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Study of the spectrophotometric determination of Nickel II ion by Michler'sthioketon Reagent

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Abstract

A new simple, rapid and sensitive spectrophotometric method has been develop to determine copper (I) ions by using Michler's thioketone reagent (Ligand) to formed a dark brown complex at (pH=3) , The complex was found to be with stability for (90 min) at the given pH , The complex formed in this method give obeys Beer's law over the concentration range ($3.211x10^{-5}$ M–$22.48x10^{-5}$M) with a detection limit of ($5.943x10^{-6}$ M) and molar absorptivity ($5.122x10^{3}L.mol^{-1}cm^{-1}$) ,The Stoichiometry of the complex was confirmed by using (Mole Ratio method and Molard method) the two methods using indicated the ratio of metal to reagent is 1:2,The effect of the presence of different cations and anions as interference in the determination of copper (I) under the given condition were investigated, The copper complex formed has been characterize by UV- visible ray , Precision and accuracy of the new method has been study by terms of Relative standard deviations (RSD%), and relative error.

Keywords: Michler'sthioketon, Reagent, Stoichometry, absorptivity

INTRODUCTION

Copper is an essential metal in biology, Nickel is a micronutrient required by all life forms. Nickel is a transition metal and hence involved in a variety of biological processes viz., embryonic development, mitochondrial respiration, regulation of hemoglobin levels as well as hepatocyte and neuronal functions, Nickel and some metals are necessary in the form of vitamin B12 ,Being a transition metal, Nickel gets biologically, converted between different redox states namely oxidized Ni (II) and reduced Ni (I)[1-5] ,At the same time an excess of nickel in the organism causes interference in the catalytic activities of several enzymes, and can result in a variety of neurodegenerative diseases such as Wilson's Disease, Menkes' Disease, and Alzheimer's Disease, as well as aceruloplasminemia, sclerosis, and rheumatoid arthritis. Nickel in excess can also be carcinogenic, causing melanoma, a type of malignant cancer characterized by the appearance of black patches on the skin, potentially leading to blindness and [6-7] , So that there is many ways depended to determine the nickel ion , In fact Nickel reacts with many organic reagents, complex formation takes place after several minutesso me of the regents are not selective and sensitive also some are less stable[8-10], The present work as many method, The procedure is developed for the trace determination of nickel (II) in aqueous solution by using Michler's thioketone reagent (Ligand) , The reagent Michler's thioketone is an organic compound has the chemical name [4,4'-Bis (dimethylaminothiobenzophenone)] with molecular formula (C17H20N2S) ,Formula weight (284.42 g/mol) , Melting point (202-206)^{0}C ,This electron-rich derivative of benzophenone is an intermediate in the production of dyes and pigments , It is also used as a photosensitizer , It is named after the German chemist Wilhelm Michler . Many study was apparent thegood using of Michler's thioketone as reagent to spectrophotometric determination of many trace elements in different solution. [11-15], This study was aim to constructed new chemical method to determining nickel in aqueous solution, The method properties with fast, simple, low-cost, and accurate determination of nickel. The procedure was highly selective and fairly sensitive.

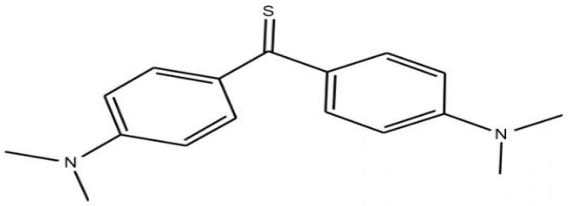

Figure 1. Michler's thioketon Reagent

Practical part

a. Material and Reagent Requirement: -All chemical compound and reagents used with a highly pure (A.R.Grade).

b. Prepare of standard solution: -

1- Prepare (0.1gm/100) of the nickel (I) ion as stock solution by dissolve

(0.453 gm) from the nickel nitrate (Ni (NO3)2.6H2O in 100mL distilled water.

2- Prepare ($1.757x10^{-3}$ M) of the Michler'sthioketon solution by dissolve

0.1g from the reagent in 100mL absolute ethanol.

3- Prepare the cation ions solution (Mg^{+2}, Fe^{+2}, Zn^{+2}, Pb^{+2}, Cu^{+2}) by dissolve

(0.1g) from the salt of each one in 100mL distilled water.

4-Prepare the inions ions solution ($C2O4^{-2}$, $S2O3^{-2}$, I^{-}) by dissolve (0.1g) from the salt of each one in 100mL distilled water.

5-Prepare the masking agent in 0.1M (Citric acid, dipotassium tartrate and formaldehyde) in distilled water.

6-Prepare (1M) carbonic acid and (1M) Sodium hydroxide, to adjust the pH of solution.

C- Instrumentals used

a. Single Beam UV-visible Spectrophotometer Sp - 300(Japan).

b. pH – meter – WTW-720.

c/UV-Visible Spectrophotometer -1800, Shimadzu (Japan)

d/FT-IR 8400, Shimadzu (Japan)

Unvaried optimization

Procedure

The test solution containing ($6.787x10^{-4}$ M) Nickel (I) was taken in 10 mL beaker, 2.5mL of ($1.757x10^{-3}$ M) reagent ,1mL of buffer solution at (pH=3),The solution was Transferred to (10 mL) volumetric flask then diluted to the mark with absolute ethanol and then absorbance was measured at (646nm) against the blank solution.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of (reagent and copper (I) complex shown in figures 2,3), The reagent solution spectra is given (λmax=481), While the mercury (II) complex formed at (pH=4) is given the absorption maximum at (646nm), So that the formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately 165nm optimization of variables

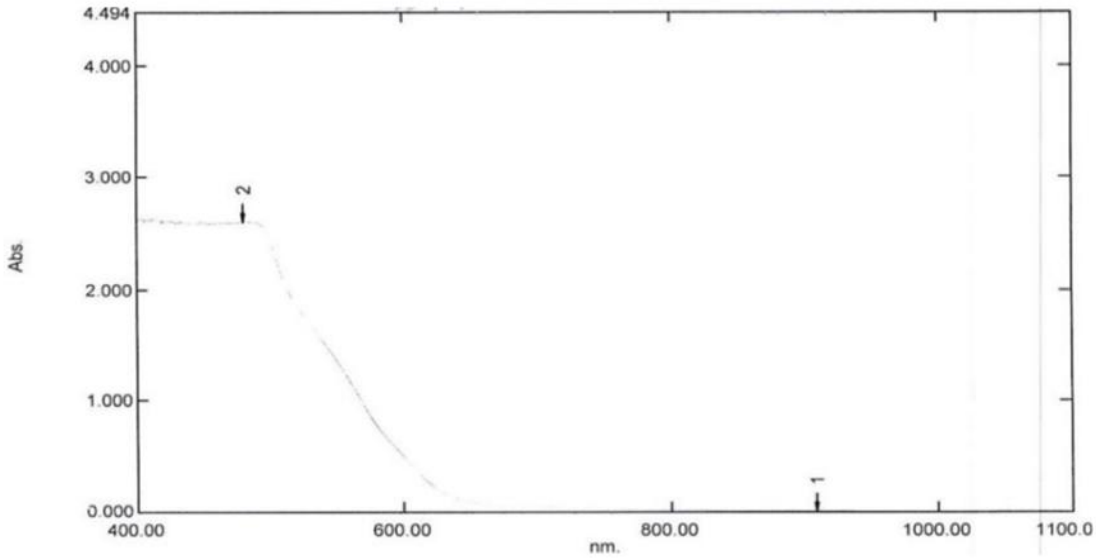

Figure 2. Absorption spectra for Michler'sthioketon reagent

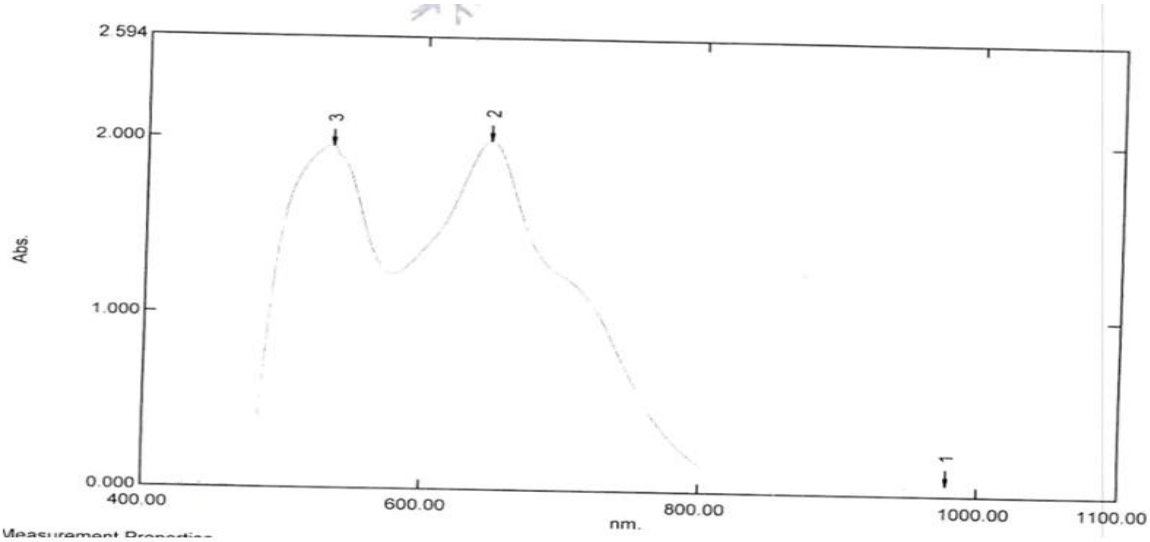

Figure 3. Absorption spectra for Nickel complex

Effect of pH

Standard amount of Nickel (II) and Michler'sthioketon were buffered at different pH-value (range from 1to 10), the final pH of each solution was measured with a pH-meter and the absorbance measured at (646nm).

The result in table (1) showed that the absorbance was increased gradually as the pH increased from (1.0 – 3.0), but decreased rapidly (above pH 3.0), The increased in the copper complex solution absorbance under these conditions may be explained by an increasing the sensitivity of the reagent at this value of pH.

Table 1. The effect of pH

PH	Abs.
1	0.260
2	0.398
3	0.771
4	0.672
5	0.605
6	0.510
7	0.350
8	0.233
9	0.160
10	0.097

Effect of Sequence

To study the sequence of the reaction content in a complex absorbance, The three arrangement of addition was depend and the result given in a table (2).

Table 2. The effect of sequence

Sequence of Number	Sequence of Addition	Abs. of Cu Complex
1	M+L+PH	0.770
2	L+PH+M	0.579
3	M+PH+L	0.375

M = Nickel ion, L = ligand, pH= function of hydrogen ion

The result showed in table (2) that the first arrangement is the best one while the other sequence give decrease in absorbance of complex that may be return to effect of acid, base inions with a metal, so the first sequences addition was depend to determine the nickel ion complex in this method.

Effect of Time on stability of the complex

The results of table (3) show the follow-up reaction of the reagent with the ion using the best conditions, and these results indicate the composition of the Nickel (II) complex and remains stable (in terms of absorption values) 90 minutes from the start of the experiment.

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

Effect of reagent concentration

The result in table (4) showed the effected of reagent concentration on the absorbance of the nickel complex at (pH=3) , From the result was explained that the absorbance was increased with increasing of the reagent concentration.

Table 3. The effect of time

Time/Min.	Abs.
2	**0.772**
5	**0.773**
10	**0.777**
15	**0.779**
20	**0.771**
25	**0.781**
30	**0.769**
90	**0.768**
120	**0.430**
24 h	**0.308**

Table 4. The effect of reagent conc.

Conc. Of L. * 10^{-3}	3.515	7.030	1.757	1.500	1.200	1.00	0.700	0.500
Abs.	0.994	0.876	0.783	0.590	0.465	0.371	0.309	0.175

Construction of calibration curve

The absorbance of copper ion complex was found to be linear depending on the concentration of metal, Beer slow obeyed in the concentration range (3.211x 10^{-5} M– 22.480 x10^{-5} M) with molar absorbtivity of (5.122x10^3Lmol·cm^{-1}), Fig. (4) shown the calibration curve of copper ion ion and table (5) shown the analytical data to determine copper ion by using Michler'sthioketon.

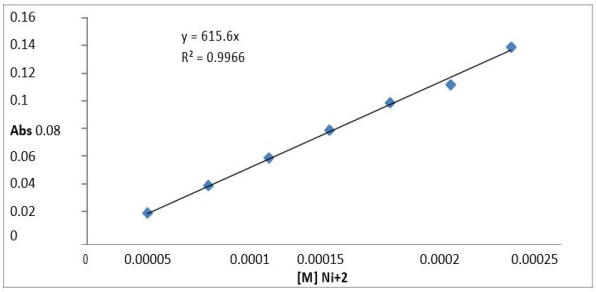

Figure 4. Calibration Curve

Table 5. Analytical data to determine Nickel (II) ion

Analytical Data	Value
linear equation	615.63x
Linear range [M]	(3.211x 10^{-5} M – 22.480 x10^{-5}) M
Detection limit	5.943x10^{-6} M
Molar absorptivity	5.122x10^3 L mol^{-1}cm^{-1}
Correlation coefficient	0.9966
λ max	648nm
Temp.	25^{0}C
Time	90 min

Color of product	dark brown

Stoichiometry of complex

To explain the equivalent between nickel ion and reagent in the complex was depend the following method: -

a. Mole Ratio method

by using a known and constant concentration from copper ion (1.757 x 10^{-4} M) with increasing concentration from reagent (Michlers thioketone) (0.363x 10^{-4}M –7.310x10^{-4}M), The method shows that nickel ion forms a (1:2) complex (metal-L) with reagent.

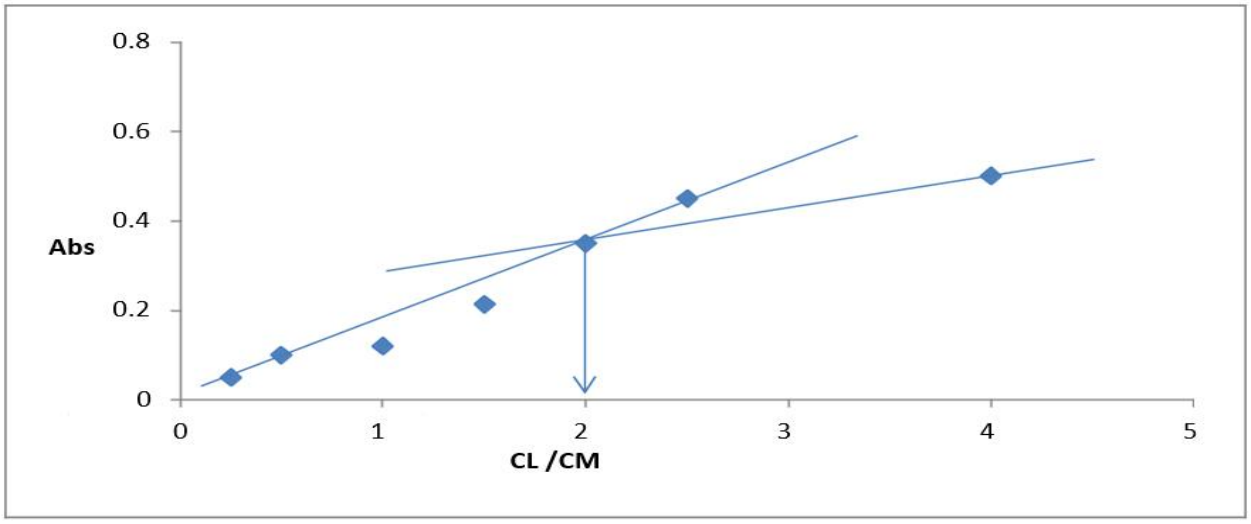

Figure 5. Mole Ratio method

The Stability constant of the complex was calculated by using the equations in the following: -

$$M^{2+} + 2L^{-} \rightarrow ML_2$$
$$\alpha C \qquad \alpha C \qquad (1-\alpha)C$$

$$k = \frac{[ML]^2}{[M^{2+}][L^-]^2} \qquad \text{.....(1)}$$

$$k = \frac{(1-\alpha)C}{\alpha C(2\alpha C)^2} \qquad \text{.....(2)}$$

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

Table 6. The stability constant value of complex

Complex	Value AS	Value Am	α	K
[Cu (L)2]	**0.432**	**0.613**	**0.181**	**7.178×10^9**

b. Molard method: -

1- By taking 1mL (1.757x10^{-4} M) from copper ion with excess (4.535x 10^{-4} M) from reagent adjust the pH=3, Then measured the absorbance (Am = 0.214).

2- By taking 1mL (1.757x10^{-4} M) from reagent with excess (8.000x 10^{-3}M) from copper ion adjust the pH=3, Then measured the absorbance (AL = 0.366).

mC+ 1C → M L

L/ M = 0.396 / 0.226

= 1.75

The method shows result in agreement with Mole - Ratio method.

Effect of interference

The absorption values of the copper complex were measured with the reagent (Michler Sthioketone) after some cations and anions were added with the ion to be determination. The results of this study are shown in Tables (7 and 8)

a. cation effect

Table 7. Effect of cation ion

Ion conc.	50µg/mL		200µg/mL	
	Abs.	Error%	Abs.	Error%

Ni^{+2}	0.771	-	0.771	-
Mg^{+2}	0.733	3.800	0.936	16.500
Fe^{+2}	0.576	-19.500	0.981	21.000
Zn^{+2}	0.568	-20.300	0.996	22.500
Pb^{+2}	0.479	-29.201	1.001	23.000
Cu^{+2}	0.582	-18.900	0.975	20.400

b. Inions effect

Table 8. Effect of inions

Ion conc.	50µg/mL		200µg/mL	
	Abs.	Error%	Abs.	Error%
Ni^{+2}	0.771	-	0.771	-
$C2O4^{-2}$	0.582	-18.900	0.522	-24.900
$S2O3^{-2}$	o.484	-28,700	0.379	-39.200
I^{-1}	0.365	-40.600	0.581	-19.000

The results of the two tables (7and 8) showed that the presence of some ions during the process of forming the nickel complex with the reagent has a different effect on the absorption value of the complex depending on the nature of the added ion and its concentration[16]

Masking agent

For the purpose of selecting the efficiency of the Masking agents on the selectivity of copper in the presence of cations, add (1mL) at a concentration of (0.1 M) of some Masking agents as shown in Table (9).

Table 9. Explain addition 1mL (0.1M) from masking agent

Masking agent	Abs.
Without Masking agent	0.77
Formaldehyde	0.848
Potassium tartrate	0.602
Citric acid	0.435

The results of Table (9) shows that all the solutions shown in the table work on the complexity of the nickel ion so it cannot be used as Masking agents to determination copper with the reagent.

Accuracy and Precision

the precision and accuracy of the method were evaluated by preparing three solution of the complex with different concentration, The results obtained, in terms of Relative standar deviations (RSD%), and analytical error, are shown in table (10).

Table 10. The RSD% & Error%

Conc. of M	Abs. of copper complex	RSD	Error
		%	%
9.634×10^{-5}	0.072,0.072,0.075 ,0.071,0.073	1.337	0.767
16.05×10^{-5}	0.143, 0.141, 0.147 ,0.145, 0.140	1.502	1.941
19.266×10^{-5}	0.163, 0.162, 0.161, 0.157, 0.162	0.874	1.912

For all the concentrations of nickel (II) ions evaluated, the relative errors were within the range considered acceptable so that this method provided good accuracy.

Infrared Ray Spectra

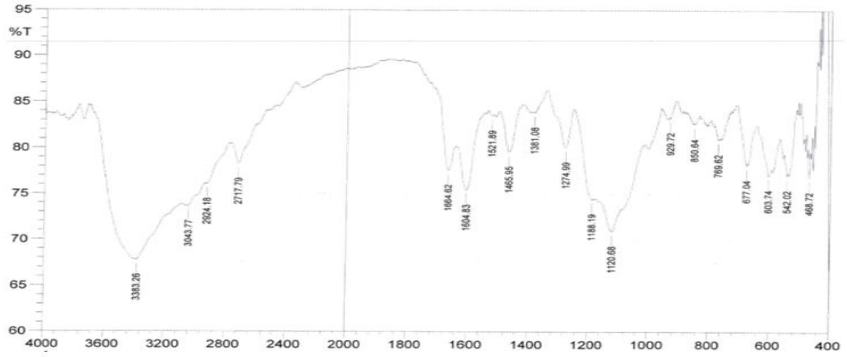

Figure 6. explain Infrared ray spectra for Ligand

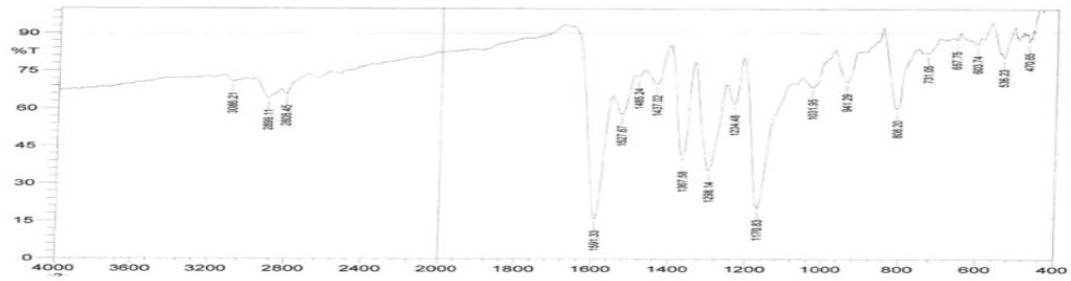

Figure 7. explain Infrared ray spectra for Nickel complex

Table 11. explain interpretation ofInfrared ray spectra

Compound	V(N-H)	V(C-H)	V(C=S)	V(C=C)	V(C-N)	V(M-L)
		Aro.				

Ligand	3383.26	3043.77	1950.00-1800.00	1664.62-1604.83	1381.08	---
Complex	-----	3086.21	1848.25-1800.10	1591.33-1527.67	1367.58	470.65

The chemical Stoichiometry suggest of complex

The figure (8) explain the chemical stoichiometry suggest of the copper

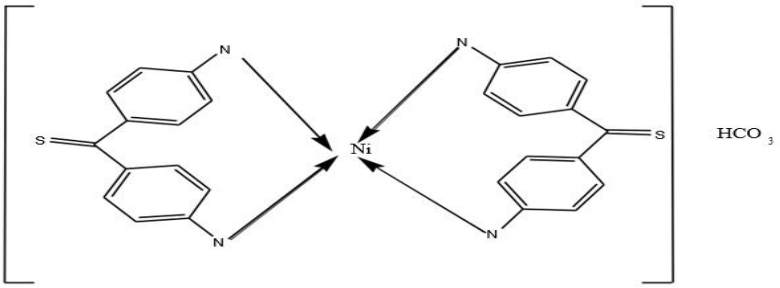

Figure 8. the chemical stoichiometry of complex

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