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RESEARCH ARTICLE

Spectrophotometric Determination of Mercury (II) With Michler'sthioketon Reagent

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Abstract

A new simple, rapid and sensitive spectrophotometric method has been develop to determine mercury (II) ions by using Michler's thioketone reagent (Ligand) to formed a dark blue complex at (pH=7), The complex was found to be with stability for(120 min)at the given pH , The complex formed in this method give obeys Beer's law over the concentration range (1.473x10-5 M–10.313x10-5M) with a detection limit of (5.235x10 -7 M)and molar absorptivity (0.339x104 L mol-1cm-1) ,The Stoichiometry of the complex was confirmed by using(Mole Ratio method &Molard method) the two methods using indicated the ratio of reagent to metal is 1:1,The effect of the presence of different cations and anions as interference in the determination of mercury (II) under the given condition were investigated, The mercury 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 analytical error.

Keywords: *Michler'sthioketon Reagent, Stoichometry, Absorptivity.*

Introduction

Mercury is one of the best know highly toxic contaminants occurring in different environments, mercury considered as carcinogenic compound, mercury accumulation in biological system leads to neurological disorder, damage of the respiratory and cardio vascular system and the gastro intestinal tract, According to the statement above the threshold limit value of mercury ion in drinking water is 2ppb , So that analysis of mercury with highly selective and sensitive was very important to avoid the clinical toxicology[1, 4], The mercury toxicity is depends on its chemical composition, Some mercury compound s are relatively non-toxic and have been used as medicines, e.g., for the treatment of syphilis [5, 6].

A wide variety of mercury determination techniques has been developed. The most of these techniques are depend on analytical instrumentation methods. The two popular methods are atomic fluorescence spectrometry and cold-vapor atomic absorption spectrometry. These methods can determine mercury with very high sensitivities. In addition to analytical instruments, various mercury sensors provide a convenient means to determine both abiotic and biotic mercury [7, 9].The present work as many method, The procedure is developed for the trace determination of mercury (II) in aqueous solution by using Michler'sthioketone reagent (Ligand), The reagent Michler's thioketone is an organic compound has the chemical name [4,4'-Bis (dimethylaminothiobenzophenone)] with molecular formula ($C_{17}H_{20}N_2S$), Formula weight (284.42g/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 the good using of Michler's thioketone as reagent to spectrophotometric determination of many trace elements in different solution [10, 14], This study was aim to constructed new chemical method to determining mercury in

aqueous solution, The method properties with fast, simple, low-cost, and accurate determination of mercury. The procedure was highly selective and fairly sensitive.

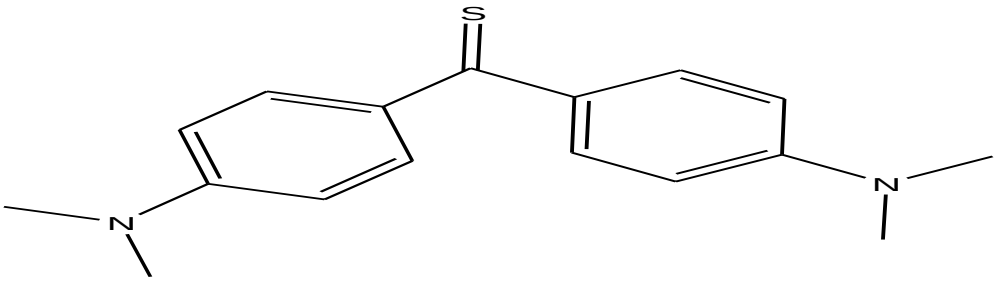

Fig 1: Michler's thioketon Reagent

Practical Part

Material and Reagent Requirement

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

Prepare of Standard Solution

- Prepare $3.683x10^{-3}$M of the mercury (II) ion as stock solution by dissolve 0.1g) from the mercury chloride $HgCl_2$ in 100mL distilled water
- Prepare $1.757x10^{-3}$ M of the Michler'sthioketon solution by dissolve 0.1g 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 the salt of each one in 100mL distilled water.
- Prepare the inions ions solution ($C_2O_4^{-2}$, $S_2O_3^{-2}$, I^-) by dissolve (0.1g) from the salt of each one in 100mL distilled water.
- Prepare the masking agent in 0.1M (Citric acid, dipotassium tartrate and formaldehyde) in distilled water.
- 6-Prepare (1M) Hydrochloric acid and (1M) Sodium hydroxide, to adjust the pH of solution.

Instrumentals Used

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

Unvaried Optimization

Procedure

The test solution containing ($2.945 x10^{-4}$ M) mercury was taken in 10mL beaker, 2.5mL of ($1.757x10^{-3}$ M) reagent ,1mL of buffer solution at (pH=7),The solution was Transferred to 20mL volumetric flask then diluted to the mark with absolute ethanol and then absorbance was measured at (626nm) against the blank solution.

Results and Discussion

Absorption Spectra

The absorption spectra of (reagent and mercury (II) complex shown in Figures (2, 3), The reagent solution spectra is given (λ_{max}=481), While the mercury (II) complex formed at (pH=7) is given the absorption maximum at (628nm), So that the formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately 147nm optimization of variables.

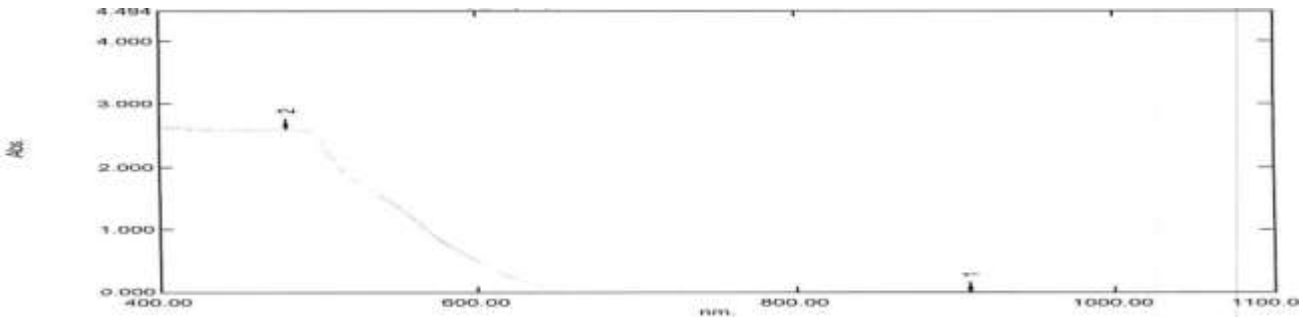

Figure 2: Absorption spectra for Michler'sthioketon reagent

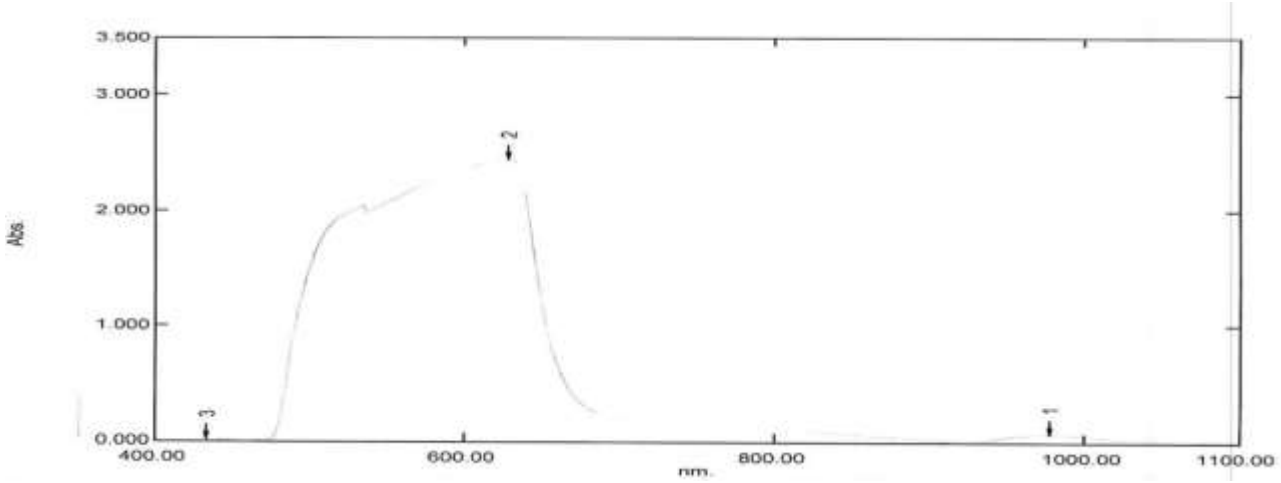

Figure 3: Absorption spectra for mercury complex

Effect of PH

Standard amount of mercury (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 (626nm).

Table 1: The Effect of pH

pH	Abs.
1	0.230
2	0.325
3	0.393
4	0.417
5	0.485
6	0.526
7	0.649
8	0.165
9	0.120
10	0.030

The result in table (1) showed that the absorbance was increased gradually as the pH increased from (1.0-7.0), but decreased rapidly (above pH 7.0), the increased in the mercury complex solution absorbance under these conditions may be explained by an increasing the sensitivity of the reagent at this value of pH.

Effect of Additive Sequencing

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: Effect of Additive sequencing

Sequence of Number	Sequence of Addition	Abs. of Cu Complex
1	M+L+PH	0.649
2	L+PH+M	0.363
3	M+PH+L	0.294

M = Mercury 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 mercury 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 mercury complex and remains stable (in terms of absorption values) 120 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 mercury parasitically.

Table 3: Effect of time of stability of the complex

Time/Min.	Abs.
2	0.649
5	0.648
10	0.649
15	0.649
20	0.648
25	0.647
30	0.640
90	0.642
120	0.640
24 h	0.271

Effect of Reagent Concentration

The result in Table (4) showed the effected of reagent concentration on the absorbance of the mercury complex at (pH=7), from the result was explained that the absorbance was increased with increasing of the reagent concentration.

Table 4: Effect of reagent concentration

Conc. of L.x 10^{-3}	3.515	7.030	1.757	1.500	1.200	1.00	0.700	0.500
Abs.	0.801	0.722	0.649	0.250	0.203	0.150	0.060	0.018

Construction of Calibration Curve

The absorbance of mercury ion complex was found to be linear depending on the concentration of metal, Beer s low obeyed in the concentration range (1.473x 10^{-5} M-10.313x10^{-5} M) with molar absorbtivity of (0.339x10^4 L $mol^{-1}cm^{-1}$), Figure(4) shown the calibration curve of mercury ion and Table (5) shown the analytacal data to determine mercury ion by using Michler'sthioketon.

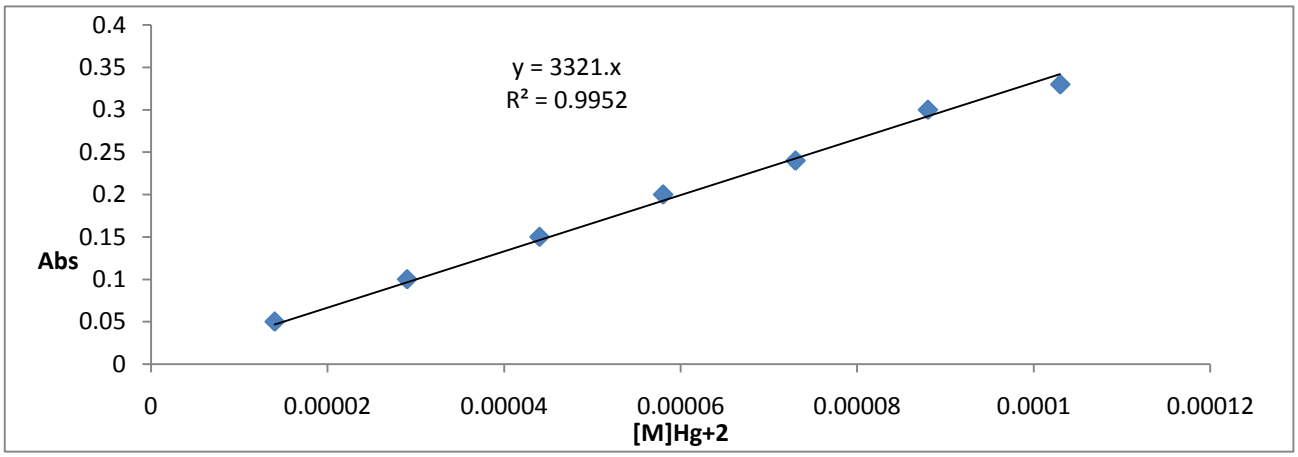

Figure 4: calibration curve of Hg2+ ion

Table 5: Analytical data to determine mercury (II) ion

Analytical Data	Value
Regression equation	3321.6x
Linear range	(1.473x 10^{-5} - 10.313x10^{-5}) M
Detection limit	5.235x10^{-7} M
Molar absorptivity	0.339x10^4 L $mol^{-1}cm^{-1}$
Correlation coefficient	0.9952
λ max	626nm
Temp.	25 ^{0}C
Time	120 min
Color of product	dark blue

Stoichiometry of Complex

To explain the equivalent between mercury ion and reagent in the complex was depend the following method: Mole Ratio method by using a known and constant concentration from mercury ion (1.757 x 10^{-4}M) with increasing concentration from reagent (Michlersthioketone) (0.363x 10^{-4}M-7.310x10^{-4}M), the method shows that mercury ion forms a (1:1) complex (metal-Ligand) with reagent.

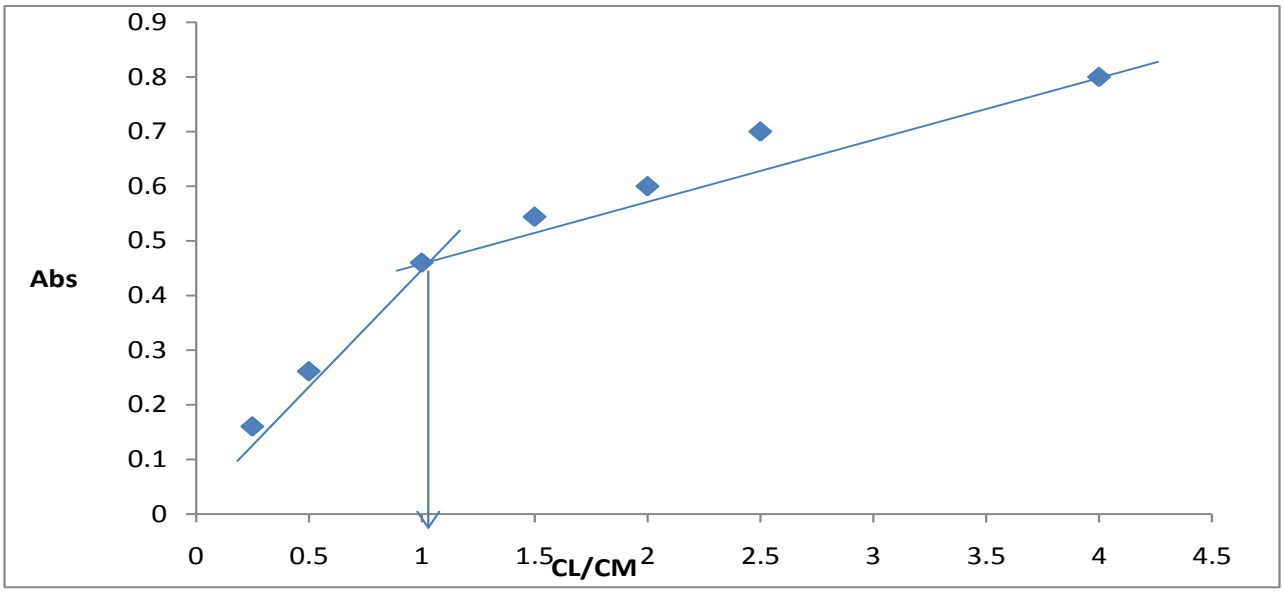

Figure 5: Mole Ratio method

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

$M^{+2} + L \longrightarrow ML$

αC+ αC (1-α)C

K = [ML] / [M] [L] ……. (a)

K= (1-α) C / α2C2 …….. (b)

α = Am –AS / Am ….. (c)

Table 6: Stability constant value of complex

Complex	Value As	Value A_m	α	K
[Hg L]	0.461	0.830	0.445	$1.594* 10^4$

Molard Method

- By taking 1mL ($1.757x10^{-4}$M) from mercury ion with excess ($4.535x\ 10^{-4}$M) from reagent adjust the pH=7, Then measured the absorbance (A_m = 0.464).
- By taking 1mL ($1.757x10^{-4}$ M) from reagent with excess ($3.683x\ 10^{-3}$M) from mercury ion adjust the pH=7, Then measured the absorbance (A_L = 0.401).

mC□□1C □□M L

L/ M =0.461 / 0.401

= 1.1

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

Effect of Interference

The absorption values of the mercury 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).

Cations Effect

Table 7: Effect of adding cations

Ion conc.	50µg		200µg	
	Abs.	Error%	Abs.	Error%
Hg^{+2}	0.649	-	0.649	-
Mg^{+2}	0.303	-53.312	0.303	-53.312
Fe^{+2}	o.433	-33.281	0.508	-21.725
Zn^{+2}	0.317	-51.155	0.395	-39.137
Pb^{+2}	0.313	-51.771	0.351	-45.916
Cu^{+2}	0.374	-42.372	0.428	-34.052

Inions Effect

Table 8: Effect of adding anions

Ion conc.	50µg		200µg	
	Abs.	Error%	Abs.	Error%
Hg^{+2}	0.649	-	0.649	-
$C_2O_4^{-2}$	0.293	-54.853	0.353	-45.608
$S_2O_3^{-2}$	0.103	-84.130	0.277	-57.318
I^{-1}	0.083	-87.210	0.160	-75.346

The results of the two Tables (7and 8) showed that the presence of some ions during the process of forming the mercury 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[15].

Masking Agent

For the purpose of selecting the efficiency of the Masking agents on the selectivity of mercury 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: Addition 1mL (0.1M) from masking agent

Masking agent	Abs.
Without Masking agent	0.649
Formaldehyde	0.825
Potassium tartrate	0.716
Citric acid	0.206

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 Accuracy and Precision studies

Conc. of M	Abs. of mercury complex	RSD%	Error%
4.419×10^{-5}	0.153 ,0.154, 0.161, 0.157, 0.150	0.374	- 1.307
7.366×10^{-5}	0.240, 0.260 , 0.250 ,0.261, 0.252	0.763	-5.250
8.839×10^{-5}	0.314, 0.321, 0.350, 0.410, 0.305	3.811	-12.73

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

Infrared Ray Spectra:

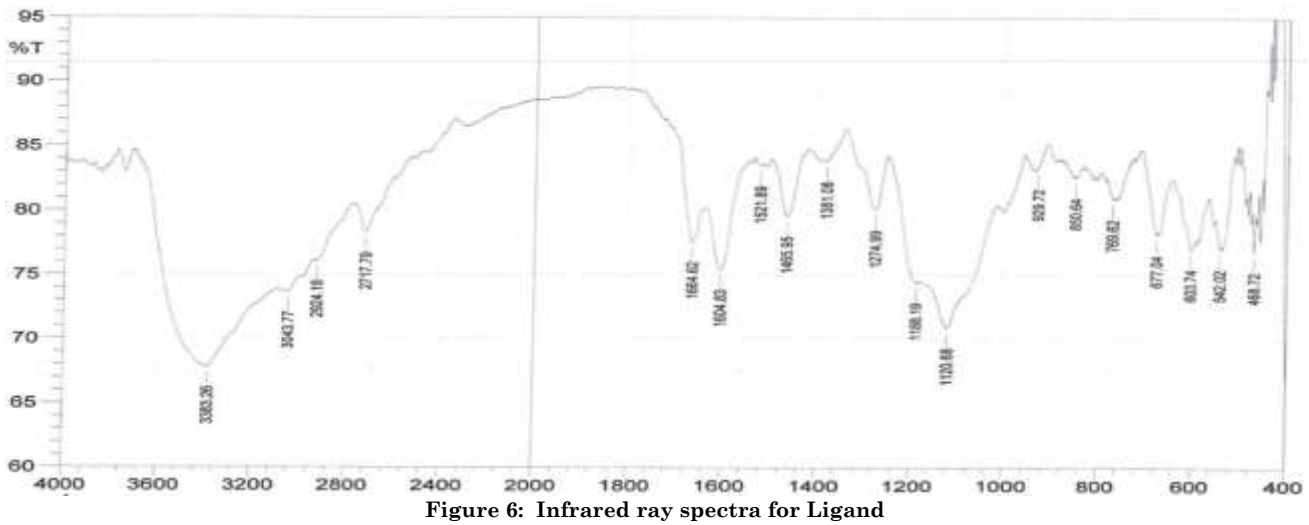

Figure 6: Infrared ray spectra for Ligand

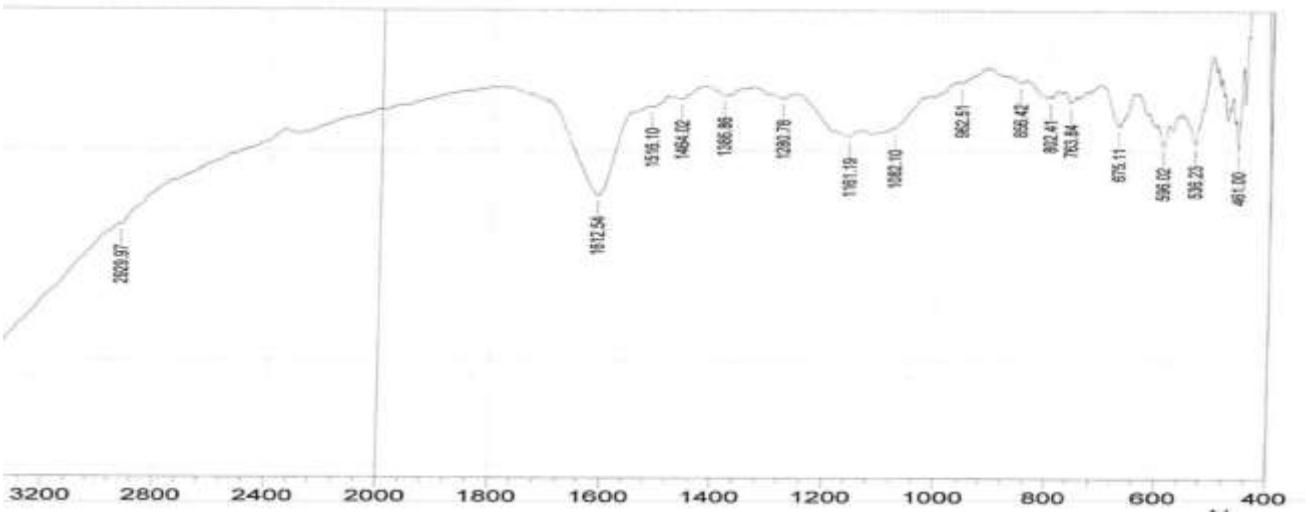

Figure 7: Infrared ray spectra for copper complex

Table 11: interpretation of Infrared ray spectra

Compound	V(N-H)	V(C-H) Aro.	V(C=S)	V(C=C)	V(C-N)	V(M-L)
Ligand	3383.26	3043.77	1950.00-1800.00	1664.62-1604.83	1381.08	---
Complex	-----	2929.97	1848.25-1800.10	1612.54- 1516.10	1280.78	461.00

The Chemical Stoichiometry Suggest of Complex

The Figure (8) explain the chemical stoichiometry suggest of the mercury complex.

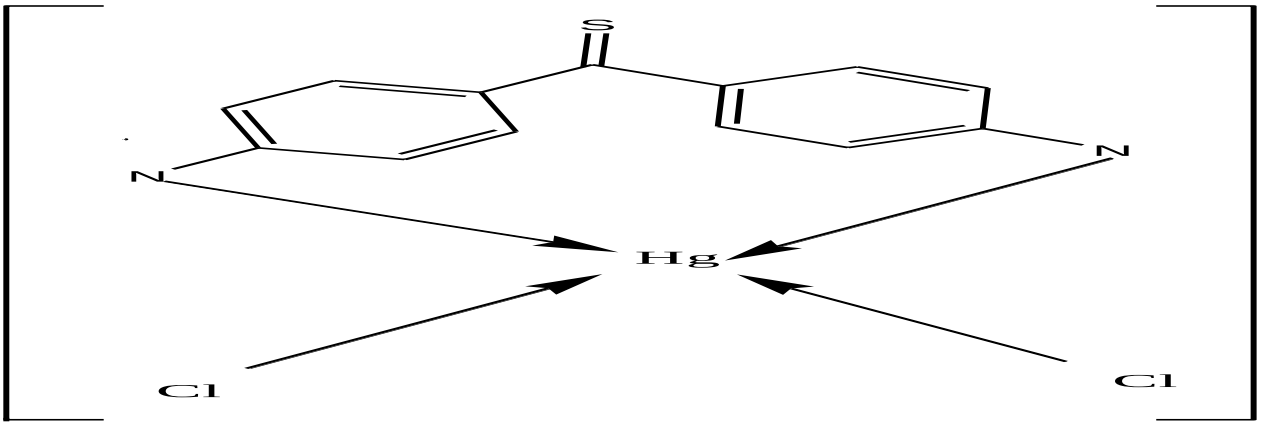

Figure 8: The chemical stoichiometry of compels

Conclusions

- The possibility of using the Reagent (Michler'sthioketon) in the spectral determination of the mercury (II) ion under optimum condition obtained was ratio of 1:1 (M: L).
- The analytical method is easy, sensitive, well-controlled and accurate. No complexity requires any complexity such as separation or other treatments.
- The formation of sharp dark blue color for the comples makes the method sitable for Spectrophotomtric analysis.

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