Area under curve and zero order spectrophotometric determination copper complexation with *N,N'*-cyclohexane-l,2-diylidene-bis(4-methaxybenzoythydrazide)

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طريقة المساحة تحت المنحني والترتيب الصفري لتقدير النحاس باستخدام التعقيد مع ن, ن- سايكلوهيكسان-1,2-دايلادين-ثنائي(4-ميثاكسي بنزويثايدرازايد) (CHMBH)

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الملخص

في هذه الدراسة طريقتان طيفيتان بسيطتان استخدمت لتقدير ايون النحاس وذالك بتعقيده مع الليكند (CHMBH)، تم تقدير النحاس بتطبيق طريقة المساحة تحت المنحني والترتيب الصفري عند الطول الموجي 415 نانومتر، بلغت الخطية لكلا الطريقيتين 24-4 مغم/ لتر, حد الكشف وحد الكمية بلغت 0.00338 و 0.01025 مغم/ لتر لطريقة المساحة تحت المنحني وبلغت 0.1677 و 0.508 مغم/ لتر لطريقة الترتيب الصفري بالتعاقب. وكانت الدقة عالية لكلا الطريقتين وبلغت % 99.356 لطريقة المساحة تحت المنحني و100.087% لطريقة الترتيب الصفري.

الكلمات المفتاحية: ايون النحاس، CHMBH، المساحة تحت المنحني، الترتيب الصفري، طريقة فاراغاس.

Abstract

This paper describes the development of a spectrophotometric for the determination of copper by coupling with ligand (CHMBH). The a maximum absorption at (415nm) .Beer's Lambert law is obeyed over the concentration (4-24 mg/L) limit of detection and limit of quantitation were found to be 0.00338 mg/L and 0.01025 mg/L for the area under curve and 0.1677 mg/L and 0.508 mg/L for zero order method, the high accuracy of both methods was 99.356 % for the area under curve method and 100.087 % for the zero order method respectively. Both methods have applied successfully to determination of copper with (CHMBH).

Keywords: Cu(ll), (CHMBH), (AUC), zero order.

1. Introduction

Copper is a heavy metal and plays an important role in biological systems. Copper has an essential micronutrient in some biological processes, and hemoglobin molecules. On the other hand, cooper is toxic above a certain concentration [1,2]. Many methods were used to determination copper such as colorimetric [3, 4], sensors [5,6], electrochemical [7-10], graphite furnace atomic [11], spectrophotometric [12,13], and liquid–liquid microextraction [14]. Solvent extraction method coupled with ICP-OES [15], and determination of serum copper using ICP technique [16]. Most of the methods are expensive or low selectivity and sensitivity. However, spectrophotometric, and derivative spectrophotometric are simple, low cost and environmentally friendly because does not request extraction using organic solvent and have extolled accuracy and precision. This current study a novel modest high sensitivity, low expensive spectrophotometric methods are determination of Cu (II) ion by complexion with the ligand CHMBH figure 1.

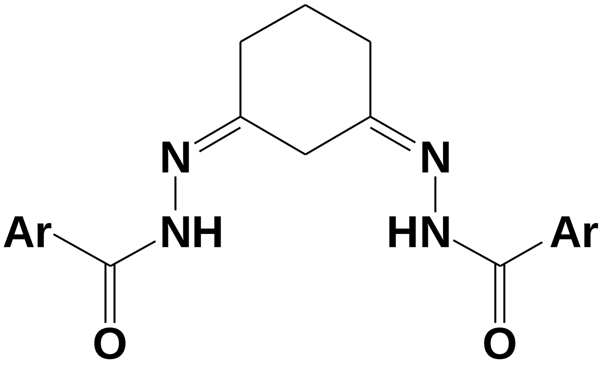


Figure 1: The structure of the ligand *N*,*N'*-cyclohexane-l,2-diylidene-bis(4-methaxybenzoythydrazide) (CHMBH).

2. Experimental Apparatus

UV-Vis spectrophotometer (VARIAN UV-visible) with 1cm path quartz cells with software program.

3. Chemicals and solutions

3.1 Preparation of the ligand

N,*N'*-cyclohexane-l,2-diylidene-bis(4-methaxybenzoythydrazide) (CHMBH) (M.Wt = 408 gm/mol) is the ligand which had prepared as the same in paper [17], 100 mg/L from the ligand CHMBH was prepared by dissolved 0.025 gm with the solvent Acetonitrile and complete the volume to 250 mL with the same volume. Then, 20 mg/L was prepared by transferred 5 ml from 100 mg/L the ligand CHMBH and complete the volume to 25 mL with the Acetonitrile.

3.2 Preparation of cooper (II) solution

$Cu(NO_3)_2.2.5\ H_2O$ standard solution was made by dissolved 0.01 gm from $Cu(NO_3)_2.2.5\ H_2O$ (sigma-aldrich) (M .Wt =232.59 gm/mol) in acetonitrile and complete the volume to 100 mL with the same solvent to obtain concentration equal to 100 mg/L.

3.3 Preparation of hydrochloric acid solution

0.1 N solution of HCl was prepared by diluting of (1.54 mL) of HCl conc. which have (37 % wt/wt) with deionized water into (250 mL) in a volumetric flask.

3.4 preparation of sodium hydroxide solution

Sodium hydroxide (0.4 gm) was dissolved in distilled water. and diluted to (100 mL) in a volumetric flask with the same solvent.

3.5 Calibration graph

Calibration graph was made by transferring 5 mL of (100 mg/L) CHMBH into a series of 25 mL volumetric flask, after that to every flask, (1, 2, 3, 4, 5, and 6 mL) from of 100 mg/L $Cu(NO_3)_2.2.5\ H_2O$ was transferred to produce concentration equal to (4, 8, 12, 16, 20, and 24 mg/L). Then, the volume was completed to mark with the acetonitrile solvent, the absorbance was recorded at 415 nm against acetonitrile as a blank.

3.6 Job's method

Job's method preparation**:** (0.2, 0.4, 0.5, 0.6, and 0.8 mL) from the 20 mg/L of the ligand CHMBH was transferred to the series of 20 mL of volumetric flask, and then added to each flask (0.8, 0.6, 0.5, 0.4, and 0.2 mL) of 20 mg/L (0.0000859 mol/L) $Cu(NO_3)_2.2.5\ H_2O$ and complete the volume to 20 mL with acetonitrile solvent.

4. Results and discission

4.1 The influence of pH

The practical pH capability determination of Cu(II) was considered and tested for many which ranges of pH we are prepared. pH 6.5 was used to maintain the optimum pH solution. This pH provides the highest absorbance value maintaining the other states permanent the pH values were varied in the capability 2-9, as display in figure 2 the inherent characteristic of the spectral curves continued nearly lower at pH 7-10. A pH of 6.5 was at randomly chosen for complete color litigation were carried out at pH 6.5.

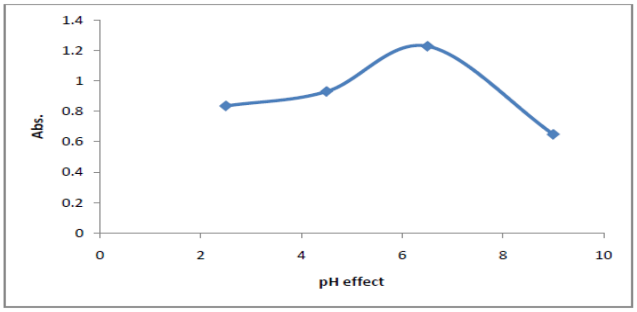


Figure 2: The influence of pH on the Cu(II)- CHMBH complex, 5mL of (100 mg/L) Cu(II), 5 mL of (100mg/L) CHMBH and 1 mL of (0.1 N) HCl or (0.1N) NaOH , at wavelength 415 nm.

4.2 The influence of the volume of the ligand

The influence of variety volumes 1-9 mL of the ligand on the absorbance of the consequential complex has been considered in figure 3. display 5 mL of (100 mg/L) CHMBH solution the best possible and it is advised for later attempts.

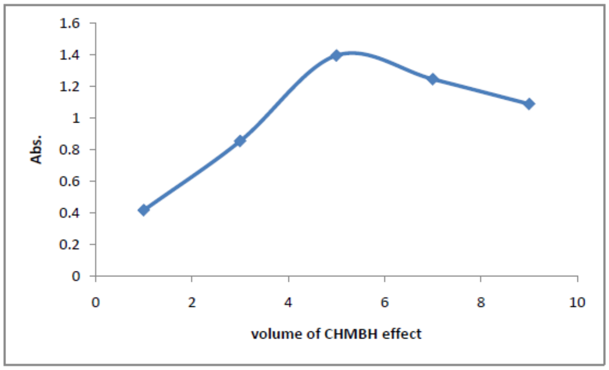


Figure 3: The influence of ligand volume on the Cu(II)- CHMBH complex, 5mL of (100mg/L) Cu(II), (1-9) mL of (100 mg/L) CHMBH at wavelength 415 nm.

4.3 The influence of the volume of metal

When the different volume of the Cu(II) metal ion was added to an affixed quantity of ligand CHMBH to continue to be the complexation is stable 5 mL of (100 mg/L) Cu(II) was provided with the best possible value as is illustrated in figure 4.

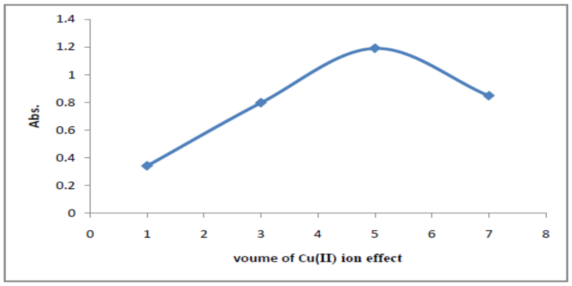


Figure 4: The influence of metal volume on the Cu(II)- CHMBH complex, (1-7) mL of (100mg/L) Cu(II), 5 mL of (100 mg/L) CHMBH at wavelength 415 nm.

4.4 Absorbance spectra

The complex of Cu(II)-GMBH which display a maximum peak at 415 nm against CH3CN as a reagent blank in figure 5.

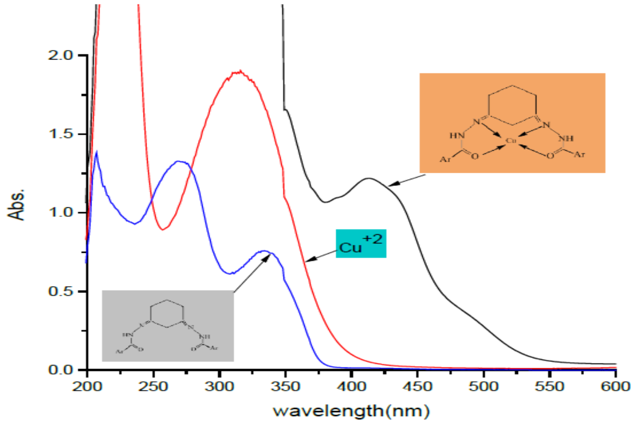


Figure 5: Absorption spectra of (20 mg/L) of Cu(II), (100 mg/L) of the ligand CHMBH and complex contained from (5 mL of 100 mg/L) of Cu(II) with (5 mL of 100 mg/L) of the ligand CHMBH at pH 6.5 against Acetonitrile as a reagent blank.

The structure of the Cu(II)-CHMBH complex was an investigation by jobs method, the stoichiometry of the Cu(II)-CHMBH complex in figure 6 that shown 1:1 Cu(II) to the ligand CHMBH.

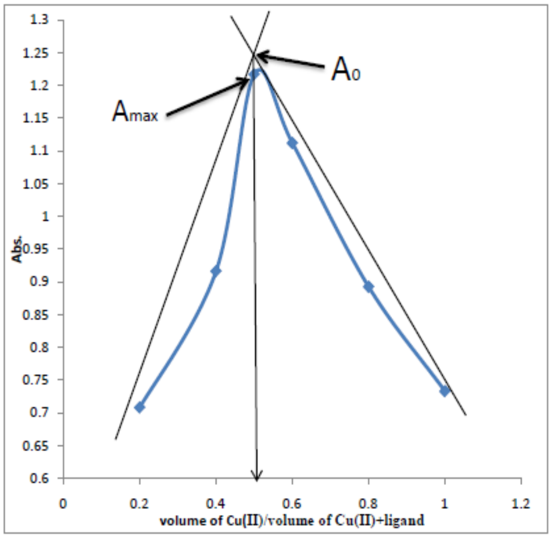


Figure 6: Job's plot for Cu(II)-CHMBH complex

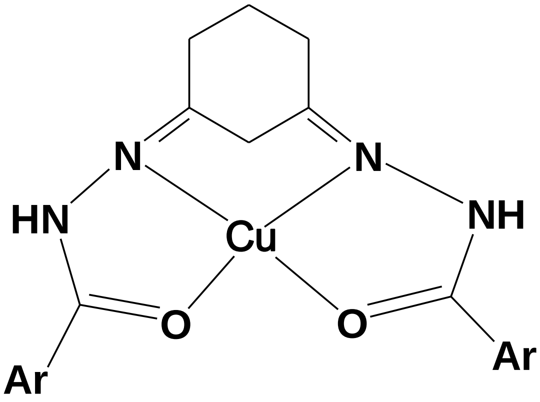
The stability constant K was calculated by using varagas method [18, 19] as the following equation:

$$K= \frac{C-\frac{A\alpha}{\epsilon}}{n^{n}(\frac{A\alpha}{\epsilon})^{n+1}} \quad (1)$$

Where, C= is a concentration of Cu(II) (0.0000859 mol/L) at stoichiometry point, ϵ = is a molar absorptivity (13242.142 L/mol.cm), n = is the no. of ligand CHMBH (1) and Aα = is the absorbance of the part of dissociated constant of Cu(II)-CHMBH complex(0.05), Aα was obtained by the following equations:

$$A_{\alpha} = A_{o} - A_{max} \quad (2)$$

Where, A_0 = is a theoretical absorbance value was obtained from jobs plot (1.25), A_{max}= is a maximum absorbance at Cu(II)-CHMBH complex (1.2). the stability constant K is found to be (578x10^{+8} L/mol), indicating that the Cu(II)-CHMBH complex is stable, The possible structure of the complex might be written as the following :



4.5 Area under curve (AUC) and Zero order methods

The area under curve and zero order spectrum for the Cu(II)-CHMBH complexation at the strength of substance (4, 24 mg/ l) are shown in figure 7 and figure 8. An area under curve is gone through the same wavelength as (415 nm) λ max of the zero order spectrum of the Cu(II) complex [20,21].

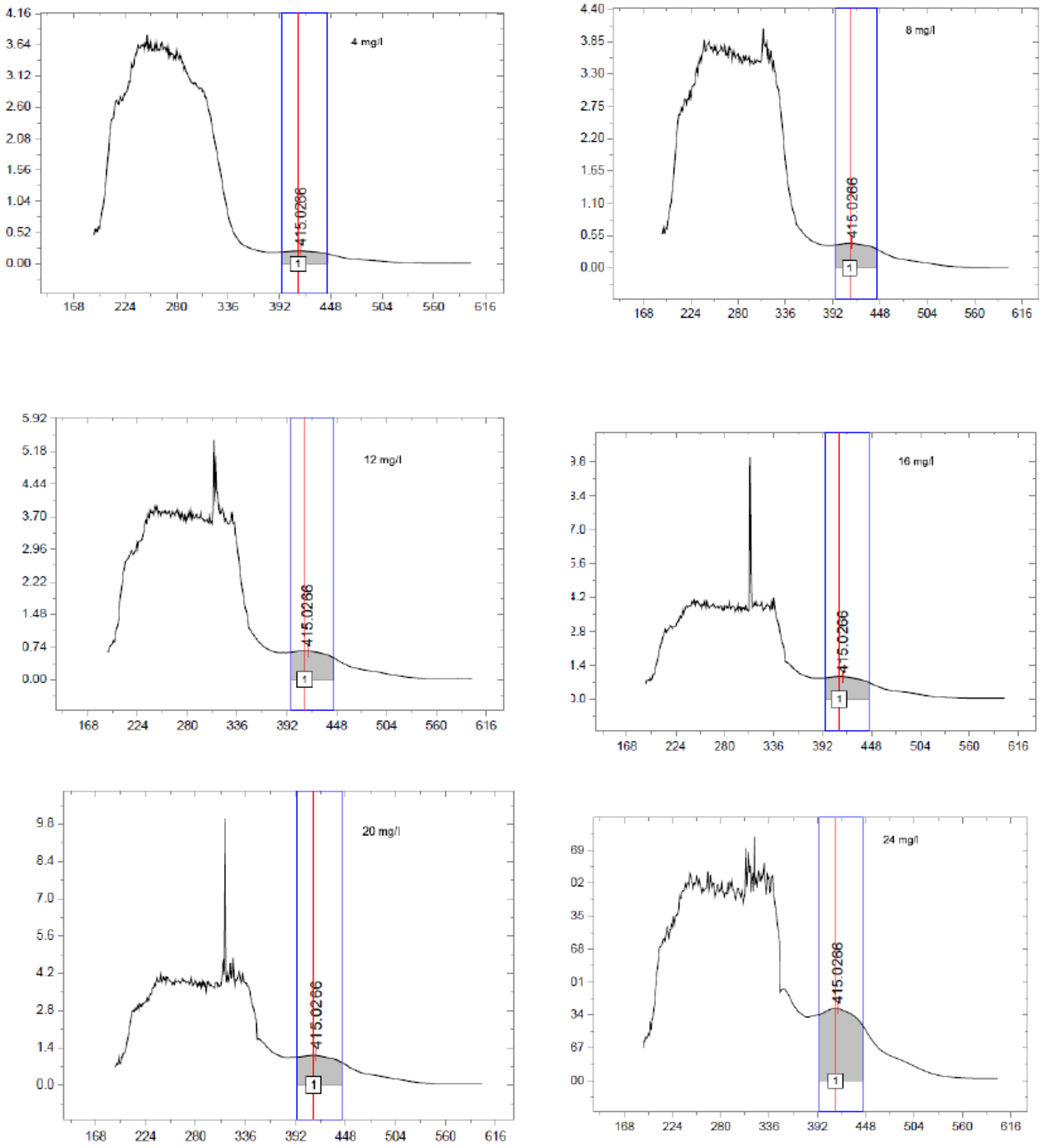


Figure 7: Spectrum of the AUC for Cu(II)-CHMBH complex

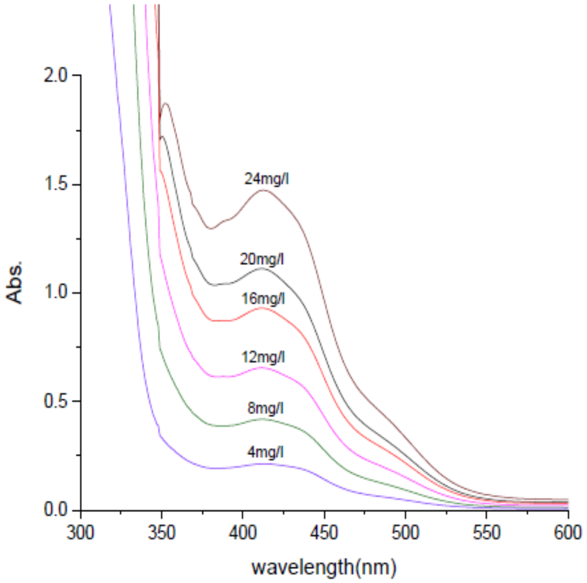


Figure 8: Spectrum of the zero order for Cu(II)-CHMBH complex.

4.6 Calibration curve

The calibration curves for the determination Cu(II) by complexion with the ligand CHMBH were created by marking the absorbance of standard solution verses the concentration of substance for the area under curve and zero order methods as displayed in figure 9 (a, b) Under the tested condition of this investigation, Molar absorptivity, Regression equation, the limit of detection and different analytical parameters are also summarized in table 1.

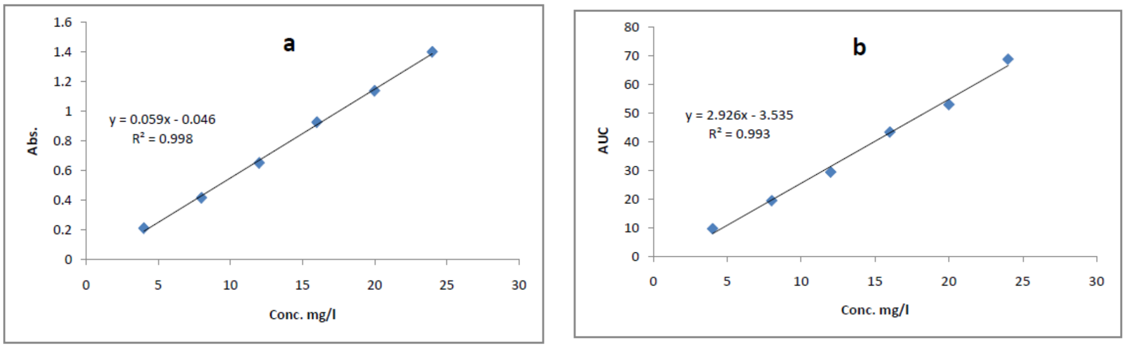


Figure 9: Calibration curves for a- the zero order and b- AUC of the Cu(II)-CHMBH complex.

Table 1: The analytical values of parameters and statistical treatment for the calibration curve.

Parameter	zero order method	AUC method
Linearity mg/l^1	4-24	4-24
Regression equation(y)	Y= 0.059x - 0.046	Y= 2.926x – 3.535
Correlation of determination (r^2)	0.998	0.993
Slope (b)	0.059	2.926
Intercept (a)	- 0.046	-3.535
Conf. limit for slope $b \pm t_{sb}$	0.059 ± 2.552	2.926± 1.926
Conf. limit for Intercept $a \pm t_{sa}$	0.046 ± 51.526	3.535± 24.834
Molar absorptivity Є (L/mol.cm)	13242.142	-
Sandell's sensitivity (mg/cm)	0.0356	-
Limit of detection LOD (mg/l)	0.1677	0.00338
Limit of quantification LOQ (mg/l)	0.508	0.01025

LOD= limit of detection= 3.3×SDb/S, LQD= limit of quantification= 10×SDb/S, SDb= 0.003= is the standard deviation of the solvent (acetonitrile solvent as a blank) (n= 3), S is the slop of the corresponding calibration curve.

4.7 Correctness and precision

The correctness and precision was determination at two concentration substance (14 and 22 mg/L) for the area under curve and zero order methods for the Cu(II)-CHMBH complexation as displayed in figures 10 and 11. Each concentration was analyzed three times, the high proportion recoveries values and low standard deviation values, displaying a good correctness and precision are summarized and listed in table 2.

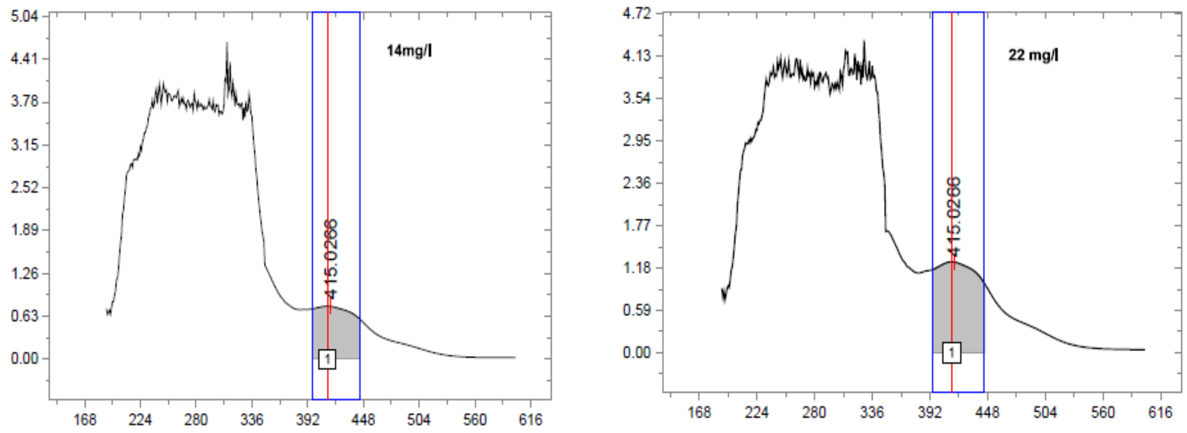


Figure 10: AUC of two concentration 14 and 22 mg/L.

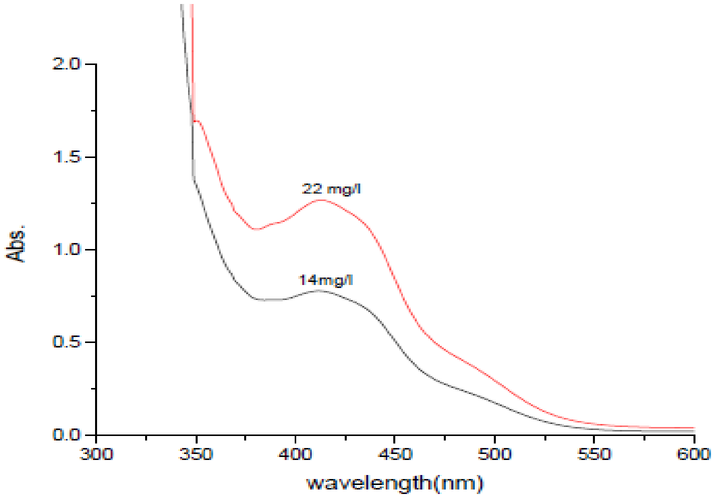


Figure 11: The zero order spectra of two concentration 14 and 22 mg/L.

Table 2: Accuracy of the AUC and zero order methods for the Cu(II)-CHMBH complex.

Methods	Pure meloxicam Conc.		E*%	Rec.*%	Average of Rec.%	RSD*%
	(taken) mg/mL	(Found) mg/mL				
Zero order	14	14.052	+0.371	100.371	99.356	1.540
	22	21.635	-1.659	98.341		0.966
AUC	14	14.106	+0.757	100.757	100.087	1.324
	22	21.872	-0.581	99.418		1.575

*Average of three determined

5. Conclusion

The proposed methods are simple and selective which used for estimation of Copper ion. The reagents used in the proposed methods are readily available and cheap. The cited methods offer the distinct possibility of assaying Copper ion without interference due to the excipients or the degradation products.

6. References

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