Spectrophotometric Determination of Micro Amount of mercury (II) Using an New of (Azo) Derivative, Study of Thermodynamic Functions and Their Analytical Application

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Abstract

In This study is preparation and diagnosis of new Ligand is 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole) (BMTI), one of the azo compounds. And that of the traditional method of azoth. The study also considered the use of this reagent to express spectroscopy for mercury (II) ion in the binary solution of water, where it was noted that the reagent be complicated the light red with the ion and shows the greatest absorption at λ_{max}= (538) nm (pH = 10). Was found to be a complex mercury duo Reagent with a stable of more than (48hours) when the pH best with compliance to Beer's law in the range of concentrations ranging between (0.2 – 9.0 µg/mL) . The effect of several factors including the value of the absorption effect of reagent concentration, reaction time, masking agent , sequences of addition and the effect of different parameters such as effect cations and anions ,and the effect of ionic strength and temperature effect . the stoichiometry of complex was investigated by ratio of the reagent - metal molar ratios, Jobs (the constant changes) mollard methods showed that the proportion of the metal regent is (1:2), with molar absorptivity ($1.31x10^4$ L mol^{-1} cm^{-1}). Limit of detection (LOD) and Limit of quantification were (0.0288 µg/mL) and (0.0952µg/mL), respectively. . As has been the preparation of complex solid was studying some of his physical characteristics such as solubility and molar conductivity and the melting point of the complex. All compound has been characterized by spectroscopic methods [HNM].[mass spctrum] [FT.IR.,UV-Vis].(UV-Vis) absorption spectra show bathochromic shift)compared with that of free reagent) the results of the accuracy and precision of the method used to estimate the value of the element mercury percentile relative deviation (RSD%) ranged between(0.71% -1.42%) while the values of the relative error(E%) between (1.24 - 4.47) . The thermodynamic functions were also calculated by studying the effect of temperature. The method was applied to some environmental and industrial models, and the results were of high accuracy and precision.

Keywords: Azo dye (BMTI), mercury (II), Wells water and Spectrophotometry.

1. Introduction

Azo compounds are chemically represented as R–N=N-R', where –N=N- is the azo group and the R or R' can be either aryl or alkyl compounds. The International Union of Pure and Applied Chemistry (IUPAC) defines azo compounds as "derivative of diazene (diimide), HN=NH, wherein both hydrogens' are substituted by hydrocarbyl group, e.g. PhN=NPh azobenzene or diphenyldiazene" (1). The word azo comes from azote, the French name for nitrogen that is derived from the Greek a (not) zoe (to live) [1]. Amongst the synthetic dyes employed in the food industry, the azo dyes constitute around 65% of the commercial dye market [2,3]. These dyes have become an industrial choice worldwide due to low cost, ease of preparation, versatility, fastness, and intensity of colors [4] . Several industries like textile, leather, printing, fast food, and cosmetics flourish due to the prevalent use of azo dyes. Though, these industries contribute notably to a nation's economy, they have become an environmental challenge due to the injudicious discharge of untreated or partially treated effluent into the water, which is often directly used for irrigation [5,6]. Azo dyestuffs have attracted a broad interest in various biological applications. They have been considered as xenobiotic substances that are highly recalcitrant against biodegradation processes. They have been applied as acid/base indicators, textile and foodstuff colorants, and biological stains [7-9]. Mercury is an element that has highly toxic effects on living organisms and the environment due to its bioaccumulation and biomagnification process [10]. In human organism, it affects the nervous, gastrointestinal, respiratory and immune systems and kidneys [11,12]. Currently, mercury control has gained increasing interest from contamination control scholars and government sectors due to the high toxicity, volatility and bioaccumulation of mercury [13,14]. Through the last decade, different spectrophotometric methods have beendeveloped for simultaneous analysis of various components present in different combined pharmaceutical dosage forms. These methods have based on the application of mathematical equations or models. They have been applied for resolving any overlapping spectra of two or more components

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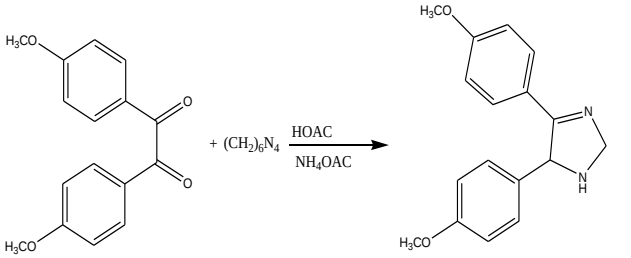
present in the same mixture or formulation without any need for chemical or physicochemical separation. Some of these methods require data processing either application of mathematical equations for the overlapped zero order absorption spectra, derivatization of the zero spectra of the components or deriving and manipulation of the ratio spectra which may be followedby extra derivatization step [15-17]

Practical part

-Preparation of the compound 4,5-dimer (4-methoxyphenyl) imidazole

In a (500mL) round flask, (2.70g, 0.01mol) of the benzyl derivative and (0.256g, 0.005mol) of hexamethylene tetraamine were mixed with (6.0g, 0.23mol) of ammonium acetate followed by adding (40ml) of acid. Ice acetic, and the solution was sublimated for a period of (90min) and after cooling the reaction product, (400g) of ice grits were added, then the ammonium hydroxide solution was added drop by drop to modify the acid function and obtain the imidazole derivative in the form of a white precipitate. The precipitate was filtered, and washed with water for several times to get rid of The remnants of the base and salts, and the product was dried and recrystallized from ethanol to obtain white crystals, dried and the melting point was measured (73-74C0), while the product was (84%).

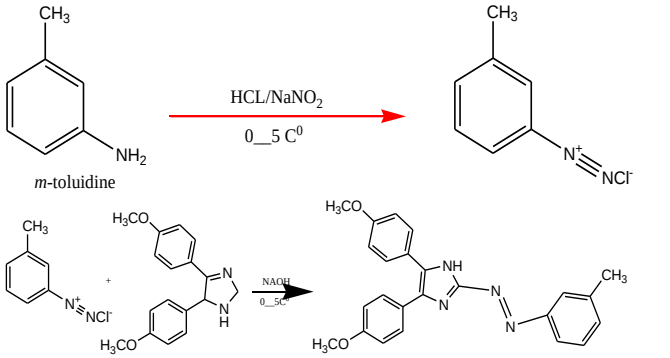


1,2-bis(4-methoxyphenyl)ethane-1,2-dione
Exact Mass: 270.09

2,5-dihydro-4,5-bis(4-methoxyphenyl)-1*H*-imidazole
Exact Mass: 282.14

A/Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (BMTI).

Synthesis of Ligand 4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole (B The new isoamidazole liquor was prepared from the diazonium salt pairs of the tlodine derivative with the derivative.Imidazole in an alcoholic medium by dissolving (1.08 ml, 0.01 mol) of methaldodine in a solution obtained by mixing (3 ml) hydrochloric acid with (50 ml) distilled water. 0.7 gm, 0.01 mol) of sodium nitrite dissolved in (10 ml) of distilled water drop by drop, taking into account stirring and maintaining the temperature below 5 C°, after which the solution was left to settle for a period of (30 minutes) to complete the nitrogenation process and obtain a solution Diazanium chloride. This salt solution was added gradually with continuous stirring to a solution (2.80 g, 0.01 mol) from the base pairs 5,4-dimethyl (methoxyphenyl) amidazole dissolved in a mixture of (150 ml) of ethyl alcohol and (15 ml). The sodium hydroxide solution (1 M) was observed to discolor the solution in an orange color. The solution was left for the next day, and the acidic function was modified down to (pH = 6) to obtain a reddish orange precipitate. The precipitate was filtered and washed with distilled water to get rid of the sodium chloride resulting from the pairs and neutralization process, and it was dried and recrystallized from ethanol to obtain the lycand in its pure form. The two equations below explain how to obtain the aforementioned licand izo.(MTI).



4,5-bis(4-methoxyphenyl)-2-(m-tolyldiazenyl)-1H-imidazole

2. Materials and Methods: B/

In this paper. All analytical reagents and solutions used in preparation are in high purity.

C/Preparation of Standard Solutions.

1-mercury (II) solution (1000µg/mL): - was prepared by dissolving(0.166 g) from [Hg(NO3)2].1/2H2O in 100 mL deionized water.

2-Sodium hydroxide solution (0.1M): - was prepared by addition of 100 mL deionized water to 0.4 g of sodium hydroxide.

3-Nitric acid solution (0.1M): - was prepared by diluting (0.18 mL) concentrated nitric acid (65%,1.41 g/cm3) in 50 ml deionized water.

4-Reagent solution (BMTI) (1000µg/ml):-was prepared by dissolving appropriate weight(0.1g) in absolute ethanol and complete the volume to(100mL)with ethanol.

Preliminary study

1ml of a solution of prepared mercury (II) (1000 µg /ml) was placed in a test tube, then 1ml of a solution prepared from a ligand (BMTI) (1000 µg / ml) was added to the test tube drop wise with shaking noting the color formation Or a precipitate, and then drops of nitric acid (0.1 M) were added to one part of this mixture and drops of NaOH (0.1 M) or HNO_3(0.1M) were added to the other part to study the effect of the acidic function. It was found that the color formed clearly in the basic medium while in the acidic medium there was a weak fading of the color

3. Results and Discussion

The spectra absorption

The absorption spectra of reagent and mercury (II) complex shown in Figures (1) ,The reagent solution spectra is given the absorption maximum at (λ_{max}=446.5),While the mercury (II) complex formed at (pH= 10) is given the absorption maximum at

(λ_{max}= 538nm), So that the formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately (94nm) optimization of variables.

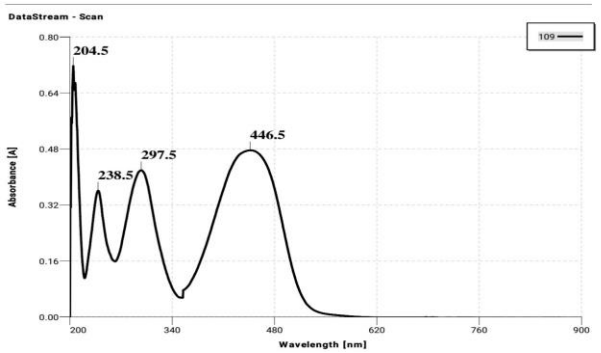


Figure (1): - The spectrum of reagent (BMTI)

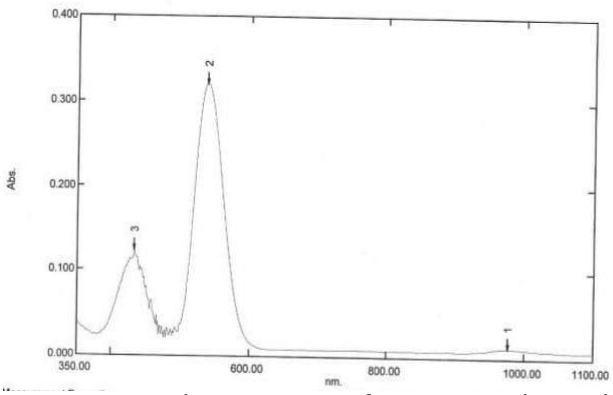


Figure (2): - The spectrum of Hg(II) complex with (BMTI) reagent.

The NMR of Reagent.

1 H-NMR

proton nuclear magnetic resonance spectrometry (1H-NMR) is an excellent tool to check the purity of the organic compounds, the 1H NMR spectrum of the ligand (L) was diagnosed in (DMSO-d6) as a solvent and at room temperature. The azo dye ligand displayed a signal singlet at 13.23 ppm (s, 1H, Ar-NH) is due to N-H in imidazole ring, and the signals due to twelve aromatic protons (m, 12H, Ar-H) have resonated as multiplets in the region (6.80-7.70 ppm) , while a proton resonated at (3.75 ppm) as singlet may be assigned to methoxy group at (s,6H,2× OCH3) Another singlet observed at (2.47 ppm) (s, 3H, CH3) , corresponds to methyl protons attached to the organic ring. Finally, the solvent signal appeared at (2.40 ppm) (DMSO).

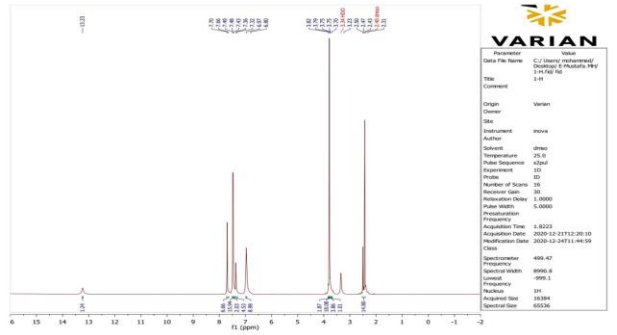


Figure3: - 1H. NMRspctrum (BMTI)

2- 13C-NMR

Ligand was diagnosed by using 13C NMR spectroscopy using DMSO-d6 as a solvent. It was observed that a signal appeared at the site (21.43 ppm) belonging to CH3 group, signal appeared at the site (55.61 ppm) belonging to OCH3 groups , signal appeared at the site (153.98) ppm belonging to (C1) , signal appeared at the site (152.95) ppm belonging to (C2), signals appeared at the site (120.65-139.43) ppm belonging to (C.Aromat) and finally, the solvent appeared at the site (40)ppm.

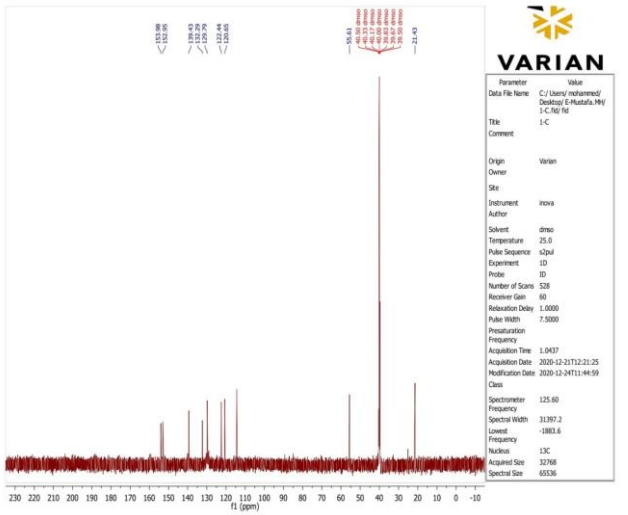


Figure4: - 13C.NMRspctrum (BMTI)

The Mass Spctrum

Ligand was diagnosed by the last sign shown in the figure (0-0), which shows the molecular weight of ligand (m/z = 398.3) [M^+].

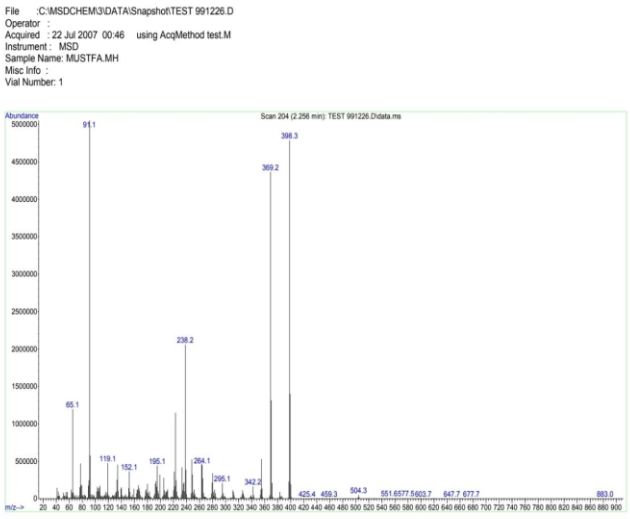


Figure5: - mass spctrum (BMTI)

Optimization of Reaction Conditions.

The pH effect.

Standard amount of mercury (ll) and reagent (BMTI) were buffered at different pH- range from (1 to 10) using HNO_3(0.1M)/ NaOH (0.1M) , the final pH of each solution was measured with a pH-meter and the absorbance measured at (538nm) at $20C^0$

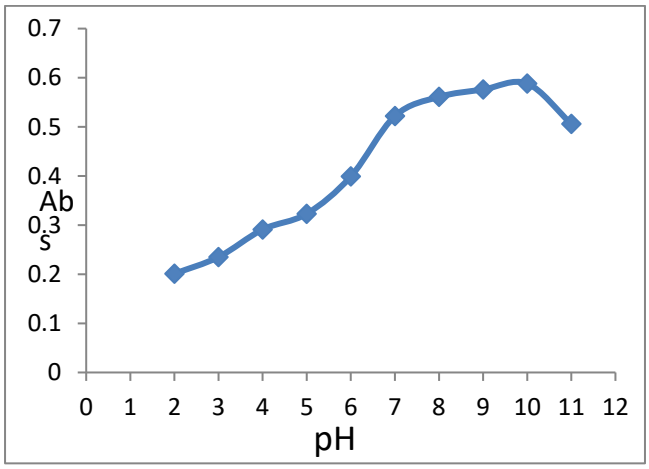


Figure (6). Effect of pH value

The result in table (1) showed that the absorbance was increased gradually as the pH increased from (2.0 – 10.0) , but decreased rapidly(above pH 11.0) , 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 [18] .

Effect of Time on stability of the complex: -

The results of table (1) show the follow-up reaction of the reagent with the ion using the best conditions, and these results indicate the composition of the mercury (II) complex and remains stable (in terms of absorption values) 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 (1):- The effect of time	
Abs.	Time/Min.
0.522	1
0.520	10
0.515	20
0.514	30
0.511	40
0.508	60
0.502	70
0.498	100
0.476	24h
0.472	48h

Effect size of reagent: -

The result in table (2) showed the effected of reagent concentration on the absorbance of the mercury complex at (pH=10) , From the result was explained that the absorbance was increased with increasing of the reagent concentration .

Table (2):- The effect of reagent concentration							
1.0	0.8	0.7	0.6	0.4	0.3	0.2	Volume Conc. of L. * 10-3
0.482	0.515	0.523	0.514	0.352	0.338	0.313	Abs.

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 (3)

Table (3) :- The effect of sequence		
Abs. of Hg Complex	Sequence of Addition	Sequence of Number
0.523	M+L+PH	1
0.512	L+PH+M	2
0.425	M+PH+L	3
M = copper ion , L = ligand , pH= function of hydrogen ion		

The result showed in table (3) 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.

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 (0.2 – 9.0 µg /mL) with molar absorbtivity of ($1.31 \times 10^4 Lmol^{-1} cm^{-1}$), Fig. (7) shown the calibration curve of mercury ion and table (5) shown the analytical data to determine mercury ion by using reagent (BMTI).

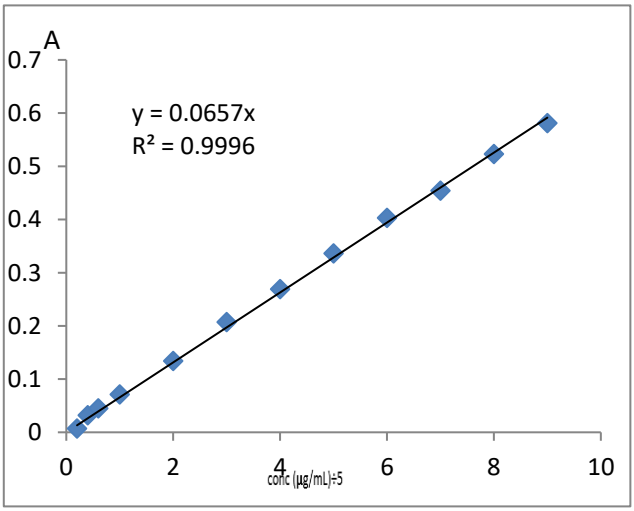


Figure 7. Calibration curve for Spectrophotometric determination of mercury(II).

Table (5) :- Analytical data to determine mercury (II)	
Value of Hg(II)	Analytical Data
Y=0.657x	linear equation
0.2 -9.0	Linear range [µg/mL]
0.0288	Detection limit(µg/mL)
0.0952	Limit of quantificationb (µg/mL)
1.31×10^4	Molar Absorpitivity ($Lmol^{-1}cm^{-1}$)
0.9988	linearity coefficient
0.042	Sandel sensitivity ($\mu g/cm^2$)
538nm	λ_{max}
20^0C	Temp.
90 min	Time
light red	Color of product

a Limit of detection (LOD)= (SD/S) *3.3

b (Limit of quantification) LOQ= (SD/S) *10

where SD is standard deviation, S is the slope of calibration curve.

Determination of Stoichiometry and Formation Constant

Mole ratio method and addition of Job`s method of continuous variations were chosen to study the composition of the complex formed, results illustrated in Figs 8 and 9. Both methods indicated that the ratio of metal ion to reagent molecules (M: L) was (1:2) at pH=10.

1- Mole Ratio method: -

by using a known and constant concentration from mercury (II) ion (3.988 x 10 $^{-5}$ M) with increasing concentration from reagent (BNTI) (1.994x10^{-5} - 13.958x10^{-5}M) ,The method shows that mercury(II) ion forms a (1:2) complex (metal -L) with reagent .

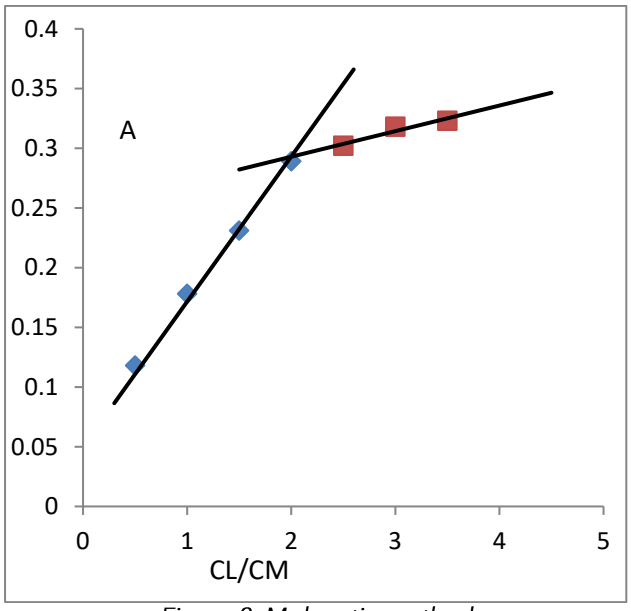


Figure 8. Mole ratio method

Mole ratio method was used to determin the stability constant of the colored complex depending on the equilibrium reaction for the complex . Calculations illustrated in Table 7.

$M^{+n} + nL^{-} \longrightarrow MLn$-----1

$K_{stability\ constant} = [ML^{+n}]/[M^{+n}][L^{-}]^{n}$ ….2

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

Where (Am) is the maximum absorption and (As) is Absorption at the stoichiometry.

Table (6) :- The stability constant value of complex				
Complex	AmValue	Value As	α	K ×10^{9}
[Hg (BMTI)$_2$]	0.323	0.2991	0.099	1.46

The results in Table 6 explain that the complex has high stability, for that it is possible to use the ligand (BMTI) in the spectral estimation of mercury(II) ion.

2- Job`s method

In this method mixture of different volumes of the solution in equal concentration (3.988x10^{-5} M) from both ion (Hg^{+2}) and ligand were mixed.

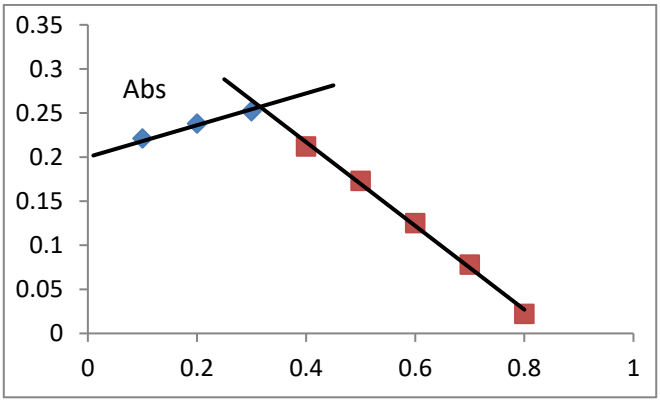


Figure 9. Job`s method of continuous variations.

The effect of add buffer solutions.

To study the effect of the type of buffer solution on the absorbance of the mercury (II) complex, three types of buffer solutions were tested and to note the difference in the absorption values of the mercury (II)ion complex with the reagent (BMTI) using optimal conditions and the results are shown in Table (7).

Table 7. The effect of adding buffer solutions.		
Abs. A	Buffer Solution	No. N
0.428	Ascorbic	1 11
0.522	Citric acid	2 2
0.376	Acetate	3
Absorption before adding to the mercury (II) complex 0.523		

From the results, we find that the absorption of the mercury (II) complex and the presence of the buffer solution is less than the absorption obtained with the use of nitric acid and dilute sodium hydroxide, so the amendment of the acidic function was limited by using an acid or base only to obtain a high sensitivity and accuracy for the determination of the mercury (II) ion

-Accuracy and Precision of the Described Method.

Accuracy and precision were determined for the applied method in term of recovery and relative standard deviation (RSD%), respectively. Results of recovery and RSD% were illustrated in table 9.

Table 9. Accuracy and precision studies.				
Error%	Recovery%	RSD%	Conc.of Hg^{+2} found[M]	Conc.of Hg^{+2} present[M]
4.47	97.40	1.42	9.711*10^{-6}	9.970*10^{-6}
3.06	99.21	1.01	1.978*10^{-5}	1.994*10^{-5}
1.24	98.24	0.71	3.918*10^{-5}	3.988*10^{-5}

Results in Table (9) explain that the developed method was precise as the value of relative standard deviation was <2.0%.

The effect of temperature on the stability constant for the Hg-BMTI complex.

The values of stability constant of Hg(II) with the reagent (BMTI) were studied at various temperatures ranged from (10-35)oC. The results are illustrated in Table (10)

Table 10. The effect of temperatures on the stability constant for Hg(II)complex.					
$K*10^{10}$	α	As	Am	T(K)	$T(C^0)$
9.454	0.1138	0.218	0.246	283	10
7.821	0.1209	0.189	0.215	288	15
6.635	0.1274	0.185	0.204	293	20
5.606	0.1344	0.161	0.186	298	25
5.010	0.1392	0.136	0.158	303	30
4.240	0.1468	0.122	0.143	308	35

Results obtained in Table 8 explained that there is a limited effect of temperatures on the stability of complex.

Thermodynamic Function of the Complex.

Thermodynamic function ΔH, ΔG and ΔS were calculated, results were illustrated in Fig 10 and Table .

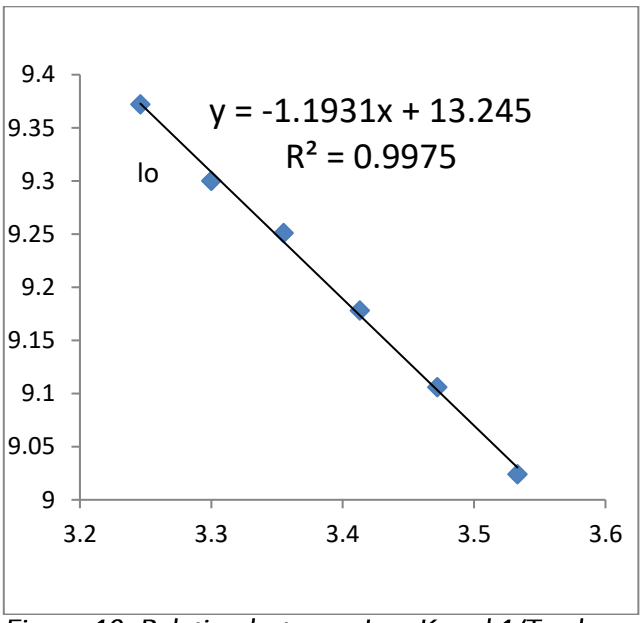


Figure 10. Relation between Log K and 1/T values for mercury (II) complex.

Table 11. The effect of temperature on thermodynamic function for mercury(II) complex.					
ΔS (K.J/mole.K)	ΔG (K.J/mole)	ΔH	log K	$1/T*10^{-3}$ (K^{-1})	T(K)
0.25350	-48.897	22.844	9.024	3.533	283
0.25367	-50.213		9.106	3.472	288
0.25369	-51.489		9.178	3.413	293
0.25378	-52.784		9.251	3.355	298
0.25345	-53.954		9.300	3.3	303
0.25361	-55.269		9.372	3.053	308

Positive value of enthalpy explained that the reaction was endothermic for that, it can be noted by inecreasing the temperature the possibility of. complex formation will increased, in addition to that the reaction was spontaneous according to the negative sign of free energy. The stability of the complex was confirmed due to the value of entropy which approach to zero(less random and spontaneous).

Study of FT-IR Spectra for Ligand and Complex

Figures 11-12 and Table 10 explain the FT-IR study and the absorption frequencies for reagent and the reagent-BMTI.

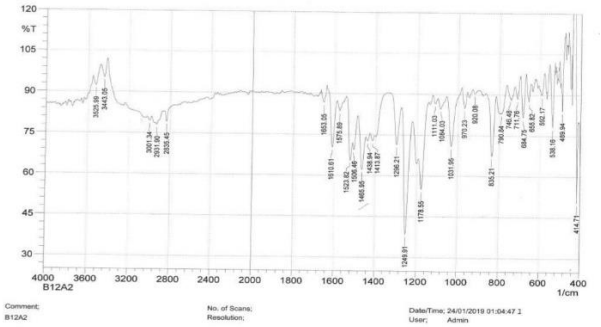


Figure 11. FT-IR spectrum of ligand.

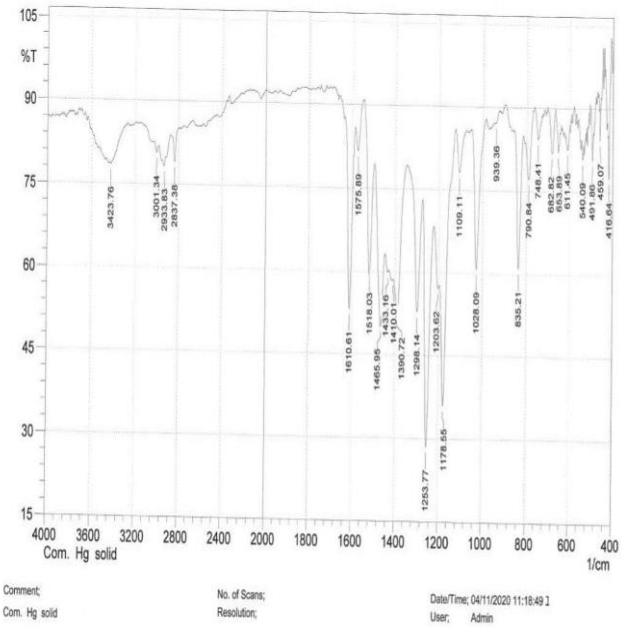


Figure 12. FT-IR spectrum Hg(II) of complex.

Application

Samples were prepared from tap water and tea leaves and then added to Ligand (BMTI) to detect mercury concentration in these samples and the results are shown in Table 12.

Table 12. Result of the application for mercury(II) in samples.		
Flam atomic absorption Hg^{+2} mol / L	Spectrophotometric method Hg^{+2} mol / L	Sample
1.330×10^{-6}	2.891×10^{-6}	Tap water
6.281×10^{-6}	10.80×10^{-6}	Ain al tamer
18.899×10^{-6}	24.27×10^{-6}	Al-gadwal gharbi

4. Conclusion

A very sensitive method for quantifying mercury in multiple samples has been developed and is also inexpensive for quantifying Hg (II). Verification and application studies demonstrated that Hg (II) can be quantified using this developed method. The results obtained showed that the reagent is able to quantify mercury (II) in many samples. Analytical parameters such as identification, detection limit, accuracy, and recovery indicate that this method can be successfully applied to determine Hg (II).

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