



An analytical study for spectrophotometric determination of cu (ii)ions in aqueous solutions using 4 hydroxy 3-2 hydroxy phenyl methyl amino benzene sulfonic acid

Dr. Mohammad Maarouf¹, Lama Debany²

¹ Professor, Department of Chemistry, college of sciences, Tishreen University, Latakia, Syria

² Ms. student, Department of Chemistry, college of sciences, Tishreen University, Latakia, Syria

ARTICLE INFO

Published on: 15-03-2016

ISSN: 0975-8216

Keywords:

Hydroxy-3-[(2- hydroxyl phenyl) methylene amino] benzene Sulphonic Acid(II)(HVMAB); simultaneousUV-Visible spectrophotometric determination of copper(II);the maximum value of absorbance ;The stoichiometric composition of complex;the detection limit; molar absorbance coefficient; complex formation constant

Corresponding author:

Dr. Mohammad Maarouf, Professor, Department of Chemistry, college of sciences, Tishreen University, Latakia, Syria

ABSTRACT

The potential formation of a colored complex between Cu^{+2} and Hydroxy-3-[(2- hydroxyl phenyl) methylene amino] benzene Sulphonic Acid(II)(HVMAB) was proposed in the spectrophotometric determination of copper in aqueous solutions. It was found that a greenish yellow colored complex of Cu^{+2} was formed in the presence of the above mentioned reagent in aqueous medium at $\text{pH}=2$. Experimentally, the spectral survey of complex solution with Cu^{+2} revealed that the maximum value of absorbance was found to be corresponded to $\lambda_{\text{max}}=430\text{nm}$ at which all quantitative parameters of the related complex were determined as follows: The stoichiometric composition of complex $\text{Cu:HVMAB}=(1:2)$, molar absorbance coefficient $\varepsilon = 1.25 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and complex formation constant $\beta_K = 1.67 \times 10^4$. Moreover, all factors effecting the complex formation were investigated where Beer Lambert Law was obeyed in the range $(0.2-8)\text{mg/l}$ and the detection limit was 0.006 mg/l . Further, it was found that, when this method was successfully applied to standard copper solutions, the relative standard deviation didn't exceed 3.89% at low concentration of copper. The higher copper concentration the lowest RSD and the highest recovery occurred, viz. at 5mg/l of copper the RSD and the recovery were 0.2% and 100.2% respectively. The minimum recovery was 96.3%.

INTRODUCTION

Copper is one of the most important metals after iron. It has a vital role in many fields either as metal or its salts⁽¹⁾ 75% copper that is extracted is used in the electrical industry, house hold-utensil, alloys and dyes⁽²⁾ Copper

plays a major role during cell respiration. It also takes part in hematopoiesis and in maintenance of vascular and skeletal integrity in addition to the structure and function of the central nervous system⁽³⁾. Copper traces are of the essential nutrients for animals and plants⁽⁴⁾

Copper deficiency causes several diseases such as anemia⁽⁵⁾ hair graying and skin aging that includes wrinkles and sagging⁽⁶⁾. The toxic effects of Copper are instant hypertension, renal failure, bronchitis, growth retard, hepatic fibrosis, Wilson's disease, major systematic denaturation that could promote the potential risk cancer such as skin cancer and collapse of bone skeletal⁽⁷⁾. Copper is considered one of the critical environmental pollutants that results from industrial wastes⁽⁸⁾. It's extremely toxic towards aquatic organisms due to its higher content that exceeds the permitted limit which is 2mg/l⁽⁷⁾. Thus, the detection of copper content using a developed method is considered as a critically urgent issues of pollution research.⁽⁷⁾ The determination of Copper was carried out based on spectrophotometrically measurement of complex that was formed between Cu and 2-hydroxy-1-(2-hydroxy-4-sulpho-1 naphthylazo-)-3-naphthoic acid (HHSNNA) the absorbance was read at 530 nm within linear range (0-15)ppm⁽⁹⁾. Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl)Methylene] (HC22HPM) was used as an extractive reagent in order to spectrophotometrically determine Cu that was analytically extracted. The measurement was done within linear range (0-10) ppm at pH=4.8⁽¹⁰⁾. In another study, Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene]HCHNM was suggested as an extractive reagent for the determination of Cu. This method was successfully applied to synthetic and commercial samples⁽¹¹⁾. Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH) was successfully utilized for the determination of traces of Cu in wine and beer in as well as for the determination of traces of Nickel Ni(II) in food oil⁽¹²⁾. Also, Diethyldithiocarbamate (DDTC) was used for the spectrophotometric measurement of analytically extracted Copper and Zinc. This method was extended to the determination of traces of copper and zinc in many soil, fertilizer, food, aquatic, biological and pharmaceutical samples.⁽¹³⁾ In the present study Hydroxy-3-[(2- hydroxyl phenyl) methylene amino] benzene Sulphonic Acid(II). (HVMAB)⁽¹⁴⁾. A new organic reagent, has been used in the calibration of Copper(II) in its standard aqueous solutions and in environmental samples at minimal competitive detection limits were considered competitive to other studies that used previously mentioned organic reagents. Thus, the aim of this study was to determine the content of Copper in environmental samples using Hydroxy-3-[(2- hydroxyl

phenyl) methylene amino] benzene Sulphonic Acid(II). (HVMAB) by UV-Visible spectrophotometry, to ascertain the optimal conditions under which the complex to be formed between the suggested reagent and Cu²⁺, to determine the linear range within which Cu+2 is quantitatively calibrated, and to find the at minimal competitive detection limits were considered competitive to other studies that used previously mentioned organic reagents. The present study was carried out during 2014-2015 at scientific research lab in college of sciences, Tishreen university

MATERIALS AND METHODS

INSTRUMENTS

Jasco V-503 UV-VIS Spectrophotometer model with Double Beam, Wavelength Range: 190 – 1100 nm, six cell holder, programmable temperature control system for the studied solution within range 20-100° C. the suggested analyses can be monitored through PC provided with a specific software. The findings can be printed via laser printer. pH meter Sartorius pp-50 provided with a glass electrode and temperature sensor py-p11. Analytical balance Sartorius Ed2245 Germany, ensures measuring accuracy of 0.0001. Double-Distillation Apparatus.

REAGENTS AND STANDARD SOLUTIONS.

All chemicals used in this study were pure:

- Hydroxy-3-[(2- hydroxyl phenyl) methylene amino] benzene Sulphonic Acid(II). (HVMAB), previously prepared, provides yield of 80%.
- Acetone 99.5%, propanol -1 95%, 1,4-Dioxane 98%, Ethanol 98%, Methanol 99.9%, Acetonitrile 99.6%, Dimethylsulfoxide.
- Hydroxide sodium 99.5%, Copper(II) chloride CuCl₂.2H₂O, hydrochloric acid (HCl)

37%, Acetic acid (CH_3COOH) 99.5%,
Phosphoric acid (H_3PO_4) 85%, Boric acid
 H_3BO_3 (99.5%), Ammonium Acetate,
Dipotassium phosphate (K_2HPO_4)

- Standard solutions prepared from Chlorides of several metals such as Fe, Zn, Cd, Pb, Mn, Ni, Ca, Al, Ba, Co, at a concentration of 1/100 mg/l

RESULTS AND DISCUSSION:

Formation of the Cu(II)-HVMAB complex.

The Formation of the Cu(II)-HVMAB complex took place in aqueous medium and in the presence of different buffer solutions of Britton–Robinson, Acetate and phosphate at different pH degrees. While the Fe ion containing solution color turned to greenish yellow, the blank solution remained pale yellow. Spectral surveying, a unique absorbance peak was detected with low sensitivity within UV-Vis field at $\lambda_{\text{max}} = 430 \text{ nm}$. The best buffer was to be found Britton Robinson RRB at pH=2 and in volume of 1 ml. as shown in Fig 1.

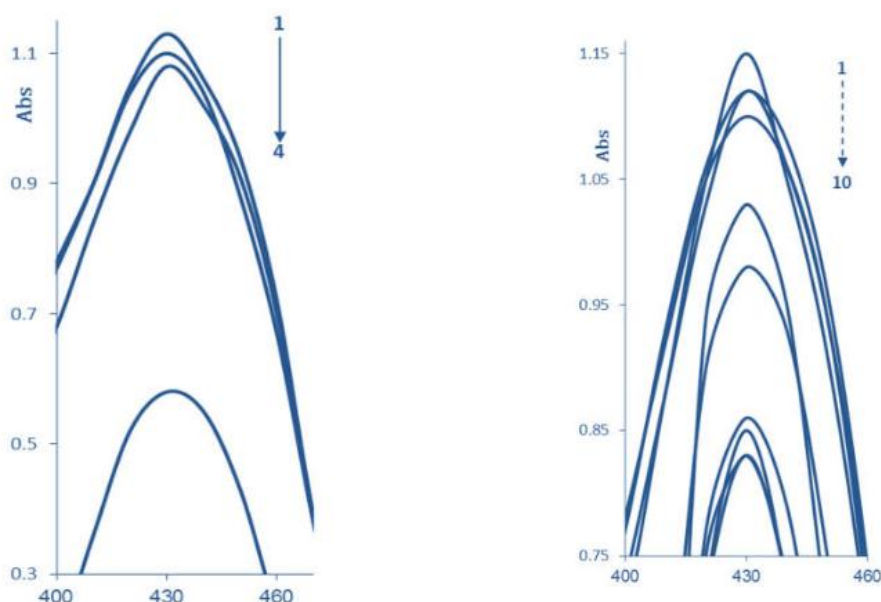


Fig 1

a-Cu(II)-HVMAB complex Spectral surveying at different pH degrees in absence and in presence of several buffer solutions such as Britton–Robinson, Acetate and phosphate

b-Cu(II)-HVMAB complex Spectral surveying in the presence of Britton–Robinson at different pH degrees accordingly, (pH): 1(2), 2(5), 3(6), 4(4), 5(9), 6(7), 7(11), 8(10), 9(8), 10(12)

$\lambda_{\text{max}} = 430 \text{ nm}$, $[\text{HVMAB}] = 7.8125 \times 10^{-4} \text{ M}$, $[\text{Cu}] = 7.8125 \times 10^{-5} \text{ M}$

Effect of reagent concentration on the absorbency of the studied complex

The effect of reagent concentration on Cu-HVMAB complex was studied by varying the reagent concentration between $(0.2344 - 4.6872) \times 10^{-4} \text{ M}$ and by two concentrations of Copper $1.1718 \times 10^{-5} \text{ M}$, 7.8125

$\times 10^{-5} \text{ M}$ at pH=2. The flask containing the solution was left at lab temperature for 20 minutes. Then the total volume was made up to the final mark of the flask with double distilled water. It was noticed that the detected absorbance values of all prepared solutions vary in accordance with the added reagent concentration Fig 2 where it shows that absorbance values proportionally

increase with excess of the reagent. The max values of absorbance were recorded at reagent concentrations of $9.3744 \times 10^{-5} \text{M}$ and $15.624 \times 10^{-5} \text{M}$ and at Cu concentrations of $1.1718 \times 10^{-5} \text{M}$, $7.8125 \times 10^{-5} \text{M}$. But the

absorbance value remained constant for a greater excess of reagent and for the two studied concentrations of Copper.

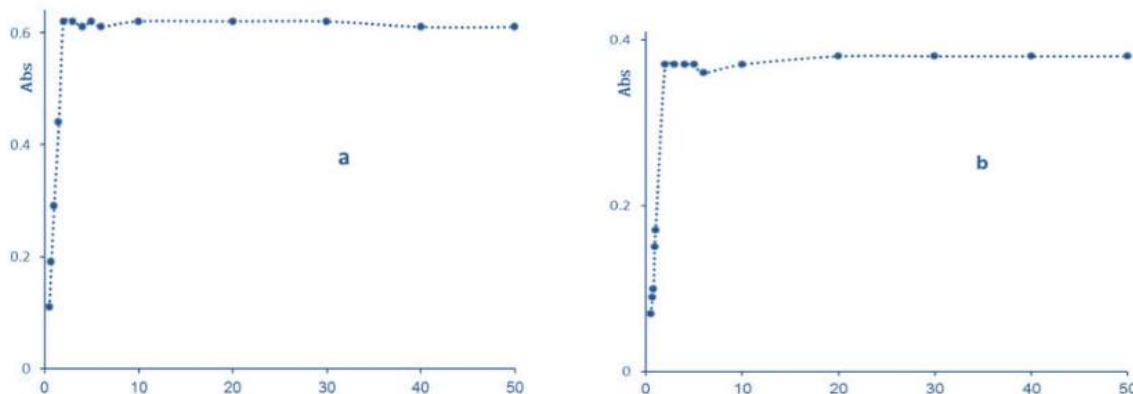


Fig2

a- The absorbance is proportional to reagent concentration at $[\text{Cu}] = 7.8125 \times 10^{-5} \text{M}$

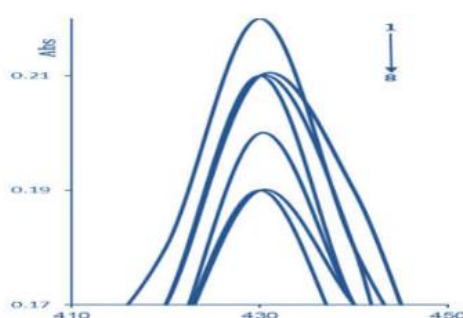
b- The absorbance is proportional to reagent concentration at $[\text{Cu}] = 1.1718 \times 10^{-5} \text{M}$

$\text{pH} = 2$, $\lambda_{\text{max}} = 430 \text{nm}$

Effect of water miscible organic solvents on the absorbency of the studied complex

Seven water miscible organic solvents of Methanol, Ethanol, Acetone, Acetonitrile, Propanol-1, 4-1 Dioxane, and Dimethylsulfoxide were used as follows : seven 25 ml flasks were filled with Cu^{+2} solutions, BRB at $\text{pH}=2$, and the suggested reagent. The flasks were left at lab temperature for five minutes. Further, excessive

volumes of the seven solvent were separately added. . Then the total volume was made up to the final mark of the flask with double distilled water. It was noticed that the detected absorbance values of complex with copper(II) ion were negatively influenced by the absence of water miscible organic solvent Fig 3. Thus, in this research work it was found that utilizing aqueous medium without any addition of organic solvent to reaction mixture was suggested.



Complex spectral surveying in absence and in presence of different solvents accordingly, Methanol, Ethanol, Acetone, Acetonitrile, Propanol-1, 4-1 Dioxane

$\lambda_{\text{max}} = 430 \text{ nm}$, $\text{pH}=2$, $[\text{HVMAB}] = 3.125 \times 10^{-4} \text{M}$, $[\text{Cu}] = 1.5625 \times 10^{-5} \text{M}$

The effect of the interfering ions

The effect of many foreign ions on the complex formation was studied at the optimal conditions. It was found that some diverse ions interfere in the complex

formation at a molar concentration equals to that of the studied ion, some ions only interfere at a concentration 4times higher. However a number of ions(anions and

cations) such as Na^+ , K^+ , HPO_4^- , CH_3COO^- , Cl^- , B^+ , PO_4^{3-} , NH_4^+ don't interfere in the complex formation. Table 2

Table 1 masking and foreign ions effecting the formation of complex

$[\text{Cu}] = 7.8125 \times 10^{-5} \text{ M}$, $[\text{HVMAB}] = 2.5 \times 10^{-4} \text{ M}$, $\lambda_{\text{max}} = 430 \text{ nm}$, $\text{pH} = 2$

Masking ions	Foreign ions			
	1 : 1	1 : 2	1 : 4	1 : 8
Na^+ , K^+ , HPO_4^- , CH_3COO^- , Cl^- , B^+ , PO_4^{3-} , NH_4^+	Zr^{2+} , NO_3^-	Cd^{2+}	Mn^{2+} , Pb^{2+} , Ba^{2+} , Al^{3+}	Ca^{2+} , Co^{2+} , Ni^{2+} , Ba^{2+}

Tab3 reveals the analysis findings for empirical samples which were prepared of standard copper solutions with different concentrations. This asserts the potential of the developed methods for analytical purposes. Besides the relative standard deviation

didn't exceed 3.89% at low concentration of copper. The higher copper concentration the lowest RSD and the highest recovery occurred, viz. at 5mg/l of copper the RSD and the recovery were 0.2% and 100.2% respectively. The minimum recovery was 96.3%.

Table 2 the analysis findings for empirical samples

The given concentrationmg/l	Determined concentrationmg/l $\bar{X} \pm X$	RSD%	Recovery %
0.80	0.77 ± 0.08	3.89	96.3
1.00	0.98 ± 0.05	2.04	98
1.50	1.48 ± 0.05	1.35	98.7
2.00	2 ± 0.05	1	100
2.50	2.49 ± 0.05	0.8	99.6
3.00	3 ± 0.03	0.33	100
4.00	3.99 ± 0.03	0.25	99.8
5.00	5.01 ± 0.03	0.20	100.2

Gradient additions of reagent to form Cu-HVMAB complex

Optimized the complex formation conditions of lab temperature , medium free of any organic solvent and with maximum value of absorbance, the validated gradient additions of reagent to form Cu- HVMAB complex was found to be as follows: reagent, buffer. Then the total volume was made up to the final mark of the flask with double distilled water.

Calculation of molar ratio of the formed complex

Continuous variation method (isomolar method)⁽¹⁵⁾

This method is based on varying the molar absorbance of the complex measured at max wave length and of series of the solutions of the studied complex where metal ion and reagent variedfor constant total concentration . The graph was constructed by plotting the absorbance against mole fraction.

$$A = \frac{[\text{Cu}]}{[\text{Cu}] + [\text{HVMAB}]}$$

Max peaks were obtained at mole fractions that were proportional to stoichiometric ratio of the formed complexes. Figure 4-a_{1,2} reveals the variation of molar UV-VIS absorbance of the formed complex indexed by the mole fraction of Cu ion. It's also noted from the mentioned figure that the curve shows a single

refraction point at mole fraction= 0.3 against both studied concentrations of Copper. Thus the stoichiometric ratio of the formed complex was (1:2) and the formula of the formed complex was Cu(HVMAB)₂.

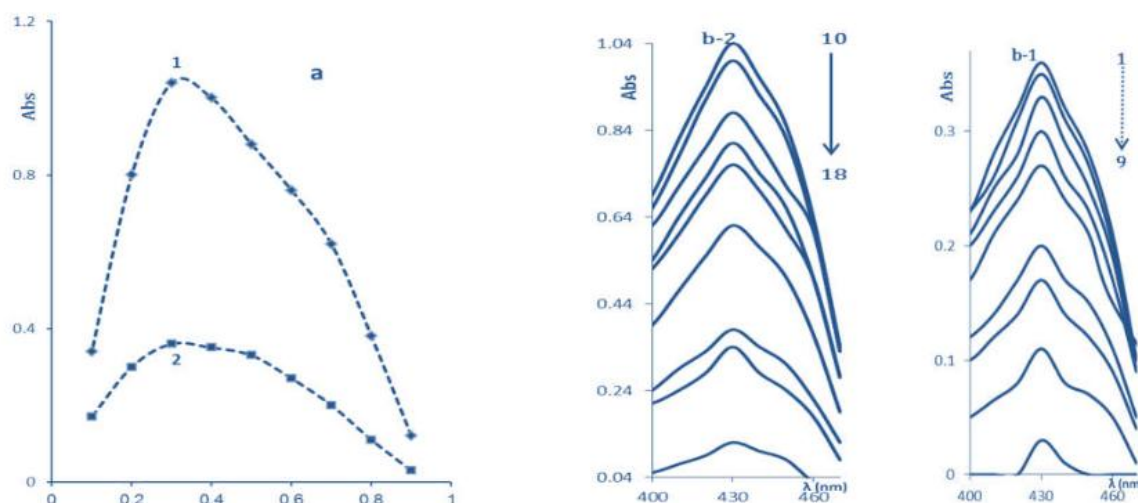


Fig4 a_{1,2} - the variation of molar UV-VIS absorbance of the formed complex indexed by the mole fraction of Cu ion. b_{1,2}-complex spectral surveying at different the mole fractions of Cu ion

$$\frac{[Cu]}{[Cu] + [HVMAB]}$$

:0.3(1), 0.4(2), 0.5(3), 0.2(4), 0.6(5), 0.7(6), 0.1(7), 0.8(8), 0.9(9), 0.3(10),

0.4(11), 0.5(12), 0.2(13), 0.6(14), 0.7(15), 0.8(16), 0.1(17), 0.9(18), $\lambda_{max} = 430nm$

Molar ratio method

This method is based on considering constant concentration of metal ion, varying reagent concentration. Then the molar absorbance of all solutions was measured at $\lambda_{max} = 430nm$

Absorbance calculated from the graph constructed by the formula against both studied concentrations of Copper ion as shown in Fig 5-a_{1,2}:

$$A = f \cdot \frac{[L]}{[M]}$$

It's noted from figure 5-a_{1,2} that both curves showed a single refraction point corresponding to mole ratio 1:2. Thus the formula of the formed complex was Cu(HVMAB)₂. Also, Figure 5-b_{1,2} reveals the spectra of the formed complex at different mole ratios against both studied copper concentrations.

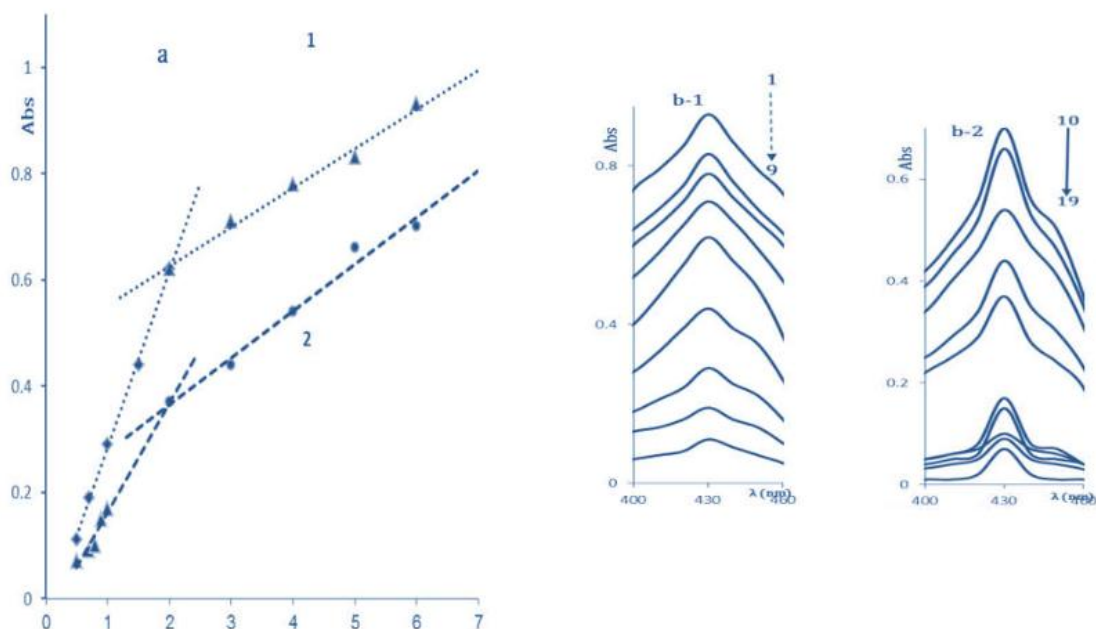


Fig 5:

- a- variation of the molar absorbance of the formed complex indexed by the mole ratio (1) $CCu = 4.6875 \times 10^{-5} M$, (2) $CCu = 7.8125 \times 10^{-5} M$
- b- the spectral surveying of the formed complex at different mole ratios $[HVMAB]/[Cu]$: 1(6), 2(5), 3(4), 4(3), 5(2), 6(1.5), 7(1), 8(0.7), 9(0.5), 10(6), 11(5), 12(4), 13(3), 14(2), 15(1), 16(0.9), 17(0.8), 18(0.7), 19(0.5), $\lambda_{max} = 430 nm$

Graphical calculation of molar absorbance coefficients of complex's formation constant β_K

Molar absorbance coefficient ϵ and stability constant of complex β_K were graphically calculated based on the formula

$$\frac{C_{Cu}}{A} = \frac{1}{\epsilon} + \frac{1}{\epsilon \beta_K (C_{HVMAB} - \frac{A}{\epsilon})} \quad (1)$$

It represents a linear equation of straight slope that crosses axis Y at a point of $\frac{1}{\epsilon}$ with a tangency of $\frac{1}{\epsilon \beta_K}$

For this purpose gradients of Fe (HVMAB) complex were prepared at optimal conditions, the absorbance was measured and the concentrations were calibrated by the equations:

$$\frac{C_{Cu}}{A} = \frac{1}{C_{HVMAB}}$$

Computerized plotting the corresponding values of $\frac{C_{Cu}}{A}$ and $\frac{1}{C_{HVMAB}}$ that were obtained by the method of least squares a straight line was given and it obeyed the equation $R^2 = 0.99, Y = 8.3 \times 10^{-9} X + 7.37 \times 10^{-5}$ where $\frac{1}{\epsilon} = 7.37 \times 10^{-5} \Rightarrow \epsilon = 1.36 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$

Based on the given value of ϵ the relation 1 was recalculated. Computerized plotting the relation $\frac{C_{Cu}}{A}$ indexed by $C_{HVMAB} - \frac{A}{\epsilon}$ using the method of least squares. A straight line was obtained and it obeyed the equation $R^2 = 0.99, Y = 5.2 \times 10^{-9} X + 7.95 \times 10^{-5}$ where $\frac{1}{\epsilon} = 7.95 \times 10^{-5} \Rightarrow \epsilon = 1.26 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$

This resulted value was too close to the previous one and the slope of the straight line (the analytical curve) was given by the following equation:

$$\frac{1}{\epsilon \cdot \beta_K} = 5.2 \times 10^{-9} \Rightarrow \beta_K = 1.52 \times 10^4$$

In purpose of assertion, β_K were recalculated saturation curve taking into consideration the balance concentration of the complex C_{eq} that given by the following relation

$$C_{eq} = C_{Cu} \cdot \frac{A}{A_{max}} \quad 2$$

Where

C_{eq} : Complex balance concentration

C_{Cu} : Copper concentration

A : Absorbance recorded at each point of saturation threshold

A_{max} : Maximum absorbance recorded at saturation threshold

The graph was plotted by the relation 2 in a new coordinate system

$$\frac{C_{Cu}}{A} \quad , \quad \frac{1}{C_{HVMAB} - C_{eq}}$$

A straight line was obtained its equation is $R^2 = 0.99, Y = 4.5 \times 10^{-9} X + 8.13 \times 10^{-5}$. It was noted that ϵ value remained constant $\epsilon = 1.23 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and approximately matched the previous one. Also, the slope of the new straight line was

$$\frac{1}{\epsilon \cdot \beta_K} = 4.5 \times 10^{-9} \Rightarrow \beta_K = 1.67 \times 10^4$$

and too close to the previous value. Thus all obtained findings matched those of reference methods that were used in the calculation of ϵ and β_K of the formed complex. It's obvious from the Table 1 the data that were used to calculate the values of ϵ and β_K accordingly

Table 3 calculation of values of β_K and ϵ based on the given data

A	$C_{HVMAB} \times 10^{-4} \text{ M}$	$\frac{1}{C_{HVMAB}}$	$\times 10^{-3} \text{ M}$	$\frac{C_{Cu}}{A}$	$\times 10^{-5} \text{ M}$	$\frac{1}{C_{HVMAB} - \frac{A}{\epsilon}}$	$\times 10^{-3}$	$\frac{1}{C_{HVMAB} - C_{eq}}$	$\times 10^{-4}$
10.2116	9.0375	12.601		6.4004		1.5624		0.62	
5.9691	5.4897	11.003		4.2669		2.3436		0.71	
4.1831	3.9196	10.016		3.2002		3.1248		0.78	
3.2002	3.0343	9.4127		2.5602		3.906		0.83	

Calibration curve method for the determination of Copper content using the reagent HVMA B

In purpose of spectrophotometric determination of Fe using the reagent HVMA B, linear Copper concentration range was determined where Beer Lambert Law was obeyed taking into consideration the optimal conditions that were set previously for the formation of HVMA B Cu II complex. Fig (a-6) shows the best straight line was obtained using Least squares Method. Beer Lambert Law was obeyed in the range (0.2-8)mg/l and the correspondent molar concentration range $(0.3125 - 12.5) \times 10^{-5}$ M, where the straight line

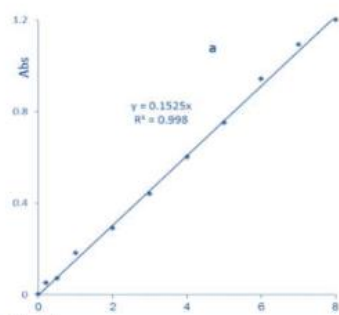
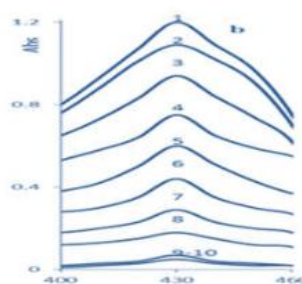


Fig6

a-linear relationship between complex molar absorptivity and copper concentration at pH=2

b-complex spectral surveying at increased concentrations of copper



C_{Cu} , mg/l : 1(8), 2(7), 3(6), 4(5), 5(4), 6(3), 7(2), 8(1), 9(0.5), 10(0.2)
 $\lambda_{max} = 430\text{nm}$, pH = 2, [HVMA B] = 2.5×10^{-4} M

CONCLUSIONS

Hydroxy-3-[(2- hydroxyl phenyl) methylene amino] benzene Sulphonic Acid(II) (HVMA B) was successfully used in the spectrophotometric determination of Cu(II) at the studied optimal conditions for the complex formation. The following conclusions were reached:

1. Greenish yellow complex was formed between the organic reagent HVMA B and the studied ion Cu^{+2} in aqueous medium at ratio ($C_{Cu:HVMAB} = 1:2$), pH=2, and lab temperature. The maximum value of

absorbance was found to be corresponded to $\lambda_{max} = 430\text{nm}$. The correlation coefficient was found to be $R^2 = 0.998$ and higher than 0.99 this finding suggests an excellent linear relationship between absorptive and concentration, asserts the correlation between absorbance and concentration where Beer Lambert Law was obeyed to a great extent within the adopted range in this study

2. Linear range was given between $(0.3125 - 12.5) \times 10^{-5}$ M, the best values for the slope and correlation coefficient were 0.1525 and 0.998 respectively.
3. The molar absorption coefficient was found to be $\epsilon = 1.25 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$, while complex formation constant was $\beta_K = 1.67 \times 10^4$ at detection limit of 0.006 mg/l
4. The reagent that was used in this study is recommended to be utilized in the determination of other transitional metals and in studying the

potential of its selectivity through adding some of the functional groups to its structure.

ACKNOWLEDGMENT

The authors acknowledge the help of Tishreen university and college of science for the financial and technical support.

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