

Analytical Study for Bismuth (III) Determination Using 3-Hydroxy-1,2-Benzoquinone Reagent with Spectrophotometric Method and Possibility to Use This Indicator for Complexometric Titration of Bismuth

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Abstract: The target of this research is to study the complex formed from Bismuth ions (III) and 3-hydroxy-1,2-benzoquinone in 10 % DMF solutions using spectrometric method, study its analytical properties and determine possibility to use 3-hydroxy-1,2-benzoquinone as new indicator with complexometric titration.

All influenced factors on formation of Bismuth-Reagent Complex were studied at maximum wavelength $\lambda_{\max} = 510$ nm. The ideal range of pH corresponding complete formation of complex was determined and it was (4-6).

The molecular absorption factor for the complex formation from reaction between 3-hydroxy-1,2-benzoquinone and iron ions (III) was determined at maximum wavelength $\lambda_{\max} = 510$ nm and it was $\epsilon_{\max} = 2666.7 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$. The constant of conditional stable for this complex was calculated and it was $\log \beta = 5.185$.

Consequently; 3-hydroxy-1,2-benzoquinone is a typical mineral indicator to determine Bismuth ions (III) using complexomeric method whereas it gives with Bismuth ions (III) reddish purple complex and at equivalence point the color changes to yellow, this change is sharp.

Keywords: Bismuth(III), 3-hydroxy-1,2-benzoquinone, direct spectrometric method to determination Bismuth (III) in visible range, complexometric titrations to determination Bismuth (III).

Introduction:

Bismuth is light and purple metal, it found in a little percent in the environment, all salts and vapor of Bismuth are poisonous, it cause kidney atrophy, but it is the lower poisonous heavy metals that used in the industry, The major poisoning come from injecting large doses of it in the closed body cavities (when used as complex solution medicine). In addition, causing a sense of unease and the descent of albumin or protein substances in the urine and severe disorders and infections of the skin.

The metal were analytically determined in many ways, including: Spectral fluorescence and atomic absorption methods, etc., and some of these methods with low sensitivity [3,4] and others will require a long time to complete the analytical work [5-6] and use other harmful substances to the environment and humans [7-8].

The other methods used in the determined bismuth, such as solvent extraction [9,10] highly sensitive but complex and require a long time, the iron was determined by flame atomic absorption spectra using graphite furnace [11] these methods is one of the best methods, but high cost.

Among the most famous and simple spectral methods to determine bismuth III in natural and industrial sources. [12] which is based on the analytical reagents such as (thiourea) that form a yellow complex with bismuth (II) in a variety of samples, and characterized as sensitive, but interferes with the bismuth and other elements of the form mostly colored complexes with the same reagents, which constitutes a bismuth with complexes that negatively affect the determine of bismuth. [13]

The method used in this research is characterized by using the new organic reagent 3-hydroxy-2,1-benzoquinone (in solutions of 10% DMF), simplicity, accuracy, and other ions do not interfere in this determination.

Experimental:

Chemicals:

All chemicals and solvents, reagents used in the present study were of analytical grade purchased from Sigma Aldrich, De Haen AG Seelze– Hannover, Avonchem and Merck, such as pyrogallol, manganese oxide, dichloroethane, ethanol, dimethylformamide DMF, binary distilled water, bismuth nitrate pentahydrate, sodium hydroxide, hydrochloric acid.

IR spectra of compounds were recorded using KBr pellets on FTIR Jasco-300E from Jasco, Melting points were measured on an Electrothermal 9200 melting point apparatus and were uncorrected, balance sensitive electronic four decimal digits from Sartorius basic were used, the elemental analyzer CHNS was Euro Elemental Analyser from Agilent, Spectrophotometer was Jasco-V650 from Jasco, UV Spectrometer Optizen 3220, PH meter (pHMi 180) from Martini.

Methods of preparation:

Preparation the reagent:

2g of pyrogallol were dissolved in a little amount of water then several drops of HCl (0.1N) were added and the solution was diluted with water (to prevent polymerization) after oxidation of the solution with (1 mg) MnO_2 at room temperature for 5 minutes, Then MnO_2 was eluted from the solution. The organic compound was extracted using CH_2Cl_2 , the solvent was evaporated then washed with distilled water and dried on air, and the resulting compound is soluble with DMF [2].

The resulting compound characterized using FT-IR and it compared with pyrogallol spectra, the infrared spectrum exhibited characteristic peak at (3600 cm^{-1}) O-H in pyrogallol length of it equal to three times the length of the resulting compound, and increasing the length of peak at (1650 cm^{-1}) of the carbonyl group - C=O in the resulting compound is twice what it was in pyrogallol as in Figures (2.1) [14].

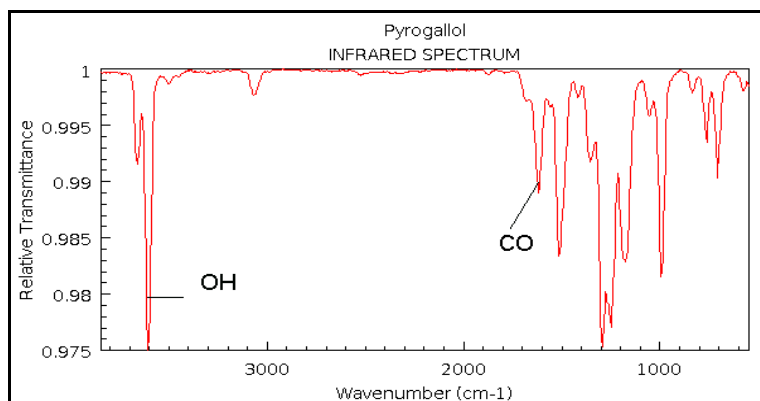


Figure 1: The infrared spectrum of the violet pyrogallol.

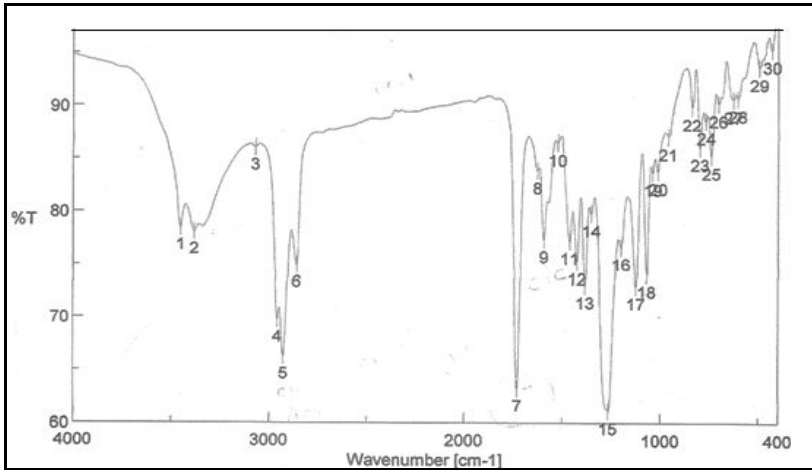


Figure 2: The infrared spectrum of the red resulting compound.

The figures 3, 4 refer ¹H-NMR spectra for pyrogallol and resulting compound.

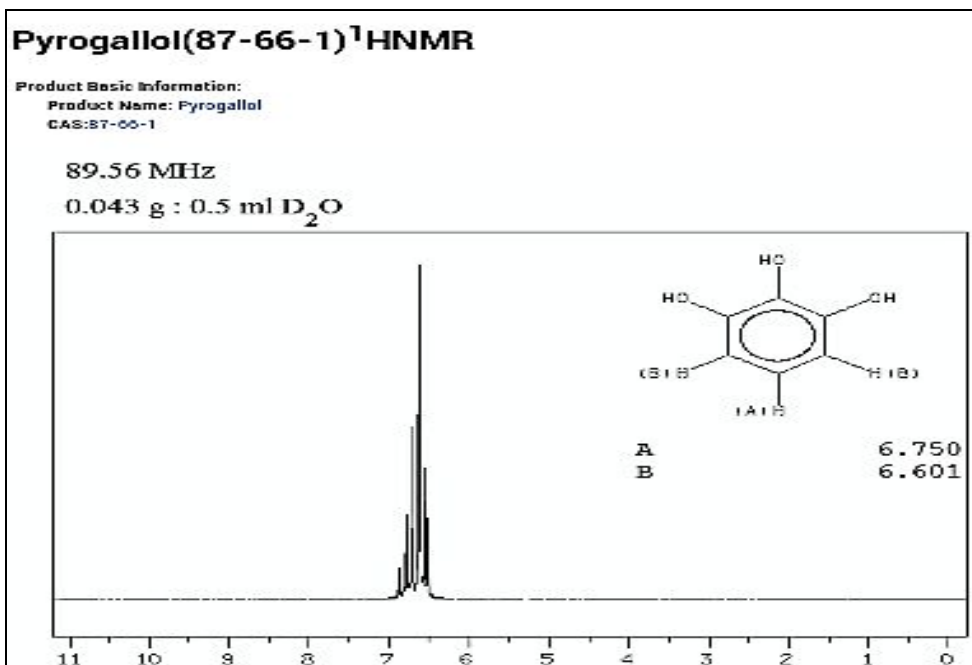


Figure 3: The ¹H-NMR spectrum of the violet pyrogallol.

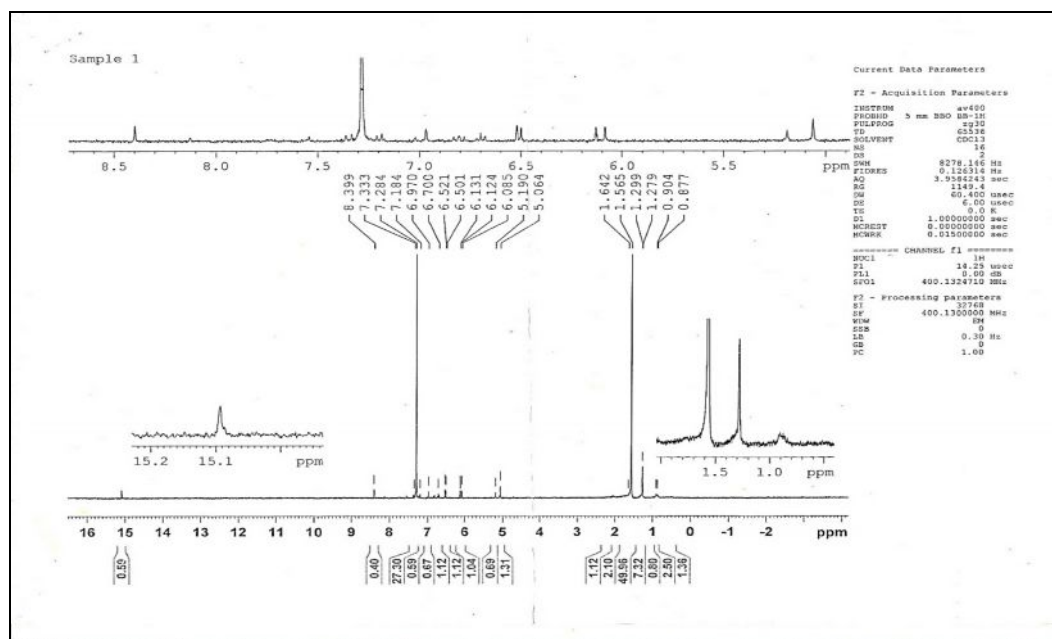


Figure 4: The ^1H -NMR spectrum of the red resulting compound.

Preparation the solutions:

1. The initial solution of bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was prepared 1×10^{-3} M, by dissolving calculated amount (0.121g) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 250 ml of distilled water.
2. The initial solution of prepared reagent ($\text{C}_6\text{H}_4\text{O}_3$) was prepared 1×10^{-3} M, by dissolving calculated amount (0.031 g) of reagent crystalline ($\text{C}_6\text{H}_4\text{O}_3$) in 250 ml of distilled water.
3. The solutions of sodium hydroxide and hydrochloric acid were prepared as initial concentrations 0.1 M and used to prepare solutions more dilution to adjust the pH values.
4. Standard solutions of chlorides and nitrate of heavy metals like Cu, Cr, Zn, Cd, Pb, Mn, Ni, Ga, Al, Co were prepared with concentrations 100 mg/l.

Result and Discussion:

1- Spectral study for complex 3-hydroxy-1,2-benzoquinone with bismuth (III):

Red soluble in water complex forms when aqua solution for a salt bismuth (III) to 3-hydroxy-1,2-benzoquinone. The visible spectrum shows maximum peak at (λ_{max} 510 nm). As the figure 5 shown.

To study the effect of pH center-absorbency complex problems between the detector and bismuth, we attended the complex mentioned at different values of the PH as follows: in a beaker with a capacity (10ml) with a focus ($M 10^{-2}$) record in DMF and added (1ml) of the visor Breton with PH = 3 then added (1ml) of ions of bismuth (III) derived from an initial solution to nitrate aqueous bismuth concentration (10^{-2} M) and waited for 5 minutes, then completed the volume with distilled water binary distillation until the signal and measured the solution after the stability of the complex color using the degree of acidity scale device meter pH and found that 3.5, we conducted the survey spectroscopy, and molecular absorption band of the complex formed in the visual field when $\lambda_{\text{max}} = 510\text{nm}$, as shown in Figure (4):

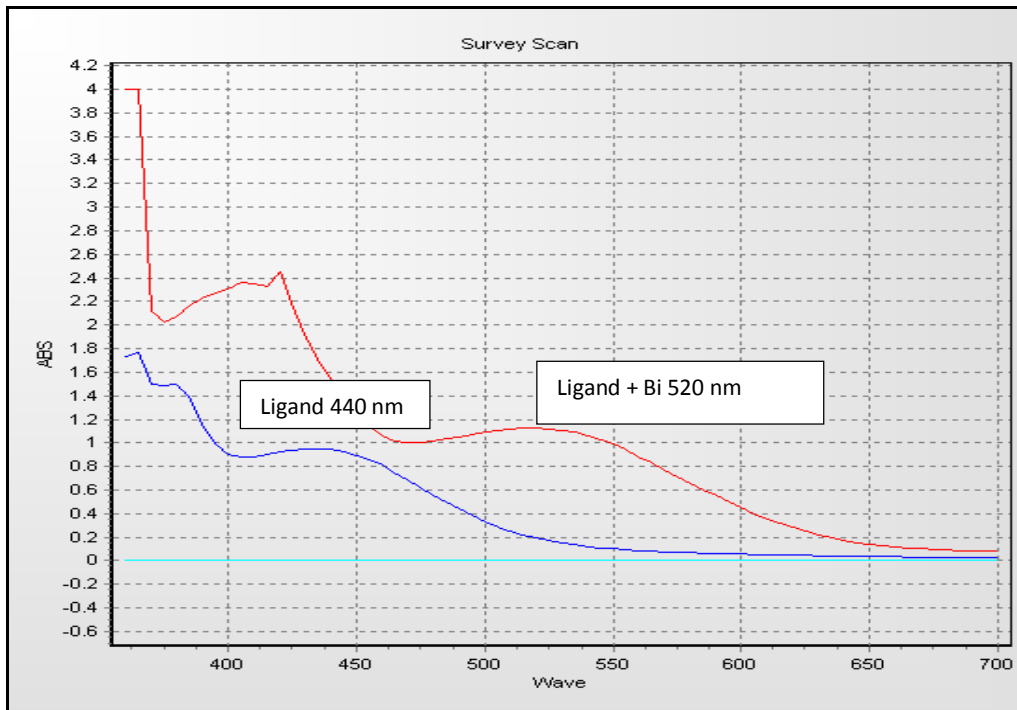


Figure 4: The spectrum of the complex formed between L and Bi (300-700 nm).PH =3.5, $C_{preton} = 0.1$, $[L] = 10^{-2}M$, $[Bi^{+3}] = 10^{-2}M$.

2- The effect of temperature on the form the complex between the Bi (III) and 3-hydroxy-1,2-benzoquinone:

The experiment has shown there is no change in absorbance (A) corresponding ($\lambda_{max} = 510$ nm) when change the temperature between (20 – 80 °C) to solution of complex between the Bi (III) and 3-hydroxy-1,2-benzoquinone.

3- The effect of solution's pH the Absorbance of the formed complex between Bi (III) & L:

(Figure 5) refer to change the molecular absorbance of the complex versus of pH, draw a relationship between the absorbency complex and the values of pH using standard solutions of HCl and NaOH were sure of the value of the pH of each solution after prepared with a pH of hydrogen pH meter when ($\lambda = 510$ nm) we get the graph shown in Figure 6.

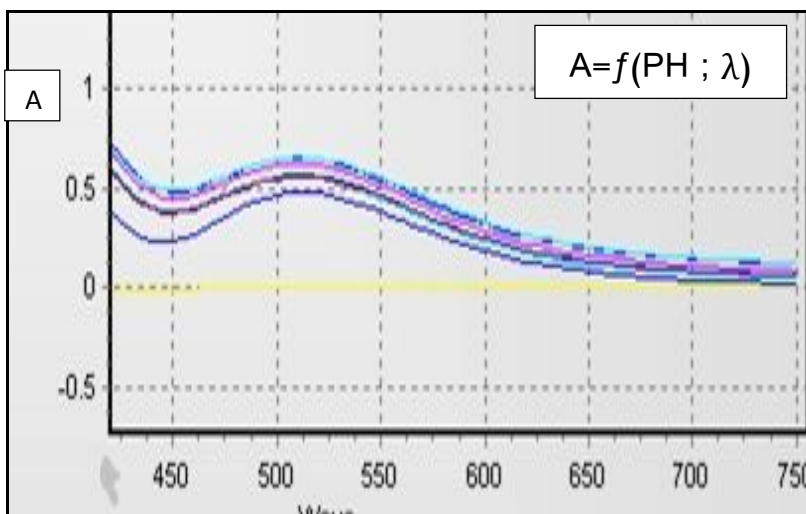


Figure5: The survey spectral complexes at different values of the PH, $C_{Preton} = 0.1M$, $[L] = 0.001M$, $[Bi^{+3}]$, $0.001M$, PH = (2,3,4,....., 9)

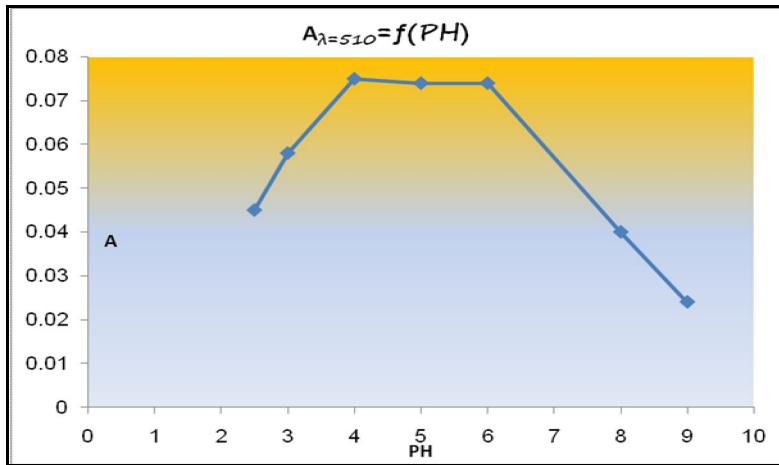


Figure 6: The relationship between the absorbency complex and PH [L] = 0.001M, [Bi³⁺] = 0.001M, Cpreton = 0.1M, λ = 510 nm.

We note that the complex is formed in small quantities when PH < 2 increases posed by the increase in the value of the PH and maintains the absorbency fixed within the domain (4-6) of the PH and then crumble absorbance at PH > 6, as shown in Figure 6. We will work within the domain (4-6) for the stability of the complex when the absorbency (PH=4).

4- The effect of increased reagent concentration in absorbency complex studied:

The effect of increasing was studied the detector on the absorbency complex formed (bismuth tri-organic reagent), except change of reagent concentration between the two values (5.10⁻⁴ -25.10⁻⁴) at a constant concentration of triple-bismuth is 5x10⁻⁴, and when the value of PH= 5 left lotions prepared within the volumetric flask in the laboratory atmosphere for 30 minutes and then complete the volume by adding water dual-distillation with the achievement of the proportion of 10% DMF until the signal was found after measuring the absorbance of all solutions prepared that the absorbance according to the concentration of reagent added changed as in Figure (4) shown in Fig. (4) The increase in the optical absorbance with the increasing concentration of the detector to reach super her when C_{ligand} = 15x10⁻⁴ and after the value of the fixed absorbance stay with the continued increase in the concentration of the detector.

5	5	5	5	5	5	5	5	5	5	5	C M.10 ⁻⁴
25	22.5	20	17.5	15	12.5	10	7.5	5	2.5		C ligand .10 ⁻⁴
1.33	1.33	1.34	1.32	1.33	1.1	0.89	0.66	0.43	0.21		A

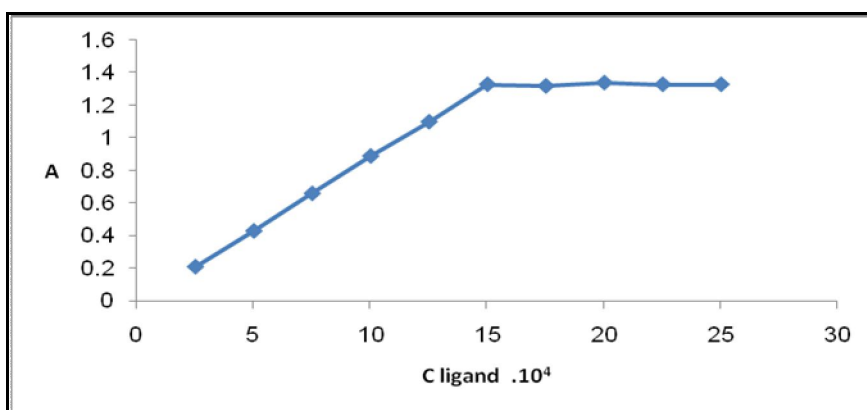


Figure.7 optical absorbance change with the change of the concentration of the detector at a constant concentration of ions Bi³⁺ = 5.10⁻⁴ when PH = 4 and in the solutions 10% DMF, λ_{max} =510 nm.

5- Calculation of Stoichiometric For the Formed Complex L-Bi(III):

A- Molar Ratio Method:

This method is summed up ratios molar take a fixed concentration of mineral ions to be forming complex with reagent-based and change the focus of the detector, and then measured the molecular absorbance of each of solutions at a wavelength corresponding to the wavelength maximum of the complex $\max \lambda$, draw graphs relationship absorbency complex versus the percentage molar concentration associated with the stray concentration of metal we will get the equation:

$$A = f([L]/[M])$$

The tendency of these linear relationship changed by changing the complex formed installation, and thus we get a straight line is growing in direct proportion with the increase in the ratio $[L]/[M]$, and then broken at that point that is compatible with the installation of the complexes formed in solution studied, Figure (8) spectral scanning change of complex molar ratios.

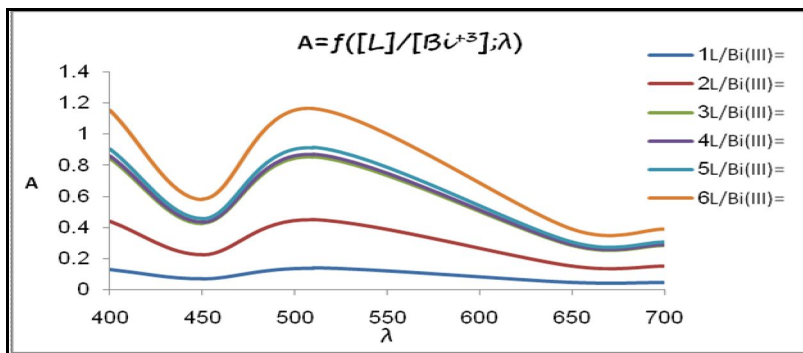


Figure 8: scanning spectroscopy for complex change molar ratios

$$, PH = 3.5 \quad , [L] = 10^{-2} \quad 1, 2, 3, 4, 5, 6 = \frac{[L]}{[M]}$$

To determine the proportion of the link we draw the relationship between the mole fraction and the absorbance as shown in Figure 9.

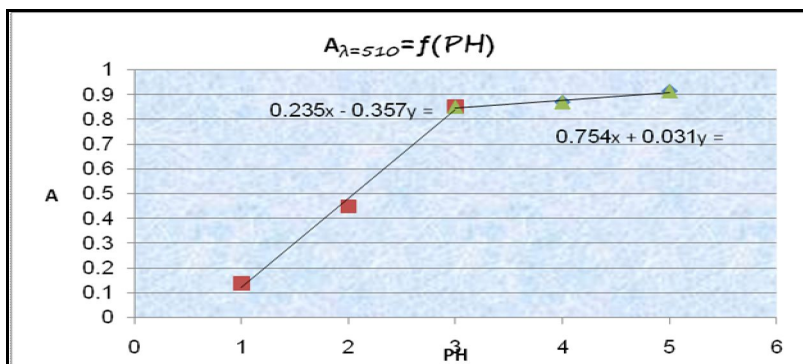


Figure 9: change the molecular absorbance of the complex versus the molar ratios / [M] [L]

$$\left. \begin{array}{l} y = 0.357X - 0.235 \\ y = 0.031X + 0.754 \end{array} \right\} \Rightarrow 0.326 X = 0.989 \Rightarrow X = 3.033 \approx 3 \Rightarrow [L]/[M] = 3$$

$[L] = 10^{-2}M, PH = 3.5, \lambda = 510nm.$

B- Continuous Variation Method:

This method is based on the change in the molecular absorbance of the complex when the length of the maximum wave and a series of solutions of the complex studied, which PH values of it fixed so that the concentration of each of the mineral stray change and associated to remain fixed their concentration. drawing curved graph between the absorbance and mole fraction determine the percentage of correlation $A = f([L] / [L] + [M])$ as Figure 10 We gets uperpeaks located at the fractures molar ratios approval for the link in the complexes formed.

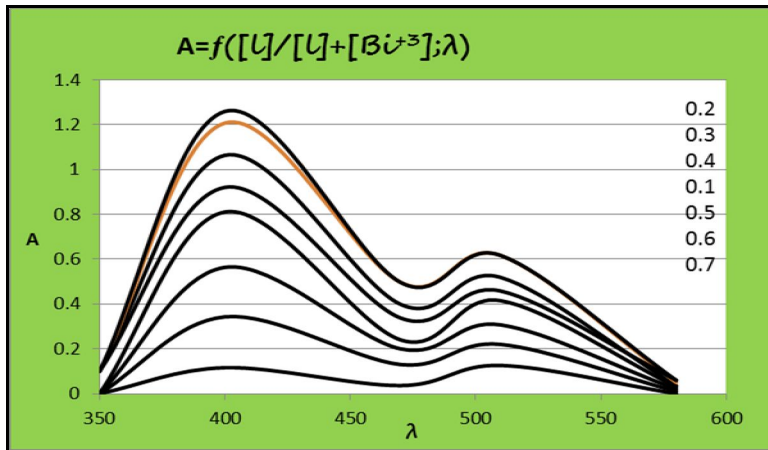


Figure 10: scanning spectroscopy for complex change molar ratios $[Bi+3]/[L]+[Bi+3]= (0,0.1,0.2,.....,1)$

To determine the proportion of the link we draw the relationship between the mole fraction and the absorbance as shown in Figure 11.

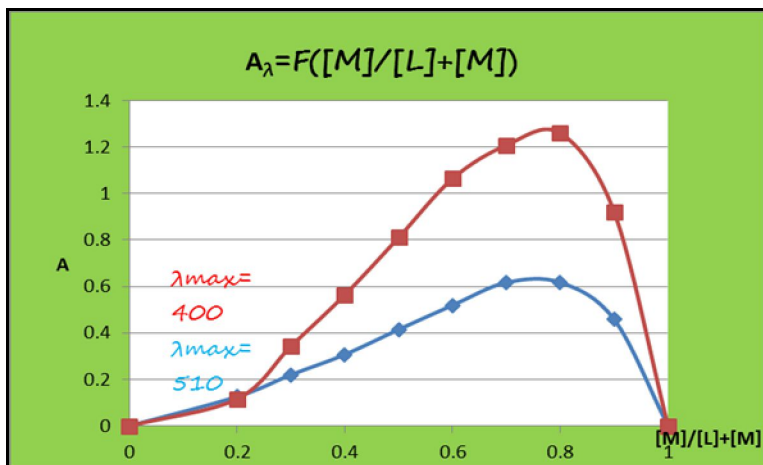


Figure 11: change the molecular absorbance of the complex in terms of the mole fraction $[M] / [M] + [L]$, PH = 3.5.

In Figure (11) note that the mixture solution which gives the highest absorption contains:

$$\frac{[M]}{[M] + [L]} = 0.24 \quad \text{Equation (1)}$$

And also:

$$\frac{[L]}{[L] + [M]} = 0.76 \quad \text{Equation (2)}$$

By dividing the equation (1) to the equation (2) we get: Equation (3)

$$\frac{0.24}{0.76} = 3.16 = \frac{1}{3} \frac{[M]}{[L]}$$

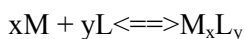
This means that the percentage of LM is 3: 1, meaning that the complicated formula of the kind ML₃.

We have thus investigated the correlation ratio between the detector and the lead duo of lead nitrate salt which is (Bi: L 3: 1) in a manner curved satiated and the method of constant changes, so the formula 3 BiL.

6- Calculation of the Molar Absorption Coefficient (ϵ) ant the Contestants Formation:

The previous two methods showed that stoichiometric complex formed from the interaction of 3-hydroxy1,2-benzoquinone with triple bismuth ions are (1:3) and approved formula (BiL₃)

According to a constant molecular absorbance Equation (1) at (λ_{\max} =510 nm) and data (Figure 12) and in line with the likes of winning the interaction between the detector and the ion bismuth triple the average value is equal to ($\epsilon. \lambda_{\max}$ = 2666.7 mol⁻¹.l.cm⁻¹)[15,16].



$$\epsilon = \frac{A \cdot y}{b \cdot C_L} = \frac{A \cdot x}{b \cdot C_M} \quad (4)$$

where A is the optical absorbance of the complex, (y, x) for stoichiometric complex formed, b layer thickness influence, CL reagent concentration mol/L, CM concentration of the metal ion mol / L.

Constant stability of a complex been a complicated calculation Bi⁺³ with m-hydroxy1,2-benzoquinone Komrea method and using the following equations described in [17,18,19].

$$\log \alpha_{Bi} =$$

$$\log \alpha_l = -$$

$$\log \beta' = \frac{\log C_{\text{complex}}}{(C_M - C_{\text{complex}})^{3.4}}$$

$$\log \beta = \log \beta' - (-\log \alpha_{pb} - \log \alpha_l)$$

$$\epsilon_{\text{complex}} = 2666.7 \pm$$

Whereas α_{Bi} represents to ion concentration ratio of bismuth (III) free when the balance the total concentration of bismuth (III).

Whereas α_{H2L} -represents to the concentration of the detector when the free balance with the total concentration of the detector, Conditional constant stability is β .

The calculations were carrying out and statistic processing for data and put in the table (2).

$\log \beta'$	$(C_M - C_{com})^2$	$C_{complex} \cdot 10^4$	A	$C_M \cdot 10^3$	$C_{ligand} \cdot 10^3$
	$.4 \cdot 10^9$				
4.924	0.94	0.83	0.22	7	3
5.49.76	0.46	0.307	0.307	6	4
5.978	0.16	0.415	0.415	5	5
6.749	0.0129	1.95	0.519	4	6

The average value of a constant stability the conditional $\log \beta'$ of the complex is equal to: $5.185 \pm$, and standard deviation, 0.515 a constant value stability $\log \beta'$:

$$\log \beta = 5.185 - =$$

Standard curve set to bismuth (III) using reagent 3-hydroxy-1,2-benzoquinone Spectral way:

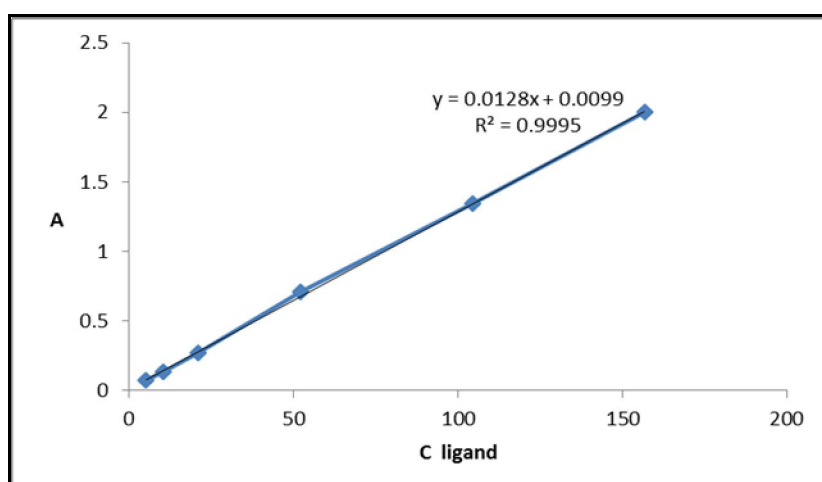
The field of concentrations of bismuth triple was studied and approved in writing Beer Law - Lambert.

In order to determine the bismuth (III) spectral way, taking into account all appropriate ideal conditions for the full form of the complex (BiL3). Shown in Figure (7) line arrange in which the check Beer Law - Lambert and humble within the range (7.5×10^{-4} - 0.25×10^{-4}) which is equivalent to (5 -150 mg /l) bismuth (III).

And that the resulting graph is a straight equation of the form is $0.009 + 0.012 X = y$

In addition, that the correlation coefficient $R^2 = 0.99$, and this shows the excellent linear relationship between the optical absorbance and concentration.

$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	C ligand
$7.5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	$0.25 \cdot 10^{-4}$	$C Bi^{+3} M$
156.68	104.45	52.23	20.9	10.44	5.22	$C Bi^{+3} mg/l$
2	1.34	0.71	0.268	0.134	0.07	A



The reagent used as indicator complex ion titration. To set the bismuth triple direct manner calibration using EDTA. [20] solution of bismuth nitrate attended the amount of 0.01 mol / l. Then dissolving 4.849 g / l and a solution of EDTA concentration 0.01 M. Attended Hairy user so by dissolving 0.5 g in binary form amide 100ml methylcellulose.

Taking 10 ml of bismuth nitrate solution was added to 2.5 ml of the reagent, and 2.5 ml of a bilateral methylcellulose pure form amide constitute a complex red color argon.

Solution of EDTA calibrated until the color from red to purple coup bright yellow color.

Calibration repeated six times and dealt with the results of statistical means. As shown in Table (3).

Table 3: Statistical processing of the results of the appointment of bismuth (III) the way complexometric titration.

V EDTA $\pm \Delta v$	$\frac{t \cdot s}{\sqrt{n}}$	$S_r = S/V$	$S_m = S/\sqrt{n}$	S	$\sum d^2$	n	\bar{V}_{EDTA}
10.01 \pm 0.049	0.049	0.0047	0.019	0.047	13.10 ⁻³	6	10.01

The use of 3-hydroxy-1,2-benzoquinone showed results that were obtained (Table 3) can be used as a reagent in the record Kmhar calibrations Alcolmbleksomitrih to set bismuth triple. Where n = 6, t = 2.57 when the reliability of 95%.

Conclusions:

1. 3-hydroxy-1,2-benzoquinone was prepared described the means adopted for the characterization of organic compounds.
2. Since the composite record reacts with ions bismuth triple and constitutes a complex undissolved water color purple has a wavelength of absorption Azami $\lambda = 525$ nm, using detector free form its (440nm, 605nm) different from the wavelength absorption of the complex, so has the study of the properties of the complex formed at a wavelength where do not affect the results that were obtained.
3. have been identified area of the ideal pH to form the complex and the proportion of conformation and the coefficient of molecular absorbance and static stability has not been a study quantifying ions triple bismuth in this way using a composite record because the constant molecular absorption of a complex formed is equal to (2666.7 mol⁻¹.L.cm⁻¹ = $\lambda \epsilon_{max}$), and such a small molecular absorption coefficient does not allow quantification values.
4. Since this is a complex compound with bismuth ions and has a triple-tinted color Mgayerllon Detector free form and constant calculated for the complex formed bismuth stability less than a fixed form (Bi - EDTA) so we suggest the use of this compound in set bismuth ions triple calibration manner pal EDTA and leave this application to the subsequent studies.

References

1. <http://ww.feedo.ne>
2. Analytical Chemistry Instrumental Analysis Written by Prof. Ibrahim Zamil Al-Zamil, Department of Chemistry, King Saud University, Dar Khurairji for publication and distribution, and the second edition in 1996.
3. Kiran, T. N. and Revanasiddappa, H. D. (2003). Rapid and Sensitive Spectrophotometric Determination of Trace Amounts of Iron (III) Using Leuco Xylene Cyanol FF. Analytical and Bioanalytical Chemistry. 376, 1126 – 1130.
4. Constantaine, D., Stalikas, A., Alexandros, C., Pappas, A., Miltlaades, I. Karyannis, A. Panayotis, G and Veltsistas, A. (2003). Simple and Selective Spectrophotometric Method for the Determination of Iron (III) and Total Iron Content, Based on the Reaction of Fe(III) with 1,2 - Dihydroxy-3,4-Diketocyclo-Butene (Squaric Acid). microchim. Acta. 142, 43.
5. Ohno, S., Teshima, N., Zhang, H., and SAKA T. (2003). Utilization of Activating and Masking Effects by Ligands for Highly Selective Catalytic Spectrophotometric Determination of Copper and Iron in Natural Waters. Talanta. 60, 1177-1185
6. Zeng, Z and Jewsbury, Y. R. (2000). Spectroscopy – Fluorimetric determination of Iron Using 5-(4-methoxyphenylazo)-8-(4-toluenesulfonamido) Quinoline. analyst. 125, 1661
7. Patel, K. S. and Shukl, A. A. (2001). A New Spectrophotometric Method for Determination of Total an Ferric Iron in Rain Water at the ppb Level. Analytical and Bioanalytical Chemistry. 369, 530 – 534.

8. Pehkonen, S., Erel, Y., and Hoffmann, M. R. (1992). Simultaneous Spectrophotometric Measurement of Fe (II) and Fe (III) in Cloud and Fogwater. *Environ. Sci. Technol.* 26, 1731-1736
9. Mohabey, H., Sharma, P. K., and Mishra, R. K., "Spectrophotometric Determination of Iron (III) with N-Hydroxy-N-Phenyl-N-(2-Methyl) Phenylbenzamidine Hydrochloride in Presence of Thiocyanate and Azide," *Proc.-Indian Acad. Sci., Chem. Sci.*, Vol. 89(2), 1980, pp. 95–99.
10. Miura, J., "Masking Agents in the Spectrophotometric Determination of Metal Ions with 2-(5-bromo-2-pyridylazo)-5-Diethylaminophenol and Non-Ionic Surfactant," *Analyst*, Vol. 114, 1989, pp. 1323–1329.
11. Krishnamurti, G. S. R. and Huang, P. M., "Spectrophotometric Determination of Fe(II) with 2,4,6-Tri(2'-Pyridyl)-1,3,5-Triazine in the Presence of Large Quantities of Fe(III) and Complexing Ions," *Talanta*, Vol. 37, No. 7, 1990, pp. 745–748.
12. Nafion –mercury coated film electrode for the adsorptive Stripping voltammetric Determination of lead and cadmium in the presene of pyrogallol red ,2012.
13. Bishop, E. (Editor), (1972) *Indicators*. Vol. 1. Pergamon Press, Oxford
14. *Organic Chemistry*, written by Morrison & Boyd, 2000, the Arab Center for Arabization, Translation, Authorship and Publication in Damascus.
15. *Chemistry of transition metals, inorganic chemistry*, "3", copyright and copyright reserved for the University of Damascus, 1992-1993.
16. Harris, D. C. , 2006, *Quantitative Chemical Analysis* , Eighth Edition , Michelson laboratory, China lake, California.
17. Inczedy, J., (1976). *Analytical Applications of complex equilibria*. NewYork: wiley.
18. Calabres, V. T., and Khan, A. C. J. *phys.chem.*2000, 104 , 1287.
19. Bulatov, M.I., Kalinkin, I.P., V(1976). *Practice scoerukovodstvopofotokolorimetrikeskim I spektrofotometrikeskimmetodom analiza.Izd.4-e,L.Himia.* 1976, 375.
20. *Complexometric Determination Of Trivalent Metal Ions Using 1,2 Naphthoquinone -4-Sulphonic Acid -2-Thiosemicarbazone As Metallochromic Indicator*, (Mrs.)S.Kesavan,B.S.Garg and R.P.Singh, University Of Delhi, India, ,pp 52- 1977-181.
