Spectrophotometric Determination of Cu(II) by Complex with Ethyl Cyano(2-Methyl Carboxylate Phenyl Azo Acetate) (ECA)

Elham Nghaimesh Mezaal
Kawther Ahmad Sadiq
Asmaa Nihad Zaki
Rasmia Mahmood Rumez
Dept. of Chemistry/ College of Education for Pure Sciences (Ibn-Al- Haitham)/ University of Baghdad
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Abstract

A new simple and sensitive spectrophotometric method for the determination of trace amount of Cu(II) in the ethanol solution have been developed. The method is based on the complexation of Cu(II) with ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ECA) in basic medium of sodium hydroxide givining maximum absorbance at (λ_{max} = 521 nm). Beer's law is obeyed over the concentration range (5-50) (µg / ml) with molar absorptivity of (3.1773 × 10^2 L mol^{-1} cm^{-1}) and correlation coefficient (0.9989). The optimum conditions for the determination of Cu(II)-complex and have been studied and applied to determine Cu(II) in synthetic water sample using simple and standard addition methods.

Keywords: Spectrophotometric, determination, copper, complex.

Introduction

Copper has Cu symbol, atomic number 29 and atomic mass 63.54 gm mol^{-1}. Copper is a reddish metal with a face centered cubic crystalline structure[1,2]. It is one of the several metals that play an important role in the biological systems, it occurs naturally which in many vegetables, meat and grains [3,4]. Copper is a mineral that nowadays possess few problems. It is widely distributed, as a component of various enzymes in foodstuffs of all kinds, at levels between 1 and 5 ppm. Milk is notably low in copper, at a round 2 ppm and mammalian liver is exceptionally high, at a round 80 ppm. The daily in take in normal adult diets is between 1 and 3 mg [5]. Methods for determination of copper were studied spectrophotometric in synthetic mixture and water samples[6], natural waters and pharmaceutical samples with chloro(pheny) glyoxime[7], determination of micro amount of copper(II) in different environmental and vital samples by new organic reagent[8], determination of micrograms of copper(II) and platinum(II)[9], complexation of cefixime with copper(II) using acetate NaOH buffer in water:methanol[10], determination of copper(II) using 5-nitrosalicyldehyde semicarbazone (NSS) as an analytical reagent[11], with 2-hydroxy-1-naphthalene carboxaldehyde phenyl hydrozone as an analytical reagent[12]. Synthesis of the ligand ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ECA) and the structure of (ECA) in Figure (1) [13]. In this work a sensitive and simple method for the determination of trace amounts of Cu(II) by UV-Vis spectrophotometry was described based on the formation of the Cu(II)-ECA complex and the influences of some parameters.

Experimental

Apparatus

- UV-Vis spectrophotometer

A shimadzu double beam UV-Vis spectrophotometer model UV-1601 (Kyoto, Japan) working at wavelength of 190-1100 nm.

-Digital balance

Digital analytical-Sartorius (Bp 3015-Germany).

Reagents

Copper chloride Fluka AG Buchs SG.
Sodium hydroxide Fluka AG Buchs SG.
Hydrochloride acid Riedel-Dehaen AG.

Ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ligand) (1000 µg / ml)

The ligand was prepared as same in paper [13]. A stock solution of (1000 µg / ml) of ligand was prepared by dissolving (0.1 gm) in ethanol absolute and then made up to (100 ml) in a volumetric flask and was kept ambient bottle a way from sun light.

Copper(II) (1000 µg / ml)

A stock solution of (1000 µg / ml) of Cu(II) was prepared by dissolving (0.2682 gm) of copper chloride dihydrate ($CuCl_2.2H_2O$) in ethanol absolute and diluted to (100 ml) in a volumetric flask by absolute ethanol. Working solution of (500 µg / ml) was prepared by simple dilution of stock solution with ethanol absolute.

Sodium hydroxide ≈ (0.1 M)

This solution was prepared by dissolving (0.4 gm) of sodium hydroxide in ethanol absolute and diluted to (100 ml) in a volumetric flask by the same solvent.

Hydrochloric acid ≈ (0.1 M)

This solution was prepared by diluting of (1.54 ml) of concentrated hydrochloric acid (37%) and diluted to (250 ml) in a volumetric flask by ethanol absolute.

Results and discussion

Absorption spectra

The complex is produced from the reaction between (0.5 ml) of Cu(II) (500 µg / ml) with (0.5 ml) of ligand (1000 µg / ml) in a volumetric flask (5 ml) and diluted to ethanol absolute giving maximum absorbance at λ_{max} = 521 nm an in Figure (2).

Optimum conditions for regulation reaction

There are many parameters affecting on the complexation reaction and absorbance of complex which is produced.

Effect of ligand volume

When a various volumes of ligand solution (0.05, 0.1, 0.15, …..0.6) ml for (1000 µg / ml) were added to (0.5 ml) of (500 (µg / ml) Cu(II), solution was found that (0.5 ml) of ligand is enough to give a maximum absorption and was considered to be optimum for concentration range of (5-50) (µg / ml) of Cu(II). The results were shown in Table (1).

Effect of hydrochloric acid volume

Existence of hydrochloric acid (0.1-1) ml of (0.1 M) in reaction solution effect on decreasing the intensity of absorbance for produced complex. The results were shown in Table (2).

Effect of sodium hydroxide volume

It was found that the presence of base in reaction solution effect on increasing the intensity of absorbance for the produced complex, NaOH was selected and (0.1 ml) of (0.1 M) was found to be the optimum volume. This base gives high sensitivity which was selected in subsequent experiments the results were shown in Table (3).

Effect of order of addition

To obtain optimum results, the order of addition of base should be the first followed by addition of ligand and Cu(II). The results were shown in Table (4).

Effect of temperature

The resulting complex of the proposed method was studied at room temperature (25 ˚C), the absorbance values remain constant. The results were shown in Table (5).

Effect of time on the complex formation

The results show that the complex produced was stable between (5-60) minutes, the absorbance value was stable. The results were shown in Table (6).

Calibration graph

The content of series of (5 ml) calibration flasks containing (0.1 ml) of (0.1 M) NaOH and (0.5 ml) of ligand (1000 µg / ml) with different concentrations (5-50) (µg / ml) of Cu(II) (500 µg / ml) were diluted with ethanol absolute. The absorption spectra were recorded against blank at temperature 25 ˚C. A linear calibration graph for Cu(II)-complex is obtained (Figure 3), which shows that Beer's law is obeyed.

Precision and accuracy

Under the optimum condition, the precision and accuracy of the method was calculated. The results were shown in Table (7).

Structure of the complex

The stoichciometry of the complex between Cu(II) and ligand was investigated using Job's method and mole ratio method; the results show that 1:2 Cu(II) to ligand complex was formed. The formation of the complex produced suggest occurring as follows, Figure (4)[14].

Effect of interference elements

We have studied the effect of interference elements (Zn(II), Na(I), K(I), Mg(II), Ca(II)), on the complexation of Cu(II). A stock solution of each element (10000 µg / ml) was prepared by dissolving (2.0845 gm) $ZnCl_2$, (2.5421 gm) NaCl, (1.9067 gm) KCl, (2.7691 gm) $CaCl_2$ and (3.9173 gm) $MgCl_2$ in ethanol absolute and then made up to (100 ml) in volumetric flask with the same solvent working solution of (1000, 500, 50) µg / ml of each element was prepared by simple dilution for primary stock solution (10000 µg / ml) in a volumetric flask (5 ml) which contains (0.1 ml) NaOH, (0.1 M), (0.5 ml) ligand (1000 µg / ml) and (0.5 ml) Cu(II) (500 µg / ml) diluted up to the mark with ethanol absolute. Taken absorbance of each solution in (λ_{max} = 521 nm) against blank. The results showed that interference elements are not affected on to determination of Cu(II) as ECA complex, Table (9).

Application

Two methods were successfully applied, (simple method and standard addition method) for determination of Cu(II) in synthetic a river water. The sample Cu(II) in synthetic a river water (1000 µg / ml) was prepared by taking (0.2682 gm) of $CuCl_2.2H_2O$ dissolving in a river water and transferred in a volumetric flask (100 ml) diluted up to the mark with same solvent. Simple method transferred (0.25 ml) of Cu(II) in synthetic a river water (1000 µg / ml) to a volumetric flask (5 ml) contains (0.1 ml) NaOH (0.1 M) and (0.5 ml) ligand (1000 µg / ml) diluted up to mark with ethanol absolute. Taken absorbance of solution in (λ_{max} = 521 nm) against blank. The results were shown in Table (10). Standard addition method transferred (0.25 ml) of Cu(II) in synthetic a river water (1000 µg / ml) to each volumetric flask (5 ml) contains (0.1 ml) NaOH (0.1 M) and (0.5 ml) ligand (1000 µg / ml) and various concentrations of Cu(II) solution (5-50) µg / ml diluted up to the mark with ethanol. Taken absorbance of each solution in (λ_{max} = 521 nm) against blank. The results were shown in Figure (5) and Table (10).

Conclusion

A new simple and sensitive spectrophotometric method for the determination of trace amount of Cu(II) in the ethanol solution. The method is based on the complexation of Cu(II) with ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ECA).

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Table (1) Effect of ligand volume of absorbance value of complex at temperature (22 ˚C)

Vol. of ligand (ml)	Absorbance
0.05	0.039
0.10	0.075
0.15	0.101
0.20	0.110
0.25	0.113
0.30	0.125
0.35	0.137
0.40	0.140
0.45	0.147
0.50	0.149
0.55	0.148
0.60	0.147

Table (2) Effect of hydrochloric acid volume on absorbance value of complex at temperature (20 ˚C)

Vol. of hydrochloric acid (0.1M) (ml)	Absorbance
0.0	0.145
0.1	0.103
0.2	0.101
0.3	0.098
0.4	0.090
0.5	0.088
0.6	0.086
0.7	0.085
0.8	0.083
0.9	0.075
1.0	0.070

Table (3) Effect of sodium hydroxide volume on absorbance value of complex at temperature (20 ˚C)

Vol. of sodium hydroxide (0.1 M) (ml)	Absorbance
0.0	0.145
0.1	0.219
0.2	0.199
0.3	0.198
0.4	0.196
0.5	0.193
0.6	0.187
0.7	0.184
0.8	0.180
0.9	0.175
1.0	0.170

Table (4) Effect of order of addition on absorbance value of complex at temperature (21 ˚C)

Order of addition	Absorbance
Cu(II) + ligand + NaOH	0.220
Cu(II) + NaOH + ligand	0.201
Ligand + NaOH + Cu(II)	0.090
Ligand + Cu(II) + NaOH	0.100
NaOH + Ligand + Cu(II)	0.245
NaOH + Cu(II) + Ligand	0.180

Table (5) Effect of temperature on absorbance value of complex

Temp. (˚C)	Absorbance
20	0.240
25	0.251
30	0.245
35	0.221
40	0.200
45	0.187

Table (6) Effect of time on the complex formation at temperature (20 ˚C)

Time (min.)	Absorbance
0	0.238
5	0.241
10	0.242
15	0.241
20	0.242
25	0.242
30	0.241
40	0.242
50	0.241
60	0.242

Table (7) Precision and accuracy of the method

Element	Taken (µg / ml)	Found (µg / ml)	RE %	RSD % n = 5	Recover %
Cu(II)	05	05.0	0.000	0.00000	100.0
	20	20.0	0.000	0.31494	100.0
	50	50.2	-0.400	0.12577	100.4

Table (8) Method validation of the spectrophotometery determination of Cu(II) with ligand in ethanol absolute

Parameter	Value
λ_{max} (nm)	521
slope	0.0050
intercept	0.0000
R^2	0.9980
r	0.9989
ε_{max} (L mol^{-1} cm^{-1})	3.1773×10^2
sandell index (µg cm^{-2})	2.0000×10^2

Table (9) Effect of interference elements on the determination of Cu(II) as (ECA) complex

Element of interference	Conc. element interference (µg / ml)	Found as	Taken of Cu(II) (µg / ml)	Found of Cu(II) (µg / ml)	RE %	Recover %
Zn(II)	50	$ZnCl_2$	50	49.8	0.040	99.6
	500		50	50.0	0.000	100.0
	1000		50	49.6	0.080	99.2
Na(I)	50	NaCl	50	50.0	0.000	100.0
	500		50	49.6	0.800	99.2
	1000		50	49.6	0.800	99.2
K(I)	50	KCl	50	50.2	-0.400	100.4
	500		50	50.0	0.000	100.0
	1000		50	50.0	0.000	100.0
Ca(II)	50	$CaCl_2$	50	49.8	0.040	99.6
	500		50	49.8	0.040	99.6
	1000		50	49.6	0.080	99.2
Mg(II)	50	$MgCl_2$	50	50.2	-0.400	100.4
	500		50	49.6	0.800	99.2
	1000		50	49.6	0.800	99.2

Table (10) Results for analysis of Cu(II) in a river water by two methods

Element	Method of analysis	Taken (µg / ml)	Found (µg / ml)	Regression equation	R^2	r	RE %	Recover %	RSD % n = 5
Cu(II)	Simple method	50	50.2	y=0.0050x+0.0000	0.9980	0.9989	-0.400	100.4	0.12577
	standard addition method	50	50.0	y=0.0050x+0.2500	0.9980	0.9989	0.000	100.0	0.00000

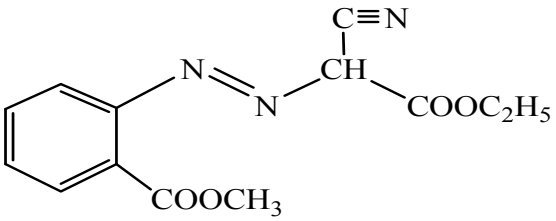

Figure (1) Structure of (ECA)

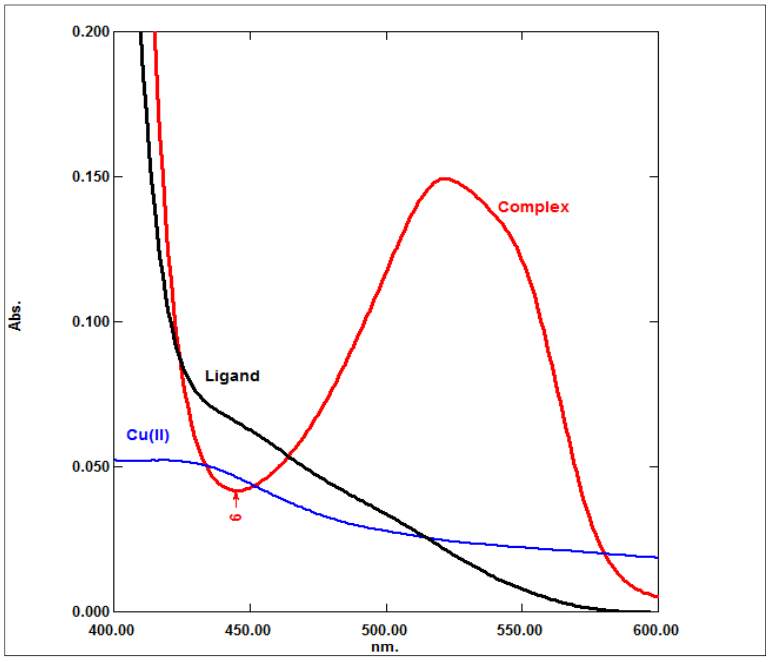

Figure (2) Absorption spectra of (a) 50 (µg / ml) of Cu(II) (b) 100 (µg / ml) of ligand (c) 50 (µg / ml) of Cu(II) with 100 (µg / ml) of ligand against reagent blank

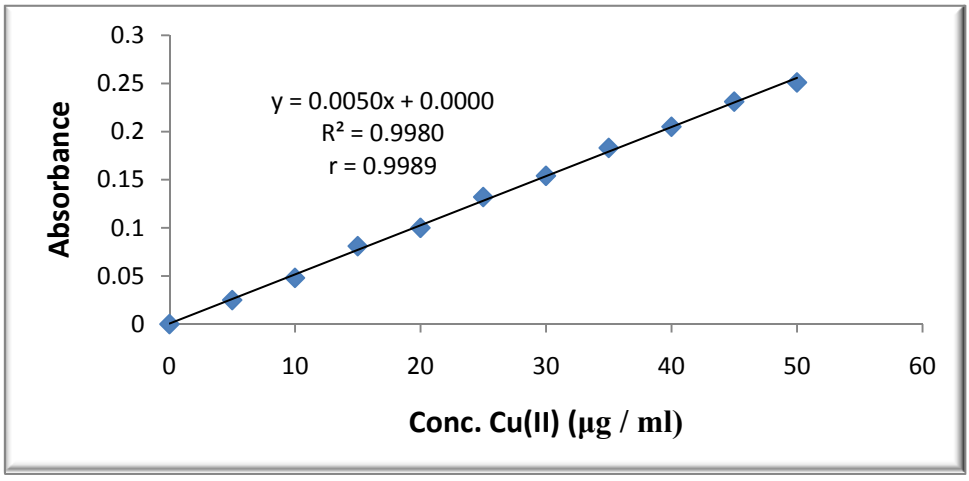

Figure (3) Calibration graph of Cu(II)-complex

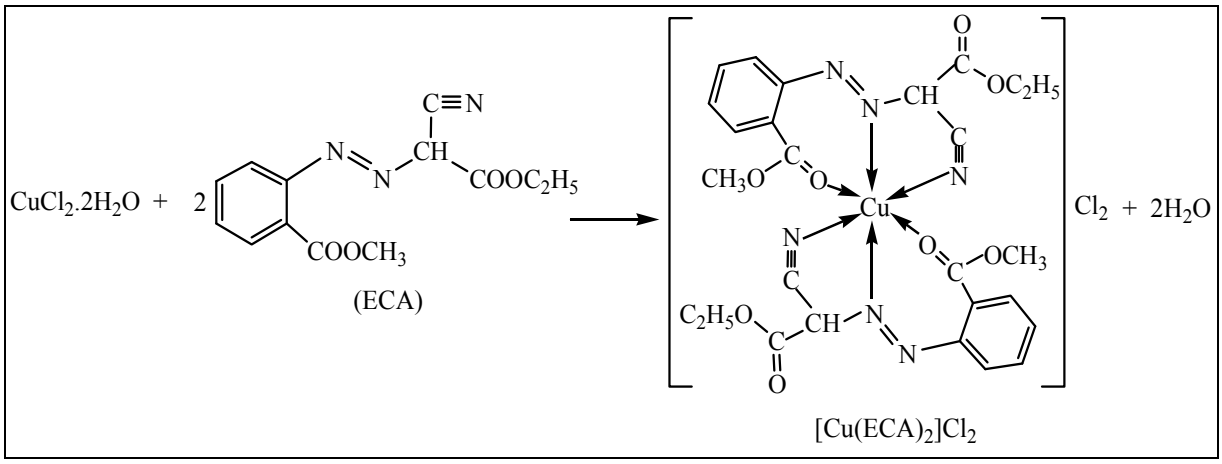

Figure (4) Suggest product formation pathway

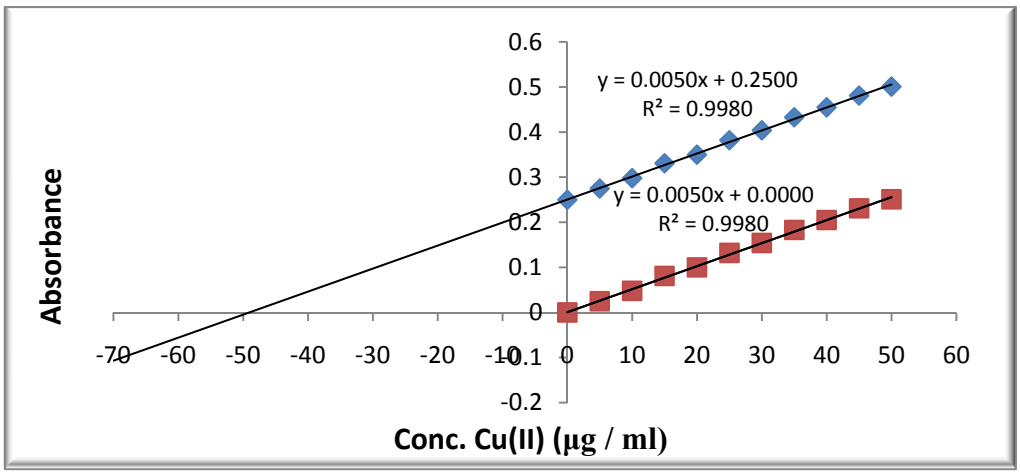

Figure (5) Results for analysis of Cu(II) in a river water by two methods

التقدير الطيفي للنحاس الثنائي بوساطة تكوين معقد مع اثيل سيانو (2- مثيل كاربوكسليت فنيل ازو خلات)

الهام نغيمش مزعل
كوثر أحمد صادق
أسماء نهاد زكي
رسمية محمود رميز
جامعة بغداد / كلية التربية للعلوم الصرفة (ابن الهيثم)/ قسم الكيمياء
استلم في:22/شباط/2016،قبل في:11/أيار/2016

الخلاصة

تم تطوير طريقة طيفية جديدة بسيطة وحساسة لتقدير كميات قليلة من النحاس الثنائي في المحلول الكحولي. تعتمد الطريقة على تكوين معقد بين النحاس الثنائي و اثيل سيانو (2- مثيل كاربوكسليت فنيل ازو خلات) في وسط قاعدي من هيدروكسيد الصوديوم الذي يعطي اعظم امتصاص عند الطول الموجي 521 نانوميترا". وجد انه يطيع قانون بير ظمن التراكيز (5-50) مايكروغرام / مللتر وقيمة الامتصاصية المولارية (3.1773×10^2) لتر مول$^{-1}$ سم$^{-1}$ ومعامل الارتباط (0.9989). تم دراسة الظروف المثلى لتقدير المعقد وطبقت الطريقة لتقدير النحاس في نموذج مصنع من الماء وباستعمال الطريقة الاعتيادية وطريقة اضافات القياس.

الكلمات المفتاحية: طيفي، تقدير، نحاس، معقد.