Study of the spectrophotometric determination of Copper ion (I) by Michler’s thioketone 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 (1.943x10⁻⁶ M) and molar Absorptivity (0.622x10³ L.mol⁻¹.cm⁻¹) , The Stoichiometry of the complex was confirmed by using (Mole Ratio method & 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’s thioketone Reagent , Stoichiometry , absorptivity

1. Introduction
Copper is an essential metal in biology , Copper is a micronutrient required by all lifeforms , Copper 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, Copper and some metals are necessary in the form of vitaminB₁₂, Being a transition metal, Copper gets biologically, Converted between different redox states namely oxidized Cu (II) and reduced Cu (I)¹⁻⁵, At the same time an excess of copper 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, Copper 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 ⁶⁹, So that there is many ways depended to determine the copper ion, In fact copper reacts with many organic reagents, Complex formation takes place after several minutes some of the regents are not selective and sensitive also some are less stable ¹⁰, The present work as many method, The procedure is developed for the trace determination of copper (I) in aqueous solution by using Michler’s thioketone reagent (Ligand), The reagent Michler’s thioketone is one of an organic compounds which plays a role in extraction
of many trace elements, Michler’s thioketone has the chemical name [4,4\(^{-}\) Bis(dimethylaminothiobenzophenone)] with molecular formula (C\(\text{17H}_{20}N_{2}S\)). Formula weight (284.42 g/mol), Melting point (202-206) °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 studies appeared to show that using Michler’s thioketone as a reagent to spectrophotometric determination of many trace elements in different solutions. 13-16 This study was aimed to construct a new chemical method to determine copper in aqueous solution. The method properties with fast, simple, low-cost, and accurate determination of copper. The procedure was highly selective and fairly sensitive.

2. Practical part

2.1. Material and Reagent Requirement

All chemical compounds and reagents used with a highly pure (A.R.Grade).

2.2. Prepare of standard solution

- Prepare (8.000x10\(^{-3}\) M) of the copper (I) ion as stock solution by dissolve 0.1g from the copper bicarbonate CuHCO\(_3\) in 100mL distilled water.
- Prepare 1.757x10\(^{-3}\) M of the Michler’s thioketone solution by dissolve 0.05g from the reagent in 100mL absolute ethanol.
- Prepare the cation ions solution (Mg\(^{2+}\), Fe\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Cu\(^{2+}\)) by dissolve (0.1g) from each salt in 100mL distilled water.
- Prepare the anion ions solution (C\(_2\)O\(_4\)^{-2}, S\(_2\)O\(_3\)^{-2}, I\(^{-}\)) by dissolve (0.1g) from each salt in 100mL distilled water.
- Prepare the masking agent in 0.1M (Citric acid, dipotassium tartrate, and formaldehyde) in distilled water.

2.3. Instrumentals used

- pH-meter – WTW-720.
- FT-IR 8400, Shimadzu(Japan).
- UV-Visible Spectrophotometer -1800, Shimadzu (Japan).
- Single Beam UV-visible Spectrophotometer Sp -300(Japan).

2.4. Unvaried optimization

Procedure
The test solution containing (6.400x10\(^{-4}\) M) copper (I) was taken in 10mL beaker, 2.5mL of (1.757x10\(^{-3}\) M) reagent, Adjust the pH with 1mL of buffer solution at (pH=3). After that solution was transferred to (20 mL) volumetric flask then diluted to the mark with absolute ethanol and then absorbance was measured at (646 nm) against the blank solution.

3. Results and Discussion

3.1. Absorption spectra
The absorption spectra of [reagent and copper (I) complex shown in figures(2,3)] , The reagent solution spectra is given ($\lambda_{max}= 481$nm), While the copper (I) complex formed at (pH=3) 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.

3.2. Effect of pH
Standard amount of copper (I) and Michler’s thioketone 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).

| pH | Abs. |
|----|------|
| 1  | 0.280|
| 2  | 0.373|
| 3  | 0.783|
| 4  | 0.472|
| 5  | 0.305|
| 6  | 0.110|
| 7  | 0.050|
| 8  | 0.033|
| 9  | 0.060|
| 10 | 0.077|

Figure 2. Absorption spectrum for Michler’s thioketone reagent

Figure 3. Absorption spectrum for copper complex
3.3. 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             | 0.783              |
| 2                  | L + pH + M             | 0.379              |
| 3                  | M + pH + L             | 0.275              |

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

The result showed in table (2) 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 copper ion complex in this method.

3.4. Effect of Time on stability of the complex
The result of table (3) showed the effect of time on the complex by using the best condition. The result indicate that the composition of the copper complex remains stable (in terms of absorption values), So this study promote the use of the Michler’s thio-ketone as one reagents used to quantify the element copper parasitically.

Table 3. The effect of time

| Time/Min. | Abs.      |
|-----------|-----------|
| 2         | 0.783     |
| 5         | 0.783     |
| 10        | 0.785     |
| 15        | 0.789     |
| 20        | 0.782     |
| 25        | 0.781     |
| 30        | 0.779     |
| 90        | 0.778     |
| 120       | 0.630     |
| 24 h      | 0.148     |

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

Table 4. The effect of reagent conc.

| Conc. of L. X 10⁻³ | Abs.   |
|--------------------|--------|
| 0.500              | 0.075  |
| 0.700              | 0.159  |
| 1.200              | 0.471  |
| 1.500              | 0.565  |
| 1.757              | 0.783  |
| 3.515              | 0.876  |
| 7.030              | 0.894  |

3.6. Construction of calibration curve
The absorbance of copper ion complex was found to be linear depending on the concentration of metal Beer's law obeyed in the concentration range \((3.211 \times 10^{-5} \text{ M} - 22.480 \times 10^{-5} \text{ M})\) with molar absorptivity of \((0.622 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})\), Fig. (4) shown the calibration curve of copper ion ion and table (5) shown the analytical data to determine copper ion by reagent.

![Calibration curve](image)

| Analytical Data                  | Value                      |
|----------------------------------|----------------------------|
| Regression equation              | 615.63x                    |
| Linear range [M]                 | \((3.211 \times 10^{-5} \text{ M} - 22.480 \times 10^{-5} \text{ M})\) |
| Detection limit                  | 1.943 \times 10^{-6} \text{ M} |
| Molar absorptivity              | \(0.622 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}\) |
| Correlation coefficient \(\lambda_{\text{max}}\) | 0.9966                     |
| Temp.                            | 25°C                       |
| Time                             | 90 min                     |
| Colour of product                | dark brown                 |

3.7. Stoichiometry of complex
To explain the equivalent between copper ion and reagent in the complex was depend the following method:

3.7.1. Mole Ratio method
By using a known and constant concentration from copper ion \((1.757 \times 10^{-4} \text{ M})\) with increasing concentration from reagent (Michler’s thioacetone) \((0.363 \times 10^{-4} \text{ M} - 7.310 \times 10^{-4} \text{ M})\)

The method shows that copper ion forms a (1:2) complex (metal-L) with reagent.

![Mole Ratio method](image)
The Stability constant of the complex was calculated by using the equations in the following:

\[ M^{2+} + 2L^- \rightarrow ML_2 \alpha C \]

\[ k = \frac{[ML]^2}{[M^2]^3} \] \hspace{1cm} \ldots (1)

\[ k = \frac{(1 - \alpha)C}{\alpha C(2\alpha C)^2} \] \hspace{1cm} \ldots (2)

\[ \alpha = \frac{A_m - A_s}{A_m} \] \hspace{1cm} \ldots (3)

**Table 6. The stability constant value of complex**

| Complex      | Value \( A_s \) | Value \( A_m \) | \( \alpha \) | \( K \)   |
|--------------|-----------------|-----------------|-------------|---------|
| \([Cu (L)_2]\) | 0.352           | 0.510           | 0.309       | 1.898 \times 10^8 |

3.7.2. **Molard method**

- 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 (A_m = 0.214).
- 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 (A_L = 0.366).

\[ mC+ 1C \rightarrow M L \]

\[ L/ M = 0.366 / 0.216 \]

\[ = 1.69 \]

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

3.8. **Effect of interference**

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

3.8.1. **cation effect**

**Table 7. Effect of cation ion**

| Ion conc. | 50µg/mL | 200µg/mL |
|-----------|---------|----------|
|           | Abs.    | Error%   | Abs.    | Error%   |
| Cu⁺²      | 0.783   | -        | 0.783   | -        |
| Mg⁺²      | 0.833   | 7.000    | 0.956   | 14.942   |
| Fe⁺²      | 0.606   | -39.400  | 1.001   | 27.713   |
| Zn⁺²      | 0.590   | -24.648  | 1.080   | 37.931   |
| Pb⁺²      | 0.579   | -26.053  | 0.975   | 24.521   |
| Cu⁺²      | 0.682   | -12.899  | 0.975   | 24.521   |

3.8.2. **Anions effect**

**Table 8. Effect of anions**
The results of the two tables (7,8) showed the presence of some ions during the process of forming the copper 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\(^{(17)}\).

### 3.9. 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 | 0.783         |
| Formaldehyde        | 0.938         |
| Potassium tartrate  | 0.592         |
| Citric acid         | 0.335         |

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

### 3.10. 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% |
|----------------------|------------------------|------|--------|
| \(9.634 \times 10^{-5}\) | 0.062 , 0.062 , 0.065 , 0.061 , 0.063 | 0.637 | 0.967  |
| \(16.05 \times 10^{-5}\) | 0.103 , 0.101 , 0.107 , 0.105 , 0.110 | 0.502 | 1.941  |
| \(19.266 \times 10^{-5}\) | 0.153 , 0.152 , 0.161 , 0.154 , 0.160 | 0.374 | 2.912  |

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

### 3.11. Infrared Ray Spectrum
Table 11. Explain interpretation of Infrared ray spectrum

| Compound | V(N-H) | V(C-H) | V(C=S) | V(C=C) | V(C-N) | V(M-L) |
|----------|--------|--------|--------|--------|--------|--------|
| Ligand   | 3383.26| 3043.77| 1950.00| 1664.62| 1381.08| 1604.83|
|          |        |        | 1800.00|        |        |        |
| Complex  | 3086.21| 1848.25| 1591.33| 1367.58| 470.65 | 1527.67|
|          |        |        | 1800.10|        |        |        |

4. The chemical Stoichiometry suggest of complex
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