction is spontaneous, no positive influence of temperature changes (it is done by ice bath and hot water bath) on increasing color intensity was observed. As shown in table 4, color intensity of complex was decreased with temperature increasing because of crystals formation which is led to absorbance decreasing.

Table 4: temperature influence on decreasing color intensity of complex.

In room temperature	In ice bath	In hot water bath
0.162	0.146	0.151

VIII. Shelf life of BIPH:

Despite of that both BIPH solutions (one of them is freshly prepared and another was prepared before more than two months) have very similar spectrum with very simple exception, there was unreasonable results and nonlinear relationship were obtained when old prepared BIPH was used as an analytical reagent. Figure 7 exhibits the spectrum of both of them and the related values are listed in table 5.

Table 5: values of peaks and valleys in spectrum of fresh and old prepared BIPH.

Freshly prepared BIPH	Old prepared BIPH (since 2-3 months)
Peak 362.00, 3.462.	Peak 979.00, 0.067.
Valley 206.00, 4.000.	Peak 344.00, 3.772
	Valley 922.00, 0.063

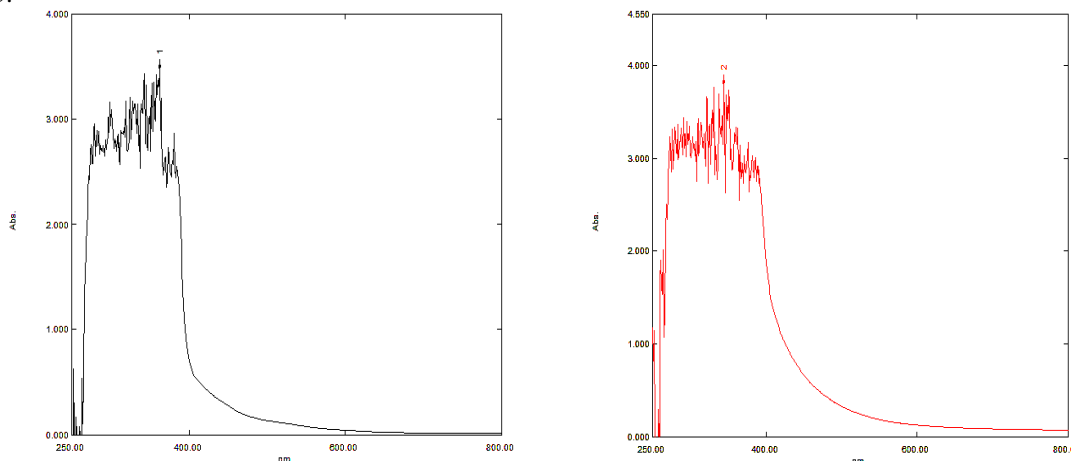


Figure 7: spectrum of 0.05N of freshly prepared BIPH in DMF solvent (in left side with black color) and prepared BIPH before one year (in right side with red color).

The optimum conditions for quantification of copper content are summarized in table 6

Table 6: the ideal reaction environmental determinates for copper complex formation

Parameter	Optimum value
Wave length	430 nm
Acidity	4
L:M fold	75:1
Sequence of chemicals addition	Ligand + buffer + metal ion
Reaction time (min.)	10 min.
Reaction temperature	Room temperature
M:L in complex composition	1:2

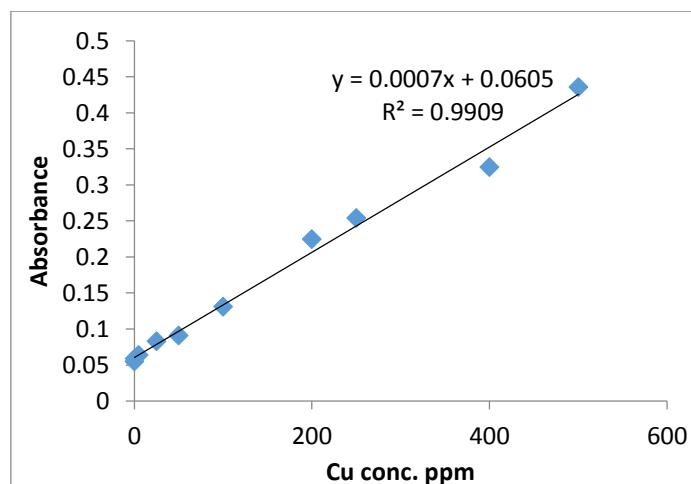


Figure 8: standard curve of Cu^{2+} determination

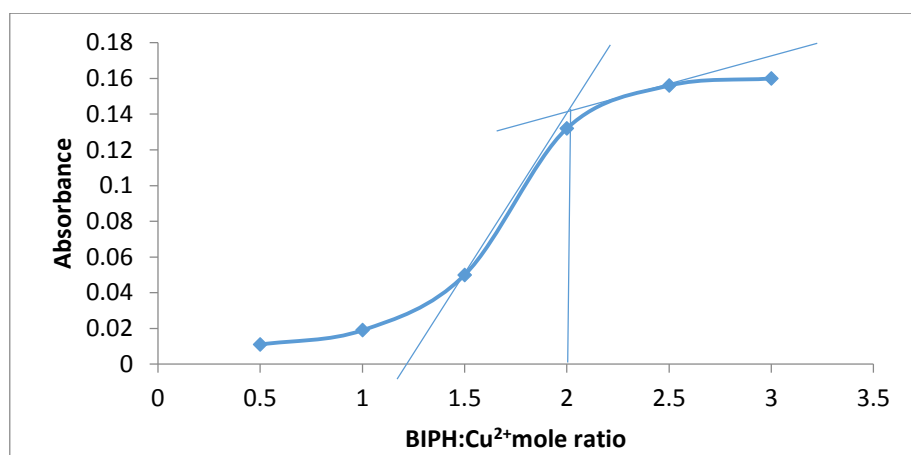


Figure 9: Determination complex compositions by mole ratio method.

3.2- Method validation:

By mixing 2ml of ligand (2000ppm) +0.5 ml buffer (pH=4) + 2ml metal with different concentrations (0.1-1500ppm) and complete volume with distilled water to 5 ml, and leaving solution mixture for 8-10 minutes to make reaction complete. The following results were

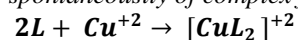
recorded, and standard curve was drawn for concentrations range (0.5-500) ppm as shown in figure 8. The statistical treatment of these values was listed in table 7:

Table 7: statistical treatment of analytical results of standard curve.

	Standard curve
Regression equation	$Y=0.0007X + 0.0605$
Correlation coefficient, r^2	0.9909
Linearity percentage, $r^2\%$	99.09
Linearity range, mg/L(ppm)	0.05-500
Molar absorptivity constant $L/mol.cm$ =slope of line (molar) ⁻¹ /path length(cm)	0.175×10^3
Slope, b	0.0007
Intercept, a	0.0605
Standard deviation of residual, $S_{y/x}$	0.0155
Standard deviation of slope, S_b	2.864×10^{-5}
Standard deviation of intercept, S_a	2.789×10^{-3}
LoD= $3S_b/b$, mg/L	0.122
LoQ= $10S_b/b$, mg/L	0.4026

3.3- Estimation of complex composition by mole ratio method: This method is done by mixing different volumes of ligand solution with the same volume of metal ions solution at each time, the absorbance of resulted complex solutions were recorded after passing reaction time of 10 minutes. It is important to prepare each of metal ions and ligand solutions in equal concentrations. As in figure below, M:L mole ratio in complex equals to 1:2.

3.4-Evaluation of stability constant and spontaneoucity of complex formation:



According to above equation the complex is formed, so stability constant K of this complex can be expressed as bellow [18]:

$$K = \frac{1-\alpha}{4 \alpha^3 C^2}$$

α : is degree of dissociation, C: complex concentration in molar (mole. L⁻¹) and equaled to 0.0013 M.

$$\alpha = \frac{A_m - A_s}{A_m}$$

A_m = absorbance at complex solution after stoichiometric M:L ratio.

A_s = absorbance of complex solution at stoichiometric M:L ratio. The spontaneoucity of complex formation reaction can be estimated based on K evaluation:

$$\Delta G = -RT \ln K$$

ΔG : Gibbs free energy, R: 8.314 joul/mol.k , T: absolute temperature

Table 8: The parameters were used to calculate complex stability constant.

A_m	A_s	α	K	$\log K$	ΔG in joule at 300k°
0.156	0.132	0.154	0.343×10^8	7.535	-43276
0.153	0.123	0.196	0.158×10^8	7.199	-41342
			Average= 0.25×10^8		Av.= -42487

3.5- Ions interference:

Effect of ions interference on copper ion quantification is studied. As in table (9), existence of some ions in medium of copper ions determination caused errors. In the table below anions which caused errors less than acceptable were listed and also the effect of some cations on complex color intensity was studied. It was found that the presence of (500ppm) sodium oxalate in 1000ppm copper sulfate solution led to completely mask of 500ppm of cadmium, cobalt, and nickel

nitrate. While addition of oxalate ion did not make interferences of lanthanum, molybdenum, ferric, barium, and aluminum ions under control range.

3.6- The applications:

Standard addition method is used to determine copper content even at low concentration and to avoid effect of matrix in different samples. The resulted values and their statistical treatment are showed in figures (10-15) and table 10 below:

Table 9: Interference ions in copper determination

Anions	Permitted conc. (ppm)	Recovery %
$Na_2S_2O_3$	<650	101.315
NaCl	<120	104.7
NaBr	<200	103.46
$Na_2C_2O_4$	<100	98.62
KI	<120	101.50
CH_3COONa	<100	99.01
NaH_2PO_4 , K_2SO_4	<10	95.62-94.19
Cations in presence of oxalate		
$Cd(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$	<500	95.18-95.45
$Ba(NO_3)_2$, $Al(NO_3)_3$, $(NH_4)_6Mo_7O_{24}$, $Fe(NO_3)_3$, $LaCl_3$	Un acceptable error at concentration 500 ppm and less despite of presence of oxalate ions.	

Table 10: application of suggested method on determination of copper ion content (ppm) in some samples.

Type of sample	Concentration of Copper ion content by another determination method (ppm)	Concentration of Copper ion content by suggested determination method	Relative error $E_{rel}\%$	Recovery%
Tap water from Al-Resafa side	0 ppm	0.035 (ppm)*	-	-
Wastewater Al-Karkh project	2.65 ppm, spectrophotometric by DR 3900 HACH instrument.	2.632 (ppm)	-0.68	99.32
Urine	100-1200 $\mu g/dL$ normal range	11.683 ppm	-	-
4% copper alloy (1)	0.028	0.02673 gm	- 4.536	95.464
4% copper alloy (2)	0.028	0.02858 gm	2.071	102.071
99% copper alloy	0.1584 gm	0.1575 gm	- 0.568	99.432

* When absorbance of analyte alone equals to zero or near to zero (negative value), and I think sample concentration is zero and no need to standard addition.

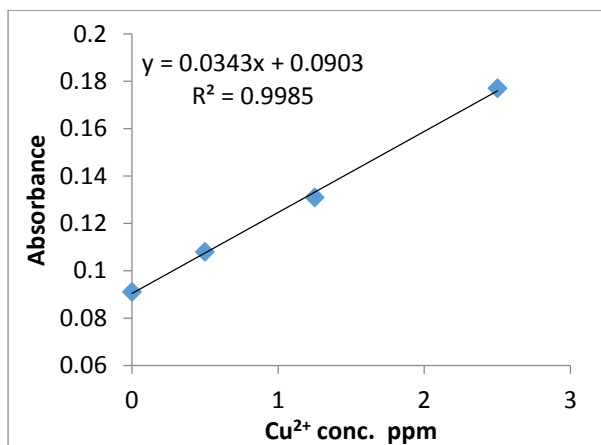


Figure 10: standard addition curve for Cu^{2+} determination in wastewater.

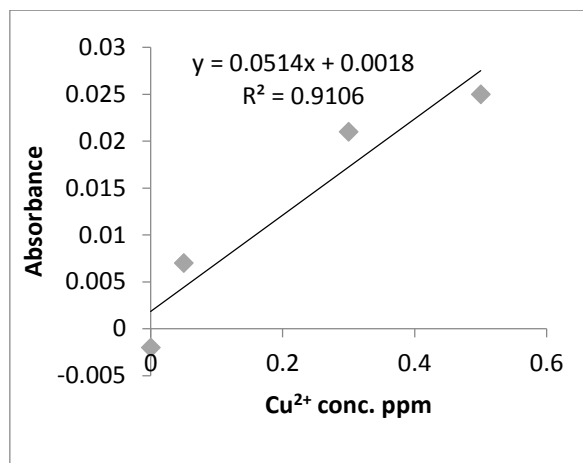


Figure 11: standard addition curve for Cu^{2+} determination in tap water.

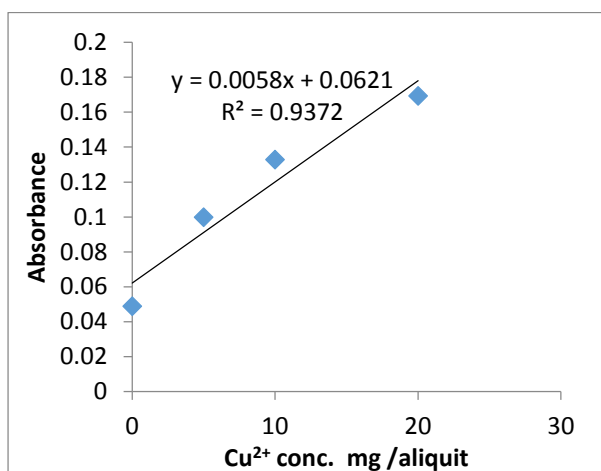


Figure 12: standard addition curve for Cu^{2+} determination in 4% copper alloy (sample 1).

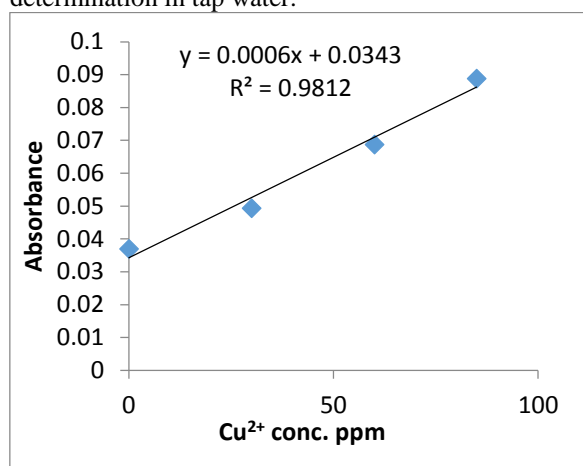


Figure 13: standard addition curve for Cu^{2+} determination in 4% copper alloy (sample 2).

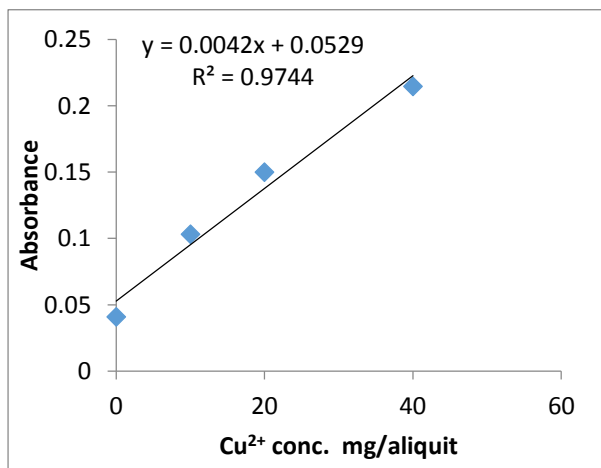


Figure 14: standard addition curve for Cu^{2+} determination in 99% copper alloy.

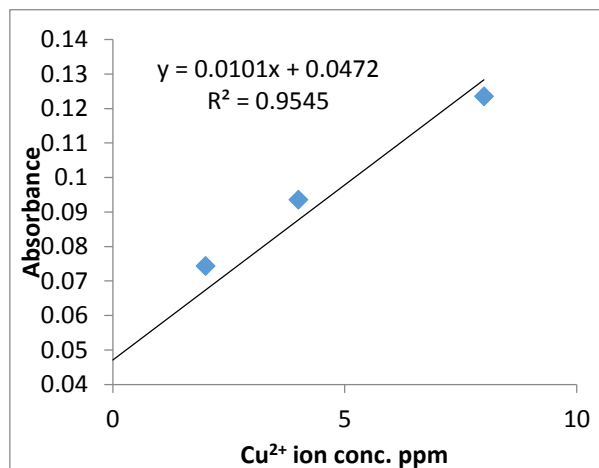


Figure 15: standard addition curve for Cu^{2+} determination in urine sample.

3.7- Identification of complex's characteristics.

a- Appearance: image 2 is included images of both BIPH ligand and its complex with copper ion.

b- HNMR spectrum: according to information of figure 16 which are summarized in table 11, magnetic spectrum of BIPH ligand improves its formation.

- c- FTIR analysis: In FT-IR spectrum, peaks shifting and appearance of new peaks in IR spectrum of complex in comparison with ligand's IR spectrum are considered as reliable evidence of complex formation as in table 12.

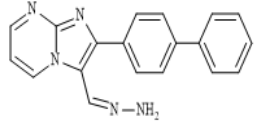
Frequency of azomethine group in ligand is shifted to less value in complex because of decreasing electronic density on nitrogen atom which is participated by its electron pair with metal ion in formation of covalent bond of complex. The positive or negative shifting values are not determined in specified limits, because

they are depending on the structure of original ligands and resulted complexes [20].



Image 2: crystals of BIPH precipitate (in left), and crystals of complex (in right).

Table 11: HNMR data of ligand.

	HNMR data in ppm	
	Multiplate 8H of aromatic rings	7.17 – 7.35
	Singlet (H) of HC=N group	2.49
	Singlet (2H) of NH ₂ group	7.05
	Doublet (1H) of HC=N group of ring	2.48
Doublet (1H) of HC=CH	4.83	

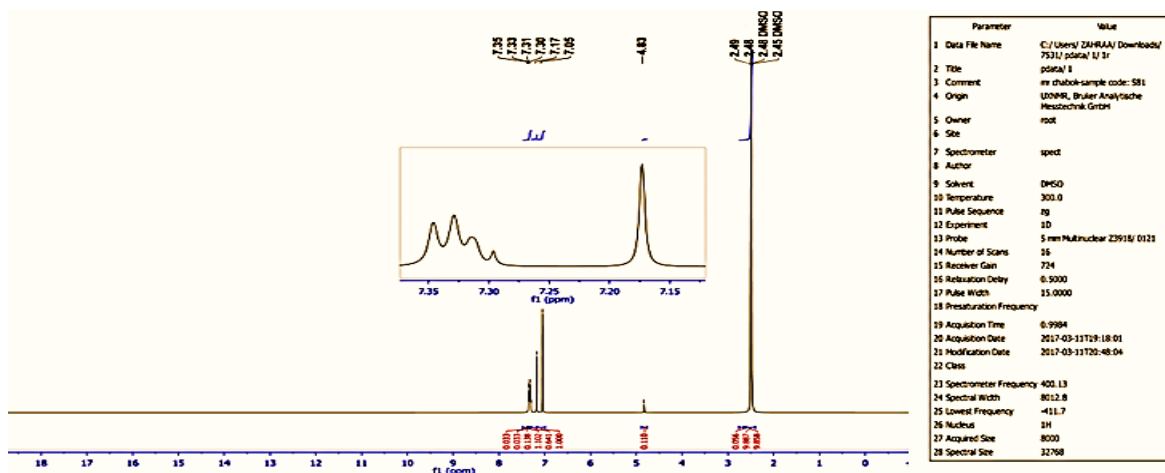


Figure 16: HNMR spectrum of ligand.

Table 12: Some of distinguished peaks in IR spectrum of ligand and complex.

Frequency of bond vibration in cm ⁻¹	v(N-H ₂)	v(C=N) azomethine	v(C-N)	v (C=C) aromatic ring	Cu-N
Ligand	3190 3311	1623	1290 1402	1542 1460	-
Complex	3238 3361	1616	1363 1402	1537 1444	476 505

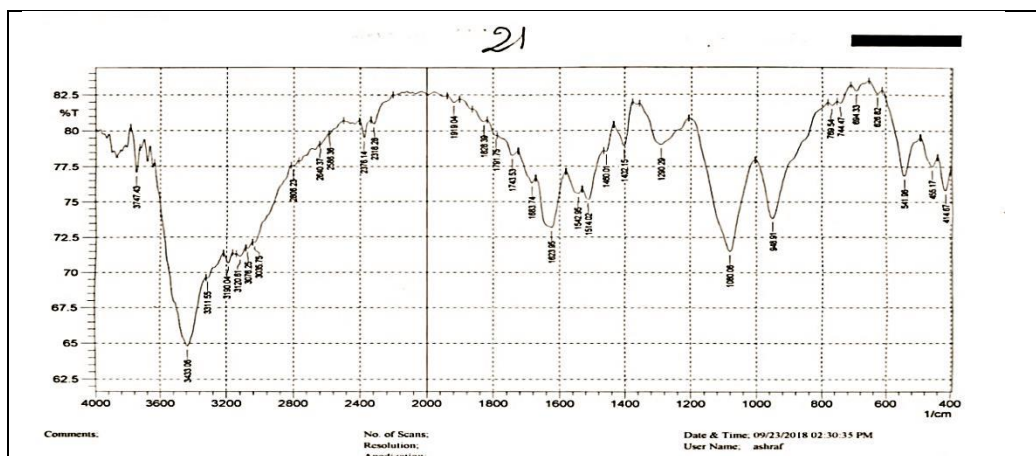


Figure 17: FTIR of 2-(4-biphenyl)imidazo[1,2-a]pyrimidine-3-hydrazone

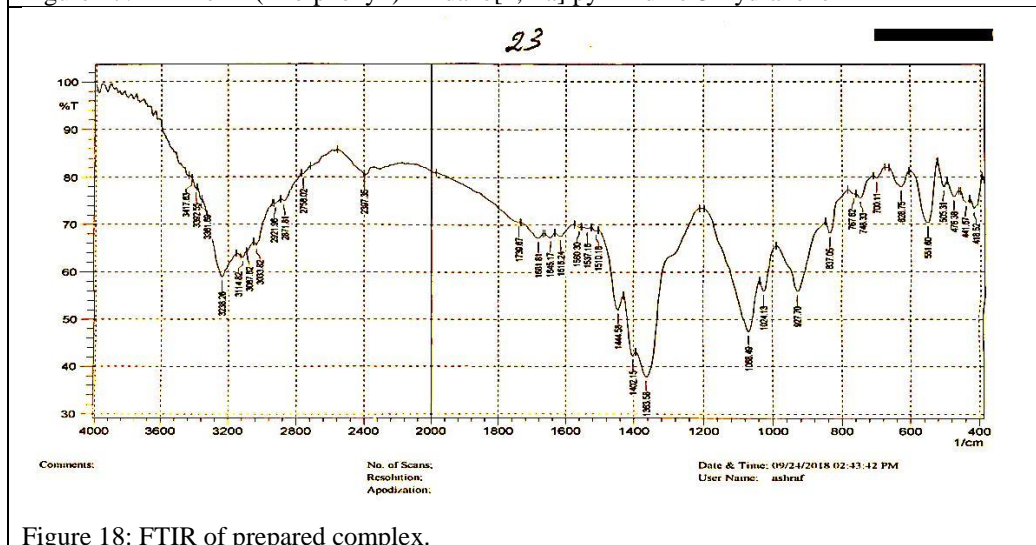


Figure 18: FTIR of prepared complex.

d- UV-Visible spectra:

By recording spectrum of both of the prepared ligand against dimethyl sulfoxide (DMSO) solvent as blank, and the same step was repeated with prepared complex (which dissolved in the same solvent) against DMSO as blank. The ligand band 239 nm is attributed to $\pi \rightarrow \pi^*$ transition of imidazole, while the band of 290 nm is due to $\pi \rightarrow \pi^*$ of other aromatic rings, and 383 nm is related to $n \rightarrow \pi^*$ of azomethine group [21-24].

Table 13: The electronic transitions in absorption spectrum of ligand and complex.

	Wave length (λ) in nm	Wave number (ν) in cm^{-1}	Assignment
Ligand	239	41841	$\pi \rightarrow \pi^*$
	290	34483	$\pi \rightarrow \pi^*$
	383	26110	$n \rightarrow \pi^*$
complex	221	45249	$\pi \rightarrow \pi^*$
	349	28653	$d \rightarrow d$ M to L charge transfer.

The $\pi \rightarrow \pi^*$ bands of ligand are shifted to lower wavelength in complex, but the transition at 349 nm is attributed to $d \rightarrow d$ transition of metal complex. While the $d \rightarrow d$ transition was appeared at 409 nm when ligand was blank.

e- Conductivity measurement

As another proof of complex formation, changing in sample conductivity from zero for ligand solution to 100 μS at 40 mg/l for complex. This increase is due to ionic nature of complex in the comparison with the covalent nature of ligand.

f- Evaluation color brightness of complex particles:

From spectrum which is plotted between variable reflectance percent (R% on y-axis) as a result of wavelength changes (x-axis) of incident light on sample surface, the color of reflected light which solid complex particles appear in and intensity of this color can be determined.

Only when angle of fallen light equals to the angle of reflected light, reflectance percent is considered [25].

R% is ratio percent of reflected light intensity to total intensity of incident light. The particles of prepared complex are transmitted light in 570-580 nm with high intensity (brightness) at R% = 89%, this region of

greenish yellow color is enriched the result of absorption spectrum for visible light by complex solution in region above 410 nm.

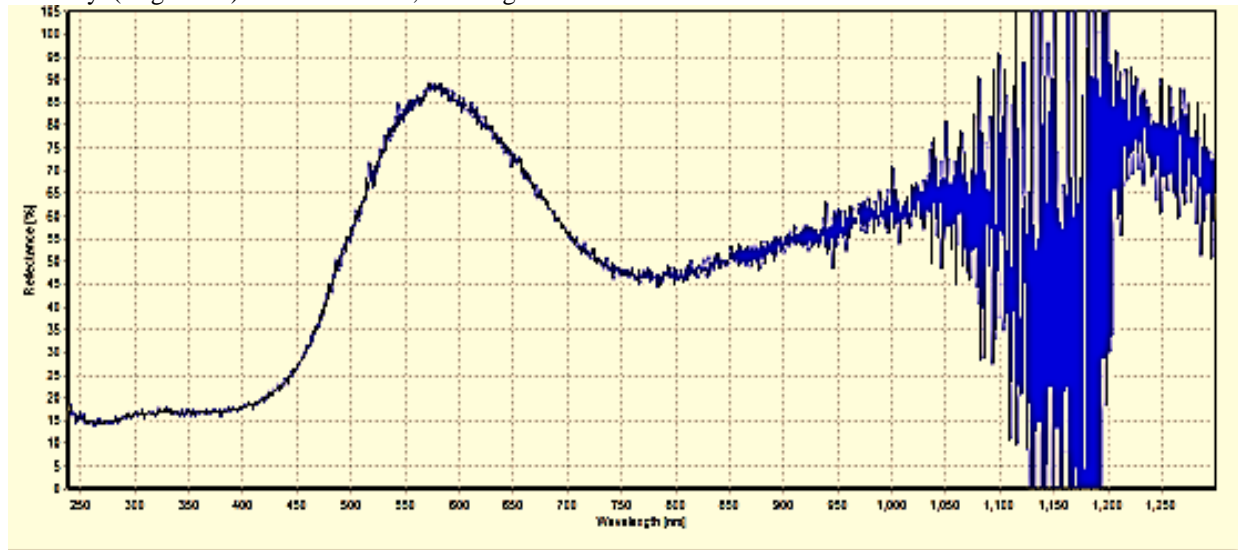


Figure 19: The reflectance spectrum of prepared complex.

g- SEMs and EDX analysis:

Based on SEM analysis, it is observed that solid complex particles have coral reef-like structure. EDX analysis is enhanced the expected complex structure by composition percent determination of complex

surface particles for all atoms (C, O, N, Cu, and S) containing in except hydrogen which cannot be recognized because of EDX technique nature. The solid particles size is $5 \mu\text{m}$ at magnification = 2×10^4 .

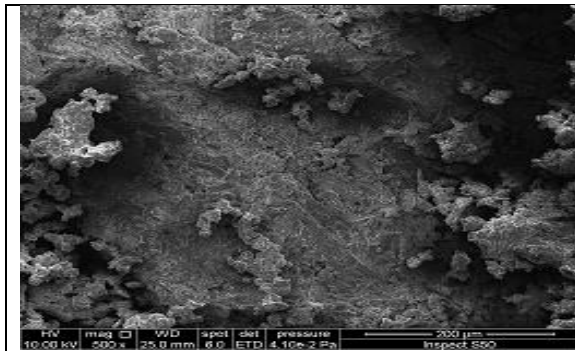
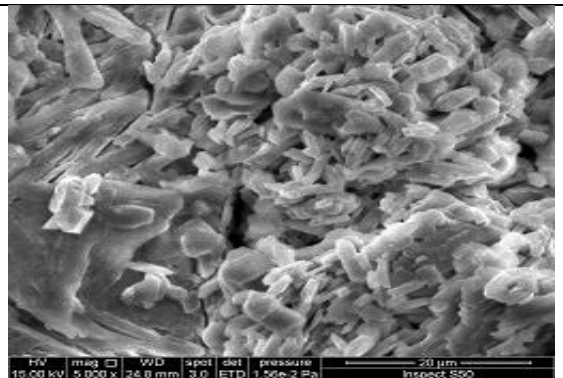


Figure 20 : SEM analysis for determination Morphology of solid complex particles. a-With 200 times magnification.



b-With 5000 times magnification.

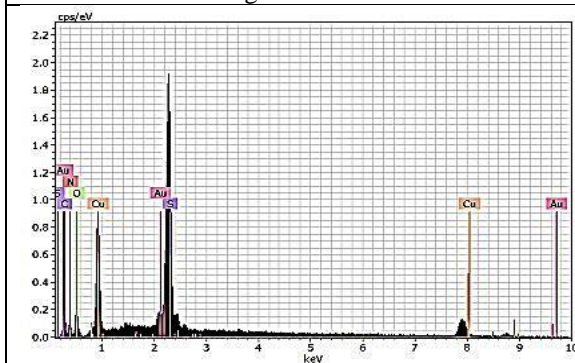


Figure 21a and b : EDX analysis for determination of surface elemental composition of solid complex.

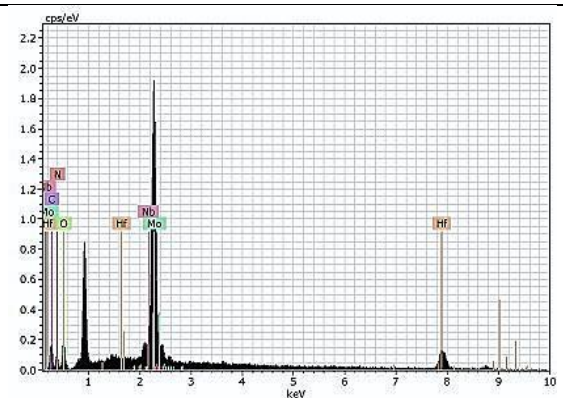


Figure 21 b

Table 14: summary of some characteristics of BIPH ligand and prepared solid complex.

Compound	Appearance	Melting point C°	Conductivity μs at 21C°	λ_{max} nm	Crystal size In μm
BIPH ligand	Yellow crystals	160-162 C°	0 μs	239 290 383	-
Cu(BIPH) ₂ SO ₄	Yellowish green crystals	184-186C°	120 at TDS= 50mg/l 100 at TDS= 40mg/l	221 349	5 μm at 2 \times 10 ⁴ magnification by SEM analysis

h- Thermal Gravimetric Analysis (TGA):

From TG analysis diagram, it is observed that complex powder lost 2.12% (calculated percent was 2.2%) of its weight as water molecules from 0 - 175 C ° and 55.23% as a result of the complex decomposition above 175 C ° until 441 C °.

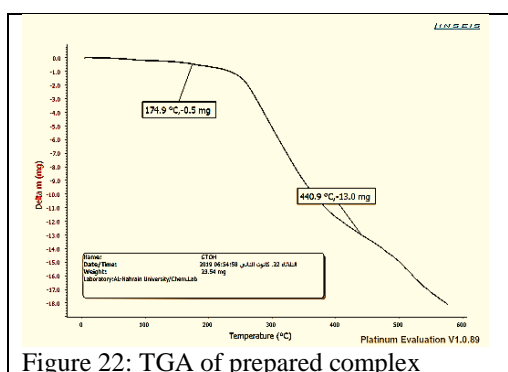


Figure 22: TGA of prepared complex

i- Evaluation of effective magnetic moment:

Gram magnetic sensitivity (X_g) was calculated using information from magnetic balance measurement of the complex, according to the below equation:

$$X_g = \frac{C \cdot L}{m \times 10^9} (R - R_0)$$

X_g =gram magnetic sensitivity, C = constant and equals to 1.5, L= lengthly and equal to 1 cm, R= sample tube reading, m= wt. of sample with tube – wt. of empty tube, R_0 = empty sample tube reading.

Table 15: Analytical results of magnetic balance of prepared f complex.

R_0	R	Wt. of tube + sample in gm	Wt. of empty tube In gm
Zero	40	1.7658	1.7030

j. The antibacterial activity:

The copper hydrazone complex has a good antibacterial activity [26, 27]. This is due to complex inhibition of bacteria active sites and to complex distribution of bacteria respiratory system. In general

this antibacterial activity of compounds is due to bacteria cell wall structure which has vital rule in its survival [28, 29].

The activity of the copper complex can be understood according to coordination concept and electrons overlap between metal ion and ligand. This electronic delocalization process of chelate ring leads to increase lipophilicity of the complex. As a result of increased permeability, the cell barrier will breakdown [30]. The inhibition zone was expressed in mm for 500 ppm of complex.

Table 16: antibacterial activity of complex.

Staphylococcus aureus	Bacillus Subtilis	E. coli
-	11	12

k- Anticorrosion activity:

It is essential for any inhibition molecule to possess atoms which can act as nucleophile centers (such as nitrogen or oxygen) to enter in bond formation by interaction with metal ions which represent electrons seeker in protection metal surface from corrosion by chemisorption [31].

As a result of inhibitor's characteristics above, Schiff bases and their complexes are expected to be good corrosion inhibitors.

The rate of mild steel corrosion was evaluated using the equation (1) below [32]:

$$W = \Delta m / S t \dots \dots \dots (1)$$

W is corrosion rate, Δm is the change in steel mass as a result of corrosion in (mg), S is the surface area in (cm²), and t is the time of immersion period in (hrs). By repeating the experiment two times and using the mean values, the inhibition efficiency percent (% IE) was determined using the equation (2) [31]:

$$\% \text{ IE} = \frac{W_0 - W_i}{W_0} \times 100 \dots \dots \dots (2)$$

Where W_0 and W_i are the weight losses in blank (uninhibited) and inhibited corroding solutions respectively.

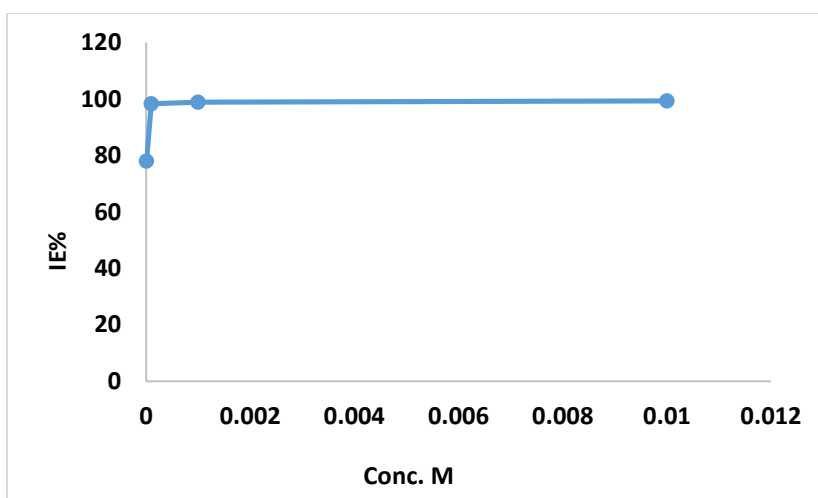


Figure 23: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 25Co in 0.1M HCl containing different concentrations of complex.

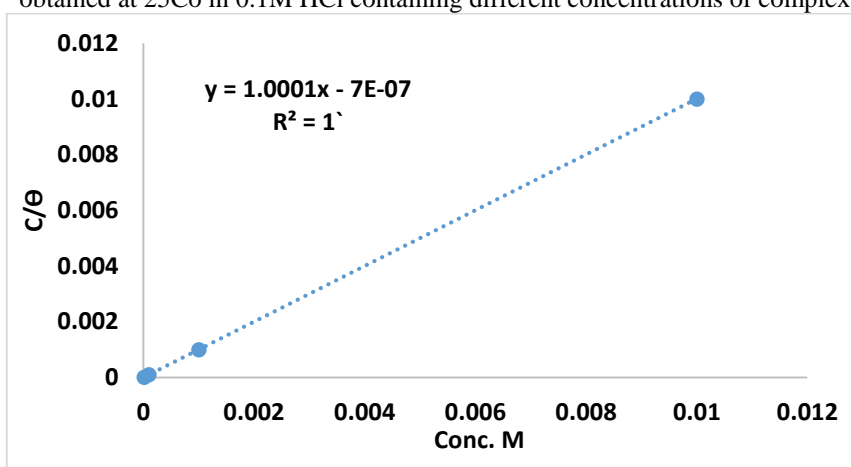


Figure 24: Langmuir adsorption isotherm plot for mild steel in 0.1M HCl solution in the presence of various concentrations of inhibitor (complex).

In order to plot the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the inhibitor in 1M HCl was achieved from weight loss measurements ($\theta = E (\%)/100$) at 25Co and tested with Langmuir isotherm relationship (3) [33]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \dots\dots\dots (3)$$

Where C is the concentration in M, K_{ads} is the equilibrium constant of the adsorption process.

K_{ads} values can be calculated from the intercepts of the straight line in figure (21). According to equation (4), Gibbs free energy of adsorption process (ΔG_{ads}) can be calculated: [34].

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \dots\dots\dots (4)$$

Where R is the gas constant (8.314 J/mol); T is the absolute temperature (K) and 55.5 is the water molar concentration. The determined $\Delta G_{ads} = -33.94$

$\text{kJ}\cdot\text{mol}^{-1}$, its negative sign is reflected the spontaneity of adsorption process [35] and its value is referred to physisorption and chemisorption participation in inhibitor work [36, 37].

3.8-The proposed structure of the complex

The suggested structure of complex is $[\text{CuL}_2]\text{SO}_4$ which in ligand is bonded to copper ion through azomethine nitrogen with high electronic density and heterocyclic secondary nitrogen. The proofs which are enriched this suggestion are:

- 1- White turbid solution was immediately resulted from reaction of 2-(4-biphenyl) imidazo[1,2-*b*]pyrimidine with copper ion, this is an evidence that two secondary heterocyclic nitrogen atoms are not the bonding atoms in greenish yellow clear solution of our complex.
- 2- No way for tertiary heterocyclic nitrogen atom to coordinate with ion.

- 3- azomethine group (1st coordinated center) has high electronic density, so it is more able to coordinate with copper ion.
- 4- Both of two secondary hetrocyclic nitrogen atoms have ability to coordinate with copper ion, but one of them is done.
- 5- Sulfate group is ionic bonded in complex structure (out of coordination core), and changing the conductivity of the ligand from zero μs to respected value of complex is conclusive evidence of suggested structure.

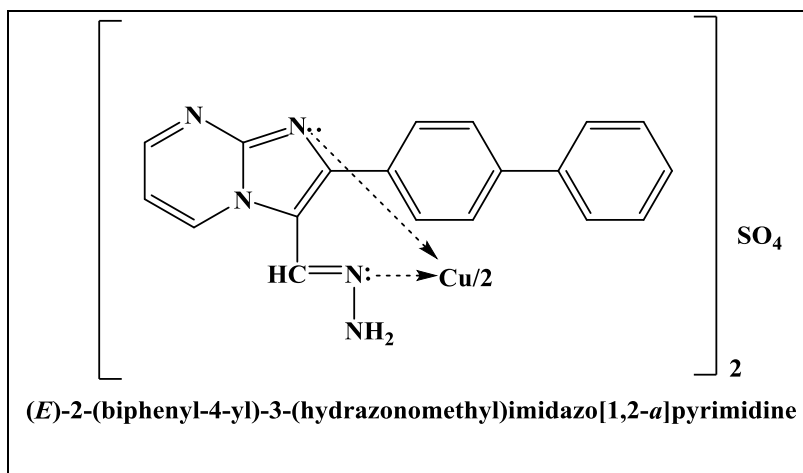


Figure 25: suggested structure of [Cu(BIPH)₂]SO₄.

Conclusion:

The proposed method has many advantages such as: Complexion reagent is inexpensive, available, and can be prepared in any scale with high purity.

There is no need to pretreatment step to increase analyte concentration, because suggested method is valid for broad range of concentrations in different samples.

Other analyses such as elemental analysis, mass spectroscopy are necessary to implement on complex to be ensure of its structure, also to open new windows on other applications of complex.

It will be good goal to look for another analytical technique which should be more economic and suitable for routine, daily analysis of different samples.

References:

- [1] B. Narasimhan, P. Kumar, and D. Sharma, "Biological activities of hydrazide derivatives in the new millennium," *Acta Pharmaceutica Scientia*, vol. 52, 2010.
- [2] V. R. de Souza, G. S. Nunes, R. C. Rocha, and H. E. Toma, "Spectroscopy, electrochemistry and catalytic properties of rutheniumII complexes containing the tetradentate Schiff base ligand N, N'-bis (7-methyl-2-pyridylmethylene)-1, 3-diiminopropane," *Inorganica chimica acta*, vol. 348, pp. 50-56, 2003.
- [3] S. Q Memon, N. Memon, A. Mallah, R. Soomro, and M. Y Khuhawar, "Schiff bases as chelating reagents for metal ions analysis," *Current Analytical Chemistry*, vol. 10, pp. 393-417, 2014.
- [4] M. García-Vargas, S. Trevilla, and M. Milla, "Synthesis and characterization of 1, 2-cyclohexanedione bis-benzoyl-hydrazone and its application to the determination of Ti in minerals and rocks," *Talanta*, vol. 33, pp. 209-214, 1986.
- [5] E. B. Sandell and H. Onishi, "Colorimetric determination of traces of metals. Part 1: photometric determination of traces of metals; general aspects," 1978.
- [6] S. Kumar, D. N. Dhar, and P. Saxena, "Applications of metal complexes of Schiff bases- A review," 2009.
- [7] R. Mohapatra, U. Mishra, S. Mishra, A. Mahapatra, and D. Dash, "Synthesis and characterization of transition metal complexes with benzimidazolyl-2-hydrazones of o-anisaldehyde and furfural," *Journal of the Korean Chemical Society*, vol. 55, pp. 926-931, 2011.
- [8] Z. Hussain, M. Khalaf, H. Adil, D. Zageer, F. Hassan, S. Mohammed, et al., "Metal Complexes of Schiff's Bases Containing Sulfonamides Nucleus: A Review," *Research Journal of Pharmaceutical Biological and Chemical Sciences*, vol. 7, pp. 1008-1025, 2016.
- [9] O. Wahba, A. M. Hassan, A. Naser, and A. Hanafi, "Preparation and Spectroscopic Studies of Some Copper and Nickel Schiff Base Complexes and their Applications as Colouring Pigments in Protective Paints Industry," *Egyptian Journal of Chemistry*, vol. 60, pp. 25-40, 2017.
- [10] A. Hassan, B. H. Heakal, A. Younis, M. A. E.-M. Bedair, and M. M. A. Mohamed, "Synthesis of some triazole Schiff base derivatives and their metal complexes under microwave irradiation and

- evaluation of their corrosion inhibition and biological activity," *Egyptian Journal of Chemistry*, vol. 62, pp. 1603-1624, 2019.
- [11] A. R. Kocharekar and N. Thakkar, "Extractive spectrophotometric determination of copper (II) and its applications in pharmaceutical samples and alloys," 2004.
- [12] B. Ashish, K. Neeti, and K. Himanshu, "Copper toxicity: a comprehensive study," *Res J Recent Sci*, vol. 2, pp. 58-67, 2013.
- [13] K. Babayeva, S. Demir, and M. Andac, "A novel spectrophotometric method for the determination of copper ion by using a salophen ligand, N, N'-disalicylidene-2, 3-diaminopyridine," *Journal of Taibah University for Science*, vol. 11, pp. 808-814, 2017.
- [14] V. Fornea, S. Trupina, A. Vasilica, and L. Bulgariu, "Spectrophotometric determination of Cu (II), Co (II) and Ni (II) ions in mono and multi-component systems," *Bul. Inst. Polit. Iasi*, vol. 62, pp. 9-20, 2016.
- [15] C. Fan, S. Luo, and R. Liu, "Optimization of an analytical method for the spectrophotometric determination of copper in tea and water samples after ultrasonic assisted cloud point extraction using a benzothiazole fluorescein derivative complexing agent," *RSC advances*, vol. 5, pp. 65321-65327, 2015.
- [16] E. Hashem, M. Seleim, and A. El-Zohry, "Spectrophotometric determination of copper (II) in pharmaceutical, biological and water samples by 4-(2'-benzothiazolylazo)-salicylic acid," *Journal of Applied Spectroscopy*, vol. 78, p. 586, 2011.
- [17] N. Al-Lami and A. S. Mahmoud, "Synthesis of some New 3-Substituted Heterocyclic Compounds Containing Bridgehead Nitrogen from 2-Amino Pyridine with Study Their Biological Activity," *Al-Nahrain Journal of Science*, pp. 26-36, 2018.
- [18] V. Devi and V. K. Reddy, "Spectrophotometric determination of iron (II) and cobalt (II) by direct, derivative, and simultaneous methods using 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone," *International journal of analytical chemistry*, vol. 2012, 2012.
- [19] T. Mohamed and S. Atwa, "Spectrophotometric microdetermination of Fe (III) and V (V) using schiff base derived from salicylhydroxamic acid," *Int J Res Stud Biosci*, vol. 1, pp. 8-13, 2013.
- [20] A. Abbas and R. S. Kadhim, "Preparation, spectral and biological studies of azo ligand derived from proline with Cu (II), Ag (I) and Au (III) metal ion," *J. Appl. Chem*, vol. 9, pp. 20-31, 2016.
- [21] M. Barwiolek, R. Szczęśny, and E. Szłyk, "Copper (II) Schiff base complexes and their mixed thin layers with ZnO nanoparticles," *Journal of Chemical Sciences*, vol. 128, pp. 1057-1066, 2016.
- [22] S. Roy, S. Choubey, K. Bhar, S. Khan, P. Mitra, and B. K. Ghosh, "Syntheses, structures, and luminescence behavior of terephthalate bridged lead (II) complexes with tetradentate N-donor Schiff bases," *Journal of Molecular Structure*, vol. 1051, pp. 328-335, 2013.
- [23] B. Hathaway, G. Wilkinson, R. Gillard, and J. McCleverty, "Comprehensive coordination chemistry," The synthesis, reactions, properties and applications of coordination compounds, vol. 5, pp. 533-774, 1987.
- [24] I. P. Ejidike, "Cu (II) complexes of 4-[(1E)-N-{2-[(Z)-benzylidene-amino] ethyl} ethanimidoyl] benzene-1, 3-diol Schiff base: synthesis, spectroscopic, in-vitro antioxidant, antifungal and antibacterial studies," *Molecules*, vol. 23, p. 1581, 2018.
- [25] S. Johnsen, "How to measure color using spectrometers and calibrated photographs," *Journal of Experimental Biology*, vol. 219, pp. 772-778, 2016.
- [26] A. M. Abu-Dief and I. M. Mohamed, "A review on versatile applications of transition metal complexes incorporating Schiff bases," *Beni-suef university journal of basic and applied sciences*, vol. 4, pp. 119-133, 2015.
- [27] Lakshmi Narayana Suvarpu, Young Kyo Seo, Sung Ok Bake, Review on Analytical and Biological Applications of Hydrazones and their Metal Complexes, *E. Journal of Chemistry*, 2012, 9(3), 1288-1304.
- [28] N. Raman, A. Kulandaisamy, A. Shunmugasundaram, and K. Jeyasubramanian, "Synthesis, spectral, redox and antimicrobial activities of Schiff base complexes derived from 1-phenyl-2, 3-dimethyl-4-aminopyrazol-5-one and acetoacetanilide," *Transition Metal Chemistry*, vol. 26, pp. 131-135, 2001.
- [29] N. Raman, S. Johnson Raja, and A. Sakthivel, "Transition metal complexes with Schiff-base ligands: 4-aminoantipyrine based derivatives—a review," *Journal of Coordination Chemistry*, vol. 62, pp. 691-709, 2009.
- [30] A. Çukurovalı, I. Yılmaz, H. Özmen, and M. Ahmedzade, "Cobalt (II), copper (II), nickel (II) and zinc (II) complexes of two novel Schiff base ligands and their antimicrobial activity," *Transition metal chemistry*, vol. 27, pp. 171-176, 2002.
- [31] I. A. Akpan and N.-A. O. Offiong, "Inhibition of mild steel corrosion in hydrochloric acid solution by Ciprofloxacin drug," *International Journal of corrosion*, vol. 2013, 2013.
- [32] E. A. Noor and A. H. Al-Moubaraki, "Corrosion behavior of mild steel in hydrochloric acid

- solutions," *Int. J. Electrochem. Sci.*, vol. 3, pp. 806-818, 2008.
- [33] E. Ebenso, N. Eddy, and A. Odiongenyi, "Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H₂SO₄," *African Journal of Pure and Applied Chemistry*, vol. 2, pp. 107-115, 2008.
- [34] O. Nwosu, E. Osarolube, L. Nnanna, C. Akoma, and T. Chigbu, "Acidic corrosion inhibition of piper guineense seed extract on Al alloy," *American journal of Materials science*, vol. 4, pp. 178-183, 2014.
- [35] S. Refaey, F. Taha, and A. Abd El-Malak, "Inhibition of stainless steel pitting corrosion in acidic medium by 2-mercaptobenzoxazole," *Applied Surface Science*, vol. 236, pp. 175-185, 2004.
- [36] G. Moretti, F. Guidi, and G. Grion, "Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid," *Corrosion science*, vol. 46, pp. 387-403, 2004.
- [37] S. K. Shukla and E. E. Ebenso, "Corrosion inhibition, adsorption behavior and thermodynamic properties of streptomycin on mild steel in hydrochloric acid medium," *Int. J. Electrochem. Sci.*, vol. 6, pp. 3277-3291, 2011.

الخلاصة

حضر مركب 2-(4-فنيل)أيميدازو(1و2)- بيرميدين 3- هيدرازون ليس تخدم ككاشف في تقدير ايون النحاس طيفيا عند اقصى طول موجي في 430 نانومتر. بعد ان حددت الظروف المثلى للتفاعل والمتمثلة بحامضية وسط مقدارها 4 و 8-10 دقائق كوقت ملائم للتفاعل, تم تحضير منحنى المعايرة القياسي والذي اظهر استجابة خطية تتراوح 0,1-1500 جزء بالمليون وحد كشف 0,057 جزء بالمليون. ولأختبار صلاحية الطريقة المقترحة في تقدير محتوى النحاس, فقد طبقت هذه الطريقة على نماذج مختلفة في طبيعتها وتركيز محتوى النحاس فيها كالنماذج الحية من مياه الصنبور, مياه الصرف الصحي, الادرار, ونماذج صناعية كسبائك النحاس 4% و 99% وبأستخدام طريقة الاضافات القياسية. وتراوح الخطأ النسبي لهذه التحاليل (-4.537)-2.071% واستعدادية مقدارها 95,46-102.07%, وقد اثبتت النتائج حساسية عالية لهذه الطريقة لمديات واسعة من تركيز النحاس. وبسبب ثابت الاستقراريه العالي للمعقد الناتج من تفاعل تقدير ايون النحاس (0,25×10⁸) وسهولة تحضيره حيث انه مجرد ترك مزيج محاليل الايون مع الليكاند لعدة ايام وبالأخص عندما يكون مذيب الليكاند مزيج من حجم قليل من داي مثيل فورماميد لضمان جودة الاذابة وحجم اكبر متبقي من الايثانول لسهولة تطايره فنلاحظ انفصال بلورات المعقد بلونها المميز وتوفر امكانية للتنقية كل ذلك ادى الى تحضير المعقد لدراسة بعض خصائصه عن طريق اجراء تحاليل اطياف ماتحت الحمراء, واطياف امتصاص منطقة تحت البنفسجية- المرئية, قياسات الانعكاسية %R, قياسات التوصيلية الكهربائية, وقياسات المسح الالكتروني المجهرى SEM, طيف الاشعة السينية مشتتة الطاقة EDX, القياس الوزني الحراري TG, قياس المغناطيسية وذلك لتعزيز المقترح الخاص بالتركيب المحتمل المعقد.