

## Spectrophotometric Determination Of Bismuth (III) Using An Organic Reagent 2-Methyl -4- (3,4- Dihydroxy Phenyl ) Thiazole Hydrochloride

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### Abstract

A preliminary study of the reaction between the reagent (2Me) 2-Methyl-4-(3,4-dihydroxy phenyl) thiazole hydrochloride as thiazole derivatives with some metal ions , and a spectrophotometric method for the determination of Bismuth (III) with this reagent was established. The wavelength of maximum absorption for the complex formed between this ion with this reagent was found to be (328) nm for bismuth, the optimum conditions for the determination of this ion was employed , such as the volume of reagent solution , time, temperature and effect of pH.

Calibration curves were constructed and Beer's law was obeyed in the range of (0.3-10) ppm for bismuth with a correlation coefficient ( $r = 0.9983$ ) with molar absorptivity  $\epsilon = 9.529 \times 10^3 \text{ L. mol}^{-1} \cdot \text{cm}^{-1}$ . The stoichiometry of the soluble formed complex was investigated by both the continuous variation and mole ratio methods , the ratio (M:L) was (1:1) for bismuth complex . The degree of dissociation ( $\alpha$ ) and the stability constant ( $K_{\text{sta}}$ ) of the complex was calculated . Where ( $\alpha = 0.160$  ,  $K_{\text{sta}} = 1.34 \times 10^5 \text{ L. mol}^{-1}$ ) for bismuth complex, this prevails that this complex have a high stability .

Precision and accuracy of the analytical procedure showed for (5.0) ppm of Bi(III) that R.S.D% was equal to (0.76)% and ( $E_{\text{rel.}}$  ,  $R_e$  )% were found to be (2.0, 102.0)% for this ion , with detection limit equal to ( 0.109) ppm for Bi(III). Its complex was showed to be neutral , by passing a solution of each complex through cationic and anionic resin.

The interferences of  $\text{Hg}^{2+}$  ,  $\text{Fe}^{3+}$  ,  $\text{W}^{6+}$  ,  $\text{Mo}^{6+}$  ions on  $\text{Bi}^{+3}$  as well as the studied ions were described , and they masked with suitable masking agents .

### الخلاصة

أجريت دراسة أولية لتفاعل الكاشف (2Me) 2-مethyl-4-(3,4-ثنائي هيدروكسي فنيل ) ثيازول هيدروكلوريد ، أحد مشتقات الثيازول مع أيون Bi(III) مع استحداث طريقة طيفية لتقديره باستخدام هذا الكاشف ، إذ كان الطول الموجي للامتصاص الأعظم للمعقد هو (328) نانوميتر ، فضلاً عن تحديد الظروف الفضلى لتقدير هذا الايون بهذا الكاشف مثل حجم محلول الكاشف ، والفترة الزمنية ، و درجة الحرارة وتأثير الدالة الحامضية . حدد منحني المعايرة للمعقد مع الكاشف فكان مدى التراكيز التي تطاوع قانون بير بالنسبة للبيزموت (III) يقع ضمن المدى (0.3-10) جزء بالمليون وبمعامل ارتباط  $(r = 0.9983)$  وقيمة معامل الامتصاص المولاري  $\epsilon = 9.529 \times 10^3 \text{ لتر. مول}^{-1} \cdot \text{سم}^{-1}$  . درست طبيعة المعقد الذائب المتكون من خلال إيجاد نسبة الايون الفلزّي إلى الكاشف (L:M) باستعمال طريقتي التغيرات المستمرة والنسب المولية فكانت تساوي (1:1) بالنسبة للمعقد البيزموت. جري حساب درجة التفكك ( $\alpha$ ) وثابت الاستقرار ( $K_{\text{sta}}$ ) للمعقد المتكون فكانت قيمتها بالنسبة للمعقد البيزموت ( $\alpha = 0.16$  و  $K_{\text{sta}} = 1.34 \times 10^5 \text{ لتر. مول}^{-1}$ ).

حدد ضبط الطريقة التحليلية المتبعة ودقتها باستعمال محاليل قياسية من هذا الايون مع تركيز قياسي للكاشف فكانت بالنسبة إلى تركيز (5.0) جزء بالمليون بزموت (III) ( $R.S.D = 0.76\%$ ) و ( $E_{\text{rel.}} = 2.0\%$ ) و ( $R_e = 102.0\%$ ) و ( $D.L = 0.109$ ) جزء بالمليون . كما عينت شحنة المعقد الذائب وذلك من خلال إمرارها على مبادل ايوني موجب وعلى آخر سالب ووجد إنها متعادلة. كما عينت التداخلات المحتملة لايونات  $\text{Hg}^{2+}$  ,  $\text{Fe}^{3+}$  ,  $\text{W}^{6+}$  ,  $\text{Mo}^{6+}$  بوجود الايون قيد الدراسة والتي يمكن أن تتداخل مع بعضها البعض ، إذ تم الحجب باستعمال عوامل حجب مناسبة .

### Introduction

Bismuth element discovered by J.Geoffroy in 1753 have a melting point equal 271.3 and the poling point equal to 1560 , its have a two equivalent state (III) and (V) (Smith 1973) and the one state it's the more common ,in recent years, a lot of

researcher determined its element because the biological important for bismuth in treatment of intestine turbulent (Nechamkin 1968) .

Therefore determined bismuth by used the (PAN) 1-(2-pyridylazo)-2-naphthol with the detection limit 0.5 ppm(Nemman and Farage 1994) , also make Shams (Shams 2001) determine of the Bi(III) by using the reagent Alizarine Red S by the linearity less than 0.03 ppm and the detection limit 0.0001ppm ,the table (1) refer to the some of the organic reagent using for determination of bismuth spectrophotometer.

**Table (1) Organic Reagent used for determination of Bi**

No.	Organic Reagent used	$\lambda$ max (nm)	Linearity ppm	$\epsilon$ L.mol <sup>-1</sup> .cm <sup>-1</sup>	Ref.
1	5-iodo-5-(dimethylamino)-2-(2-pyridylazo)phenol (IDEPAP)	590	>0.001	$6.5 \times 10^4$	Abbasi 1988
2	N,N'-bis(2-Hydroxyethyl) glycine	—	1 -70	$4.4 \times 10^3$	Lopez 1988
3	O-hydroxyhydro quinonephthalein	520	>3.5	$9.03 \times 10^4$	Mori,etal 1988
4	Cyanex 301	439	0.5 – 3.0	$5.53 \times 10^3$	Argekar and Shetty 1995
5	1(4 <sup>-</sup> -bromophenyl) 4,4,6-Trimethyl (1H,4H)-Pyrimidine-2-thiol (4bromo PTPT)	410	2 – 14	$1.5 \times 10^4$	Kolekar,etal 1998
6	1-amino-4,4,6-Trimethyl(1H,4H) Pyrimidine-2-thiol	470	7 – 24	$6.501 \times 10^3$	Gaikwad,etal 2005
7	1,2-Diaminocyclohexane-N,N,N',N' - tetraacetic acid (DACT)	267	1.67 – 8.36	□	Krzek,etal 2007
8	4-(2-pyridylazo) Resorcinol(PAR)	530	0.04 – 0.4	$2.9 \times 10^4$	Dedkova,etal 2010

## 2. Experimental

### 2.1. Apparatus

- Melting point was recorded by using Gallen kamp melting point apparatus.
- FTIR spectra were recorded as CsI discs using FTIR 8400 S Shimadzu in the range of 4000-200 cm<sup>-1</sup>.
- Electronic spectra were obtained using UV-1650 Shimadzu spectrophotometer
- Spectrophotometer PD- 303 UV From APEL

e- Elemental analyses C, H, N,S were performed using a EURO EA 3000 Single elemental analyzer.

f- Sensitive balance Sartorius.

g- PH meter WTW .

### 2.2 Standard Stock solution of ligand.:

The ligand was prepared by the dissolved of 0.0165 gram in 3 mole/L acetic acid and complete to 250 ml D.W. to prepare  $3.2 \times 10^{-4}$  mole/L.

### 2.3 Standard Stock solution of Bi ion

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (100ppm) solution was prepared by dissolving the requisite amount (0.0232 g) of salt in water, little free acid was added and used dilute to prepare other standard solution

#### procedure:-

For taking the absorbance spectra, a solution of metal ion (100ppm, 1 ml) and reagent ( $3.2 \times 10^{-4}$  M, 3 mL) was taken in a beaker and the pH was adjusted to 8 and the absorbance was measured in the range 200-800 nm

## 3. Results and Discussion:-

### 3.1. The Electronic Spectra

#### 3.1.1. Electronic Spectra of Free Ligand

The absorption spectra of the ligand in the solvent acetic acid and the complex spectra are shown in figure (1) and (2) respectively

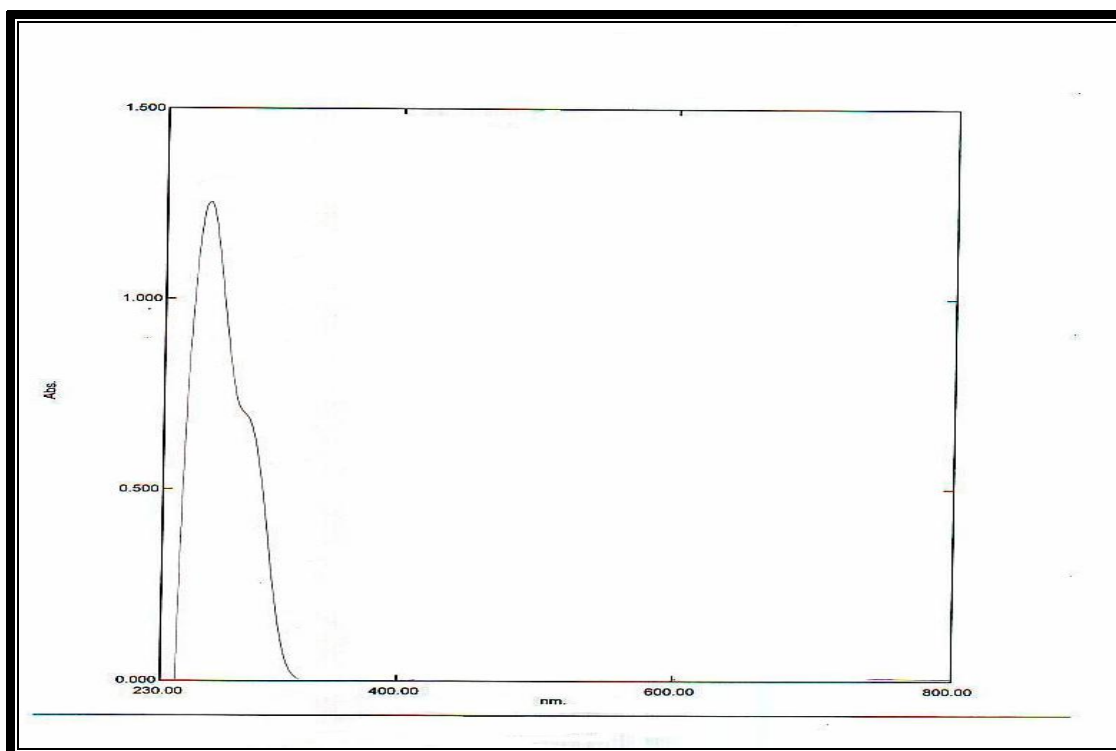
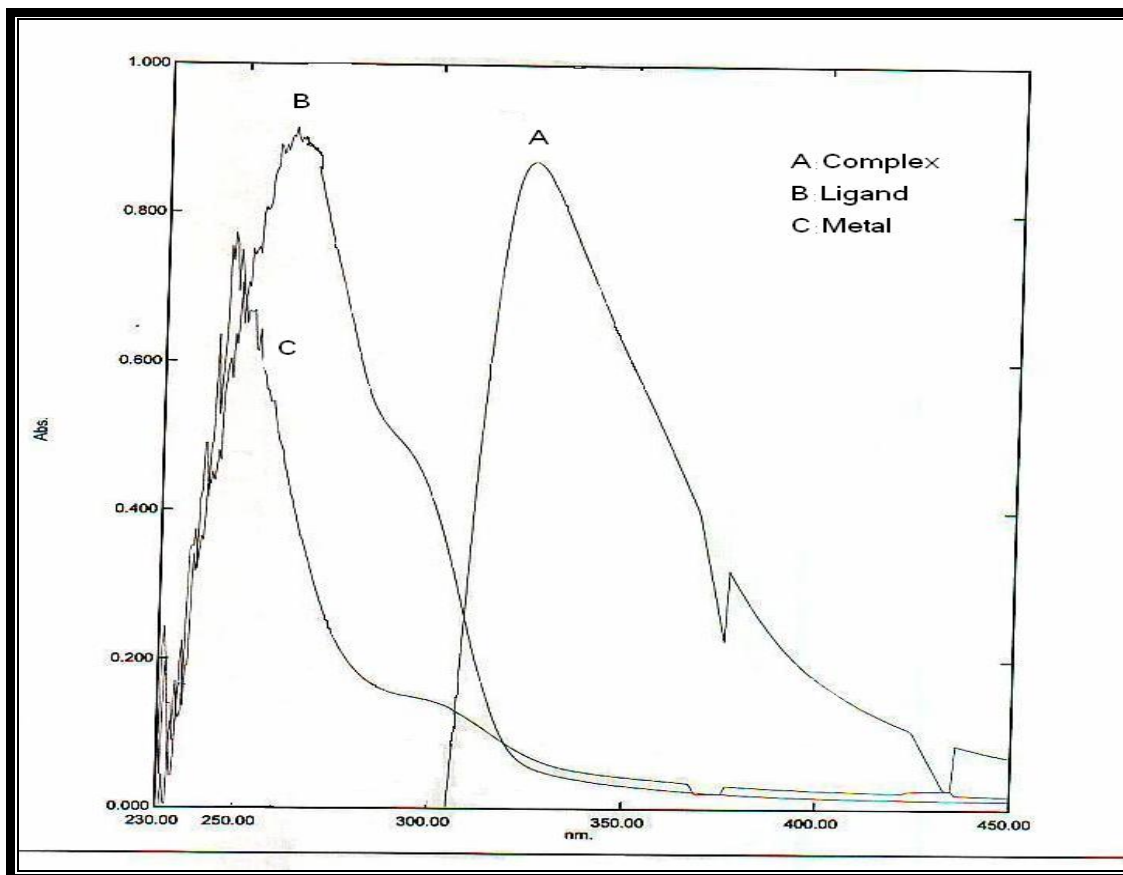


Fig.(1) absorption spectra of the ligand

### 3.1.2. Electronic Spectra of the Complexes:-



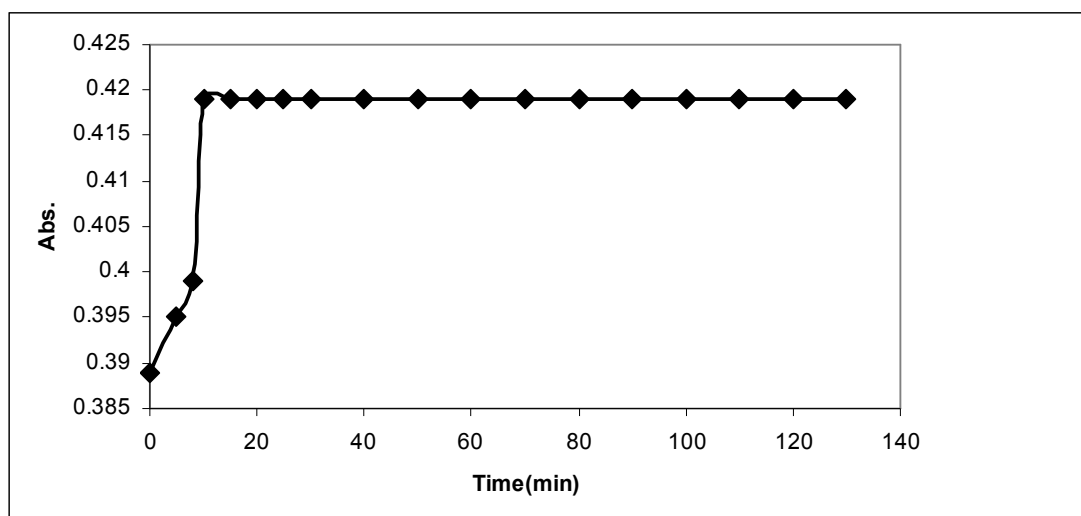
**Fig.(2) absorption spectra of the complex**

Absorption spectra show that the  $\lambda_{\max}$  of absorption of reagent is obvious at 265 nm, Bi complex at 328 nm, this new  $\lambda_{\max}$  mean the red shift in  $\lambda_{\max}$  of complex.

### 3.2 The optimum condition

#### 3.2.1 The effect of time

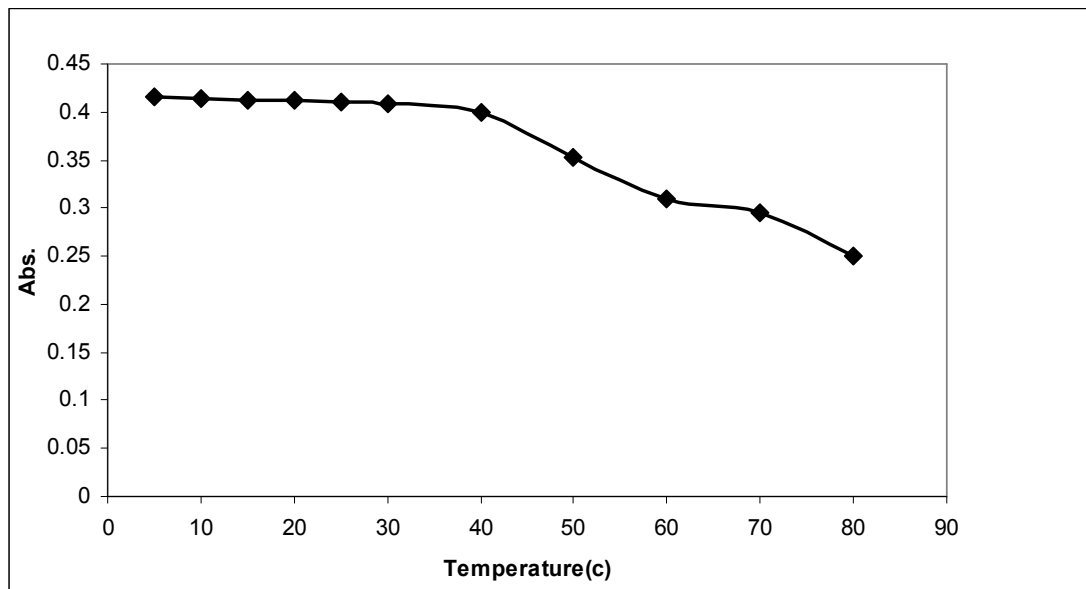
The absorbance constant to 24 hours refer to stable the complex .



**Fig.(3) Effect of time on the absorbance of bismuth complex at room temp.**

**3.2.2 . The effect of temperature**

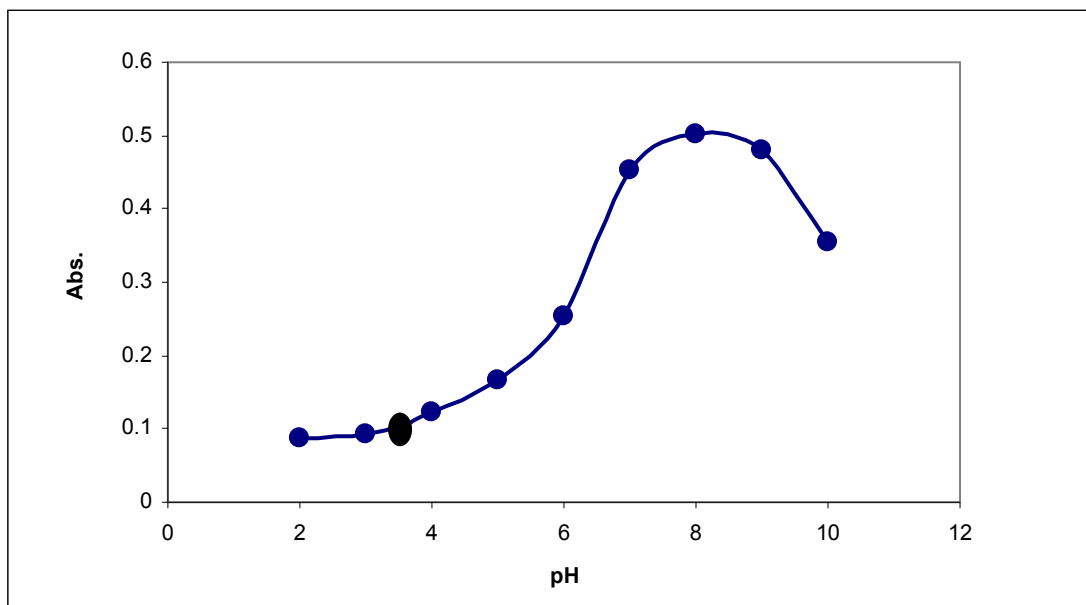
Refer to the reaction remind stable in the rang 10-40 c<sup>0</sup> and more than this led to dissociate the complex



**Fig.(4) Effect of temperature on the absorbance of bismuth complex .**

**3.2.3: The effect of pH**

The optimum pH refer to the complex formed in basic medium ,the fig (5) refer to the relationship between absorbance and pH,where the maximum absorbance obtained in the pH 8 and the pH less than 5 led to decrease the absorbance



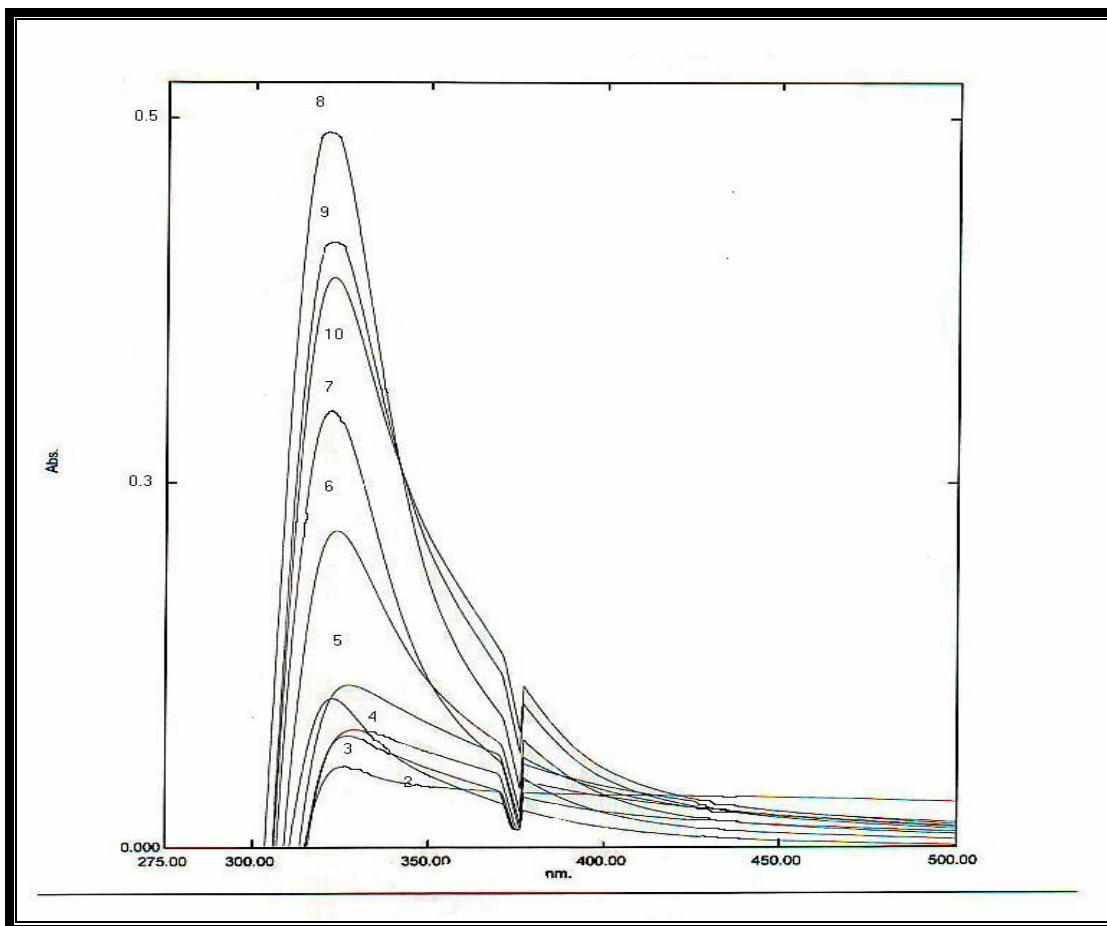


Fig.(٥) Effect of pH on the absorbance of bismuth complex .

### 3-3 Calibration Graphs

Calibration graphs for Bi (III) complex was obtained by under the These shown in figure ( 6).

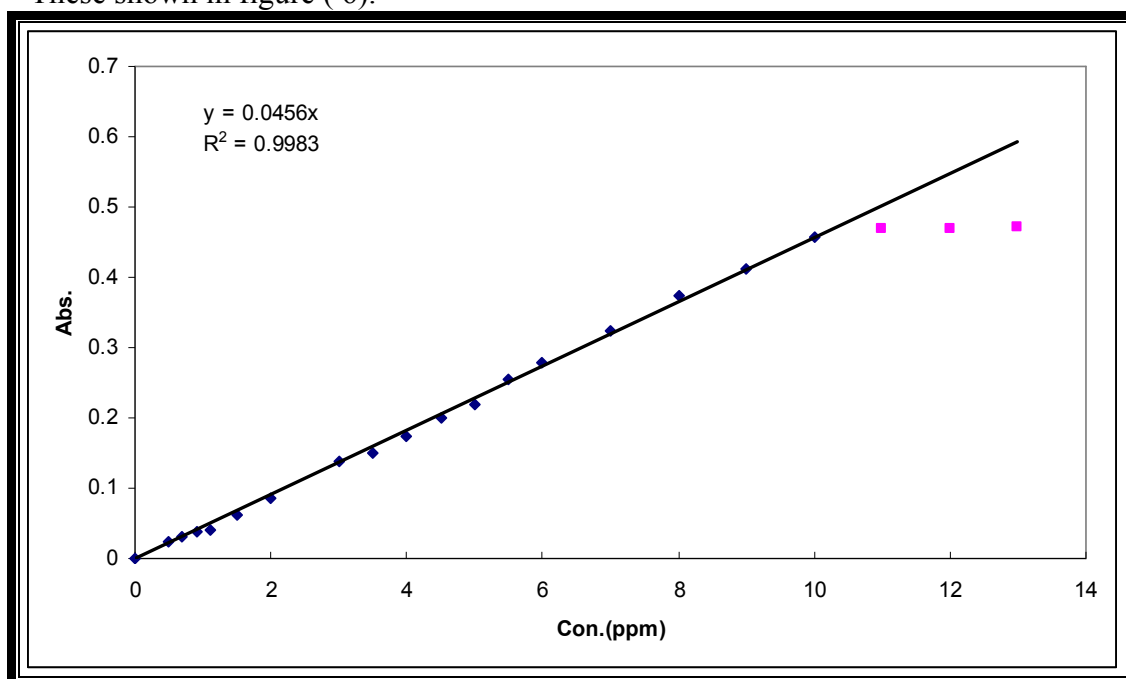


Fig.(٦) calibration graph of bismuth ion .

### 3.4 Stoichiometry of complex :-

The Stoichiometry of Bi(III) – Me complex was determined by Job’s method of continuous variation and Yoe Jone’s mole ratio method (Figure 7and 8) Both the methods gave the metal:ligand ratio of the complex as 1:1.

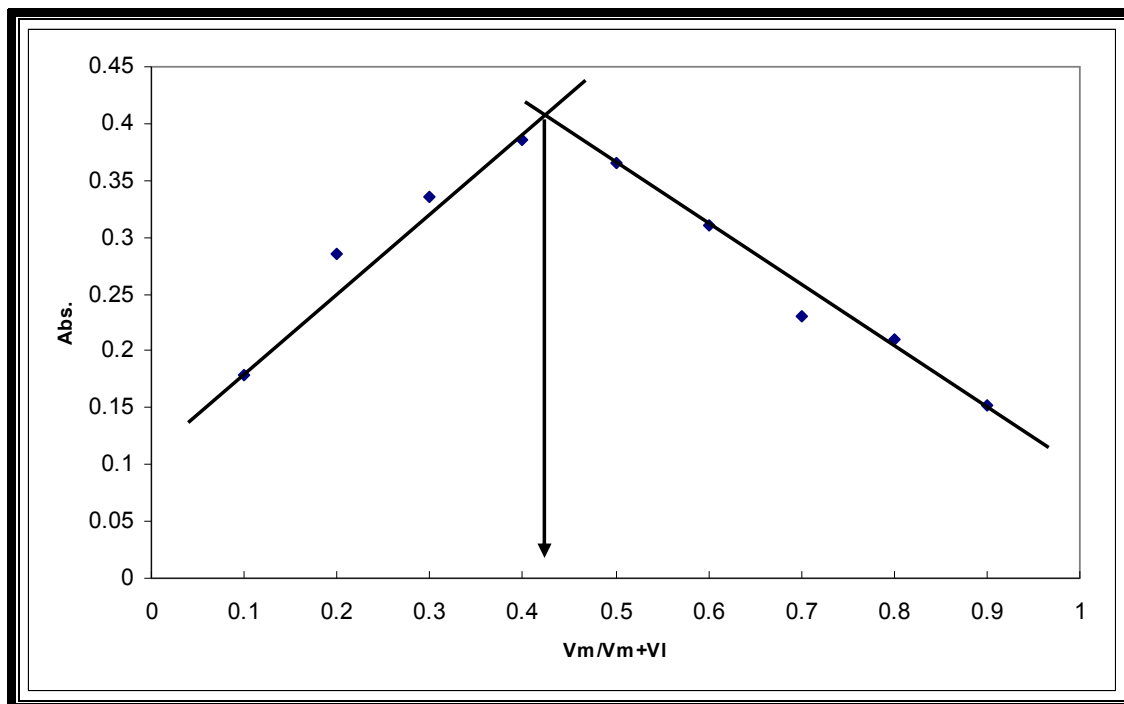


Fig.(7) continuous variation method for Bi-Me complex at optimum condition .

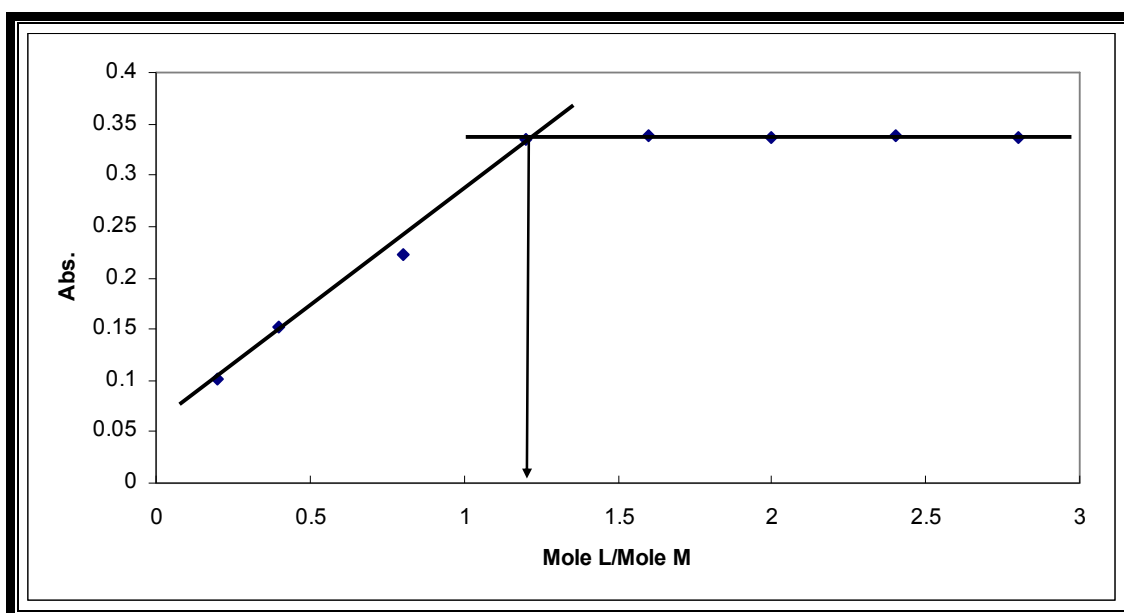


Fig.(8) molar ratio method for Bi-Me complex at optimum condition .

### 3.5 Precision and Accuracy

The precision of the present analytical method was evaluated by determining different concentration of Bi (III) analyzed (7 times), the relative standard deviation R.S.D. % was (0.76%) indicating that this method is highly precise and reproducible . The reliability of the method was tested by recovery (Ere%) was (+2.0) % for Bi (III) complex.

The precision and accuracy of the method was found to be excellent.

### 3.6 Interferences

The selectivity of bismuth complex is tested by measuring the absorbance of complex of 10 ppm at optimum condition in presence of different ions of 20 ppm which are able to form complex with the ligand .

The extent of reaction of these ion is shown in table (2) .

**Table (2) effect of interference ions**

Interference ions	Interference %
Ce(IV)	-1.6
V(V)	12.3
Fe(III)	15.4
Hg(II)	-9.3
Mo	10.1
W	-14.8

**Effect of masking agent .**

The effect of masking agent was studied to increase the selectivity of complex ,this shown in table (3).

**Table (3) the effect of masking agents**

Masking agents 0.01 M	Absorbance
Complex without any addition	0.409
Tartaric acid	0.016
EDTA	0.147
NaF	0.003
KI	0.098
Ascorbic acid	0.403
Thiourea	0.354
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.411
KSCN	0.081



The results shown in table (3) indicates that the ascorbic acid and sodium thiosulphate is the better for masking other ions .

**Effect of mixture masking agents on absorbance of vanadium complex**  
 From the table (3) , shown the Ascorbic acid and  $\text{Na}_2\text{S}_2\text{O}_3$  is not effect on the absorbance of complex , therefore make a mixture from its to increase the sensitivity of the method .

**Table (4) effect of volume of masking agent**

Volume of $\text{Na}_2\text{S}_2\text{O}_3$	Volume of Ascorbic acid	Absorbance
0.5	2	0.413
1	2	0.398
2	2	0.387
1	0.5	0.391
1	1	0.401

From this table shown the 0.5:2 is the best volume of mixture of ascorbic acid and sodium thiosulphate , therefore used its ratio to masking other ions that shown in table (5).

**Table (5) effect the best volume from masking agent**

Interference ions	Best volume by ml
Ce	3
V	2
Fe	2.5
Hg	3
Mo	1(by 0.05 M of masking agent)
W	3

### 3.7 FTIR spectrum of reagent and complex

The FTIR technique using KBr disc, fig (9) show the FTIR spectrum for each one .

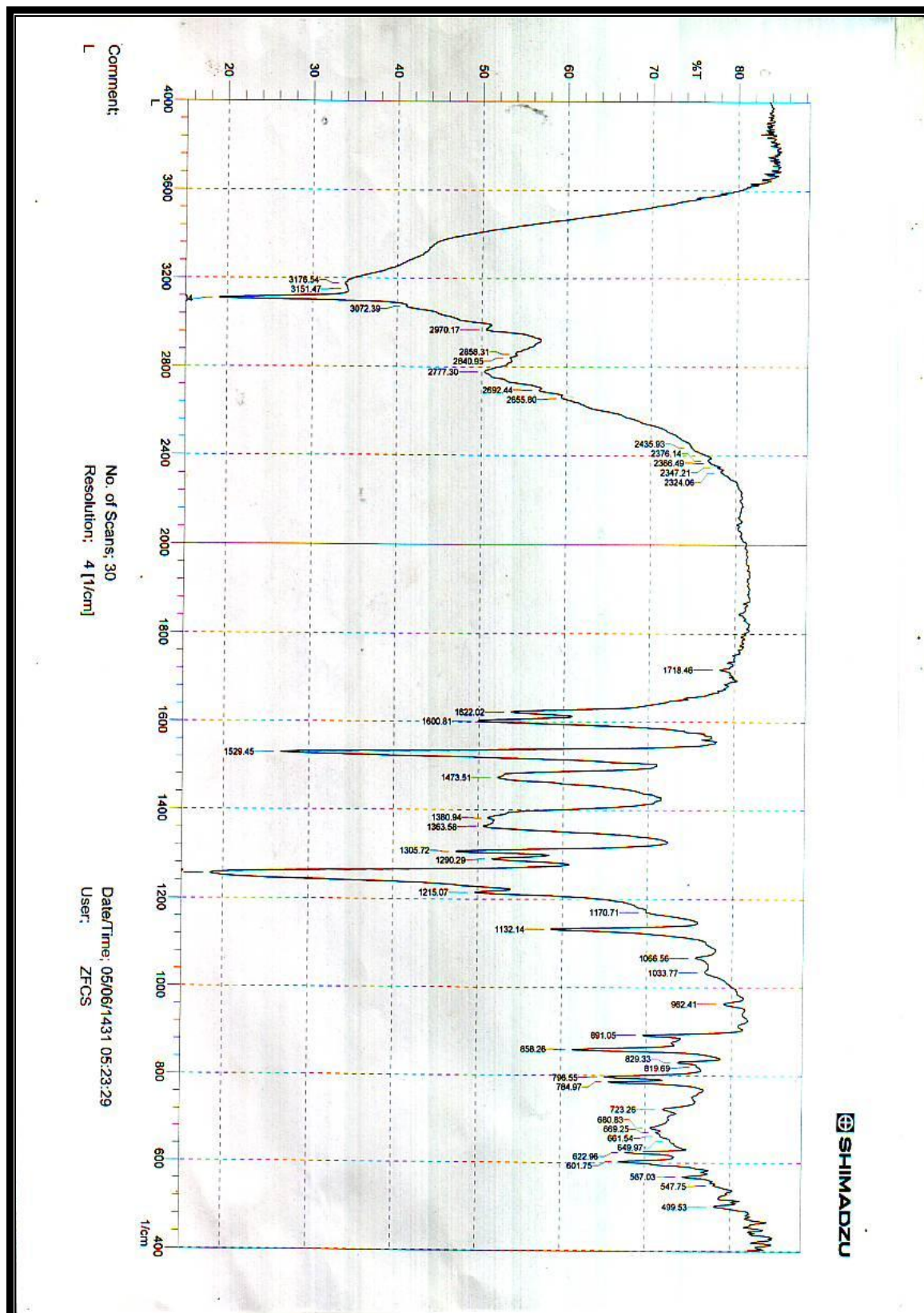


Fig.(9) FTIR spectrum of the reagent(Me) .

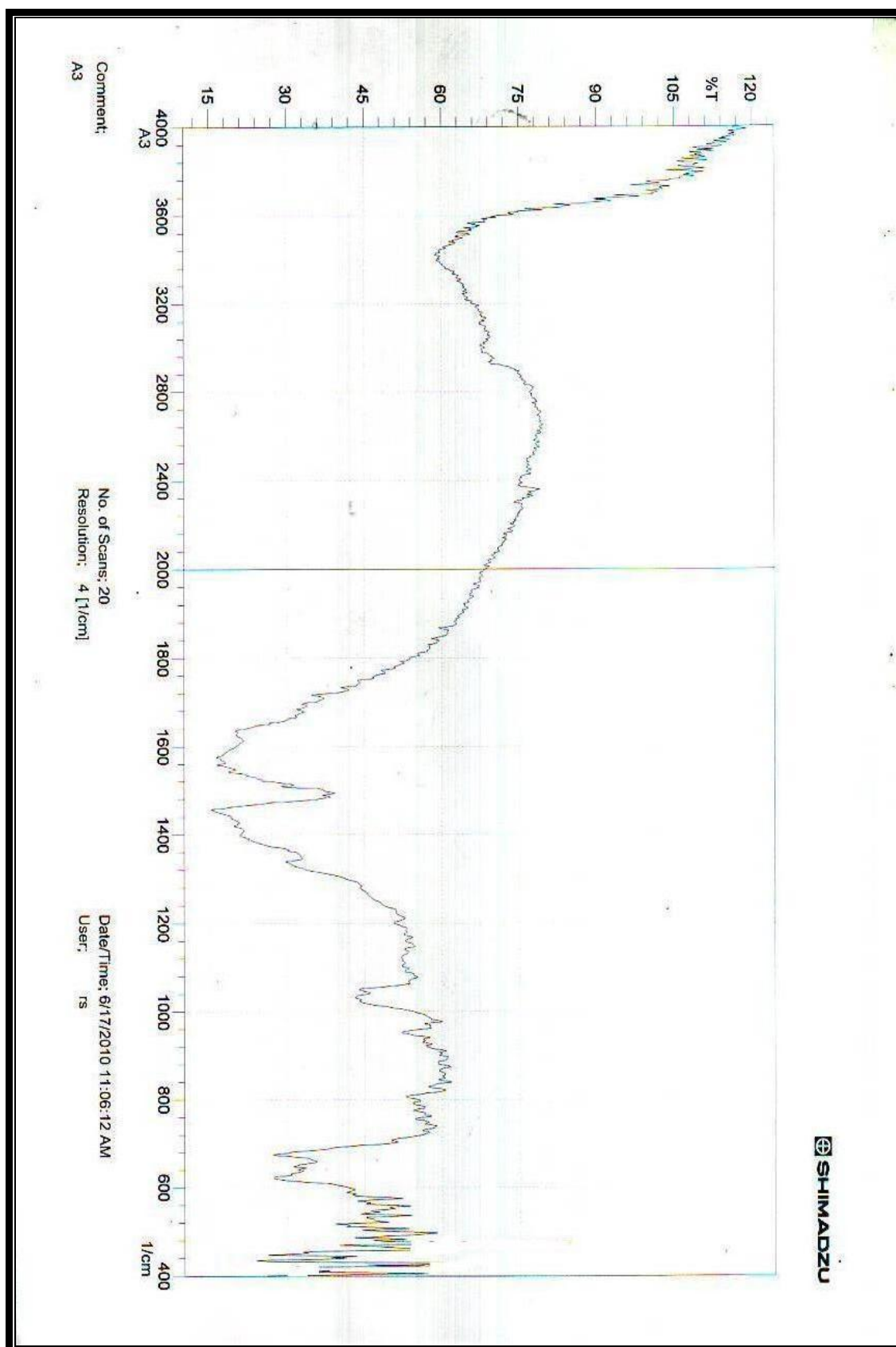


Fig.(10) FTIR spectrum of the complex .

The infrared spectrum show in figure (9) give absorption band at  $(3100) \text{ cm}^{-1}$  referred to the (OH) grope for the thiazole ring , but this absorption is hidden in complex du to information the complex, also in region between (400-1000) was formation anew band refer to the (O-M) band (Nakamoto and Betteridge 1973-1970).

3.8 C, H, N,S Analyses (%) of ligand and complex give in the table (6):-

**Table (6). C, H, N,S Analyses of ligand and complex**

element	C		N		H		S	
(L)	58.100	57.915	6.778	6.756	4.418	4.343	15.262	15.444
Complex	23.486	24.281	5.921	5.665	1.675	1.821	6.346	6.475

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