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# Synthesis of the new 2-[6-Nitro-2-benzothiazolylazo]-4-bromo phenol organic reagent for spectrophotometric determination of Zinc(II).

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**Abstract**

A new 2-[6-Nitro-2-benzothiazolylazo]-4-bromo phenol ($NO_2$BTABrP) organic reagent was synthesized. A sensitive and selective spectrophotometric method was proposed for the rapid determination of Zn(II) using ($NO_2$BTABrP) reagent .The reaction between Zn(II) and ($NO_2$BTABrP) reagent is instantaneous at pH=6.0 and the absorbance remains stable for over 24 hrs.

The Method allows for the determination of Zn(II) over the range (0.3-4.0) µg.ml$^{-1}$ ,with molar absorptivity of (6.221 x $10^{+3}$)l.mol $^{-1}$.cm$^{-1}$ and a detection limit of 0.147 µg.ml$^{-1}$.Recovery and relative error values of precision and accuracy of method were found to be R.S.D=1.6% , Re=98.84% , and Erel =-1.16% . The properties of complex was studied and show;(M:R) ratio was 1:2 at pH=6.0 ,and the stability constant of 8.23 x $10^{+9}$ l$^2$.mol$^{-2}$ . The interferences of ions ($Cu^{2+}$ , $CrO^{2-}$ , $Ca^{2+}$ , $pb^{2+}$ , $Co^{2+}$ , $Mg^{2+}$ , $Cd^{2+}$, $Ba^{2+}$ , $Bi^{3+}$) and masking agents effect on absorbance were studied .

**Introduction**

Zinc is a very important metal to human health . More than 20 metalloenzymes containing this element in low concentrations have been identified [(1)] and its considered to have an important immuno-regulatory effect on lymphocytes , lymph tissue , neutrophiles , macrophages , and plateles [(2)] .

Some chromogenic reagents have been used in spectrophotometric methods of determination of Zinc were shown in the following table ;

| chromogenic reagent | ε (l.mol$^{(-1)}$ .cm$^{(-1)}$ | $\lambda_{max}$(nm) | Determination range(ppm) | Ref. |
|---|---|---|---|---|
| 2-6-pyridine dicarboxaldehyde , phenylene diamine | 2.15 x $10^{+4}$ | 460 | 1.9 | 3 |
| 2-(3,5-dibromo-2-pyridylazo) -5-(diethyl amino phenol) | 120000 | 574 | 0.36 | 4 |
| 7-(4-Nitrophenylazo)-8-Hydroxy quinoline-5-sulfonic acid | 24000 | 505 | 0.08-0.5 | 5 |
| 4-(2-thiazolylazo) resorcinol | 33600 | 510 | 0.11-1.4 | 6 |
| 4-(2-pyridylazo) resorcinol | 1820 | 603 | …….. | 7 |

| | | | | |
|---|---|---|---|---|
| (PAR) | | | | |

Thiazolylazo compounds have attracted the attention , as they are sensitive chromogenic reagents in addition to being important complexing agents. These dyes are useful in spectrophotometric determinations due to their good selectivity over a wide range of pH and they are relatively easy to synthesize and purified [8].

In this study , a new ($NO_2$BTABrP) chromogenic reagent was synthesized for spectrophotometric determination of Zn(II) .

**Experimental**

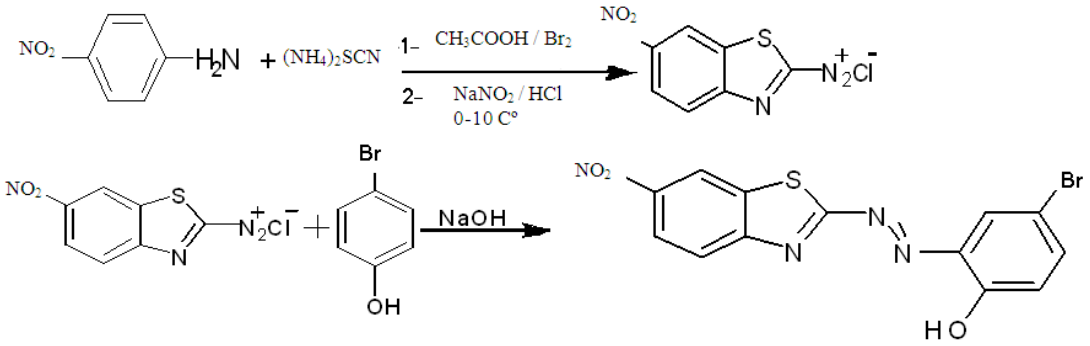
**Reagents;**

All reagents were of analytical grade. Freshly distilled and deionized water was used for solutions preparations .

**Preparation of reagent**[9]

To a mixture of {(4.3 gm of para nitro aniline and 3.8gm of ammonium thiacyanate ) in 70 ml glacial acetic acid }, was added drop by drop from burette (1.2 ml $Br_2$ + 15 ml glacial acetic acid ) keeping at temperature 10 Cº.

After 15 minutes alkaline solution was added to precipitate the thiazole derivative , 1.145 gm of thiazole and in 50 ml glacial acetic acid then add ( 5 ml conc. HCl + 25 ml water ) to the solution . After that drop by drop from burette a solution ( 0.690 gm $NaNO_2$ + 50 ml $H_2O$ ) with stirring at 10 Cº to diazonium salt , then ( 0.642 gm of para bromo phenol + 50 ml ethanol )is added to diazonium salt and 2-[6-nitro-2-benzothiazolyl azo]-4- bromo phenol ($NO_2$BTABrP) organic reagent was formed .




**Standard solution**

stock Zn (II) solution ; A solution of Zn (II) ( 100 µg.ml$^{-1}$) was prepared by dissolving ( 0.223) gm of $ZnNO_3$. $H_2O$ in (100ml) distilled water . Other standard solutions of Zn(II) were prepared by dilution of stock solution with distilled water.

-1x10$^{-3}$ M ($NO_2$BTABrP) standard solution was prepared by dissolving (0.0945)g in 250 ml of absolute ethanol .

-Buffer solution [10](pH=6.0) was prepared by mixing 12.63ml of (0.2)M $Na_2HPO_4$ (which was prepared by dissolving 2.83 gm in 100 ml distilled water) and 7.37 ml of (0.1)M Citric acid (which was prepared by dissolving 1.92 gm in 100 ml distilled water) .

**Apparatus**

Spectrophotometric measurements were made with a Shimadzo(UV-Vis.) scientific equipment with 1.0 cm cell for plot spectra .The pD-303. Spectrophotometer ,APEL

,Japan ,was used in the other measurements . The pH-meter,720 WTW, Germany , and FT-IR Spectrophotometer shimadzo., Japan .,Were used in this work .

**Procedure;**

To an aliquot containing ≤ 10µg .ml $^{-1}$ of Zn(II) in a 10-ml volumetric flask ,was added 2 ml of buffer solution , and 3 ml of ($2.5x10^{-4}$M ) of ($NO_2$BTABrP) solution .The solution was diluted to the mark with distilled water , and absorbance was measured at 25Cº and wave length of 515 nm against the reagent solution as a blank solution prepared under the same conditions.

**Results and Discussion;**

**1-FT-IR spectrum of reagent ($NO_2$BTABrP)**

The following table shows the main vibration frequencies of main absorption bands characteristic of reagent;

| Wave number (Cm $^{-1}$ ) | Groups |
|---|---|
| 3200 – 3500 | γ O-H , $H2O_{Crys.}$ |
| 2860 | γ C – H Aliphatic |
| 2950 | γC – H Aromatic |
| 1730 | γC =N |
| 1490 | γ N=N |
| 1430 | γC =C |
| 1115 | γC – S |
| 1260 | γC – O phenolic |
| 890 | γBr – C |
| 1345 | γC – N |

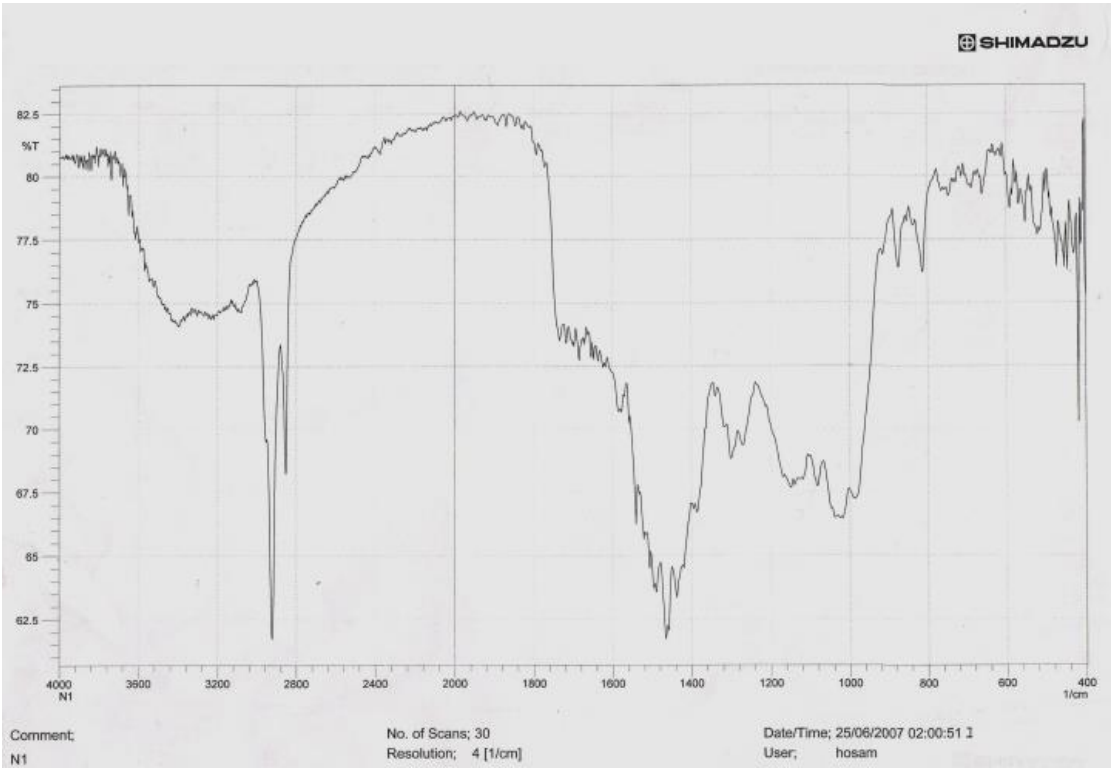
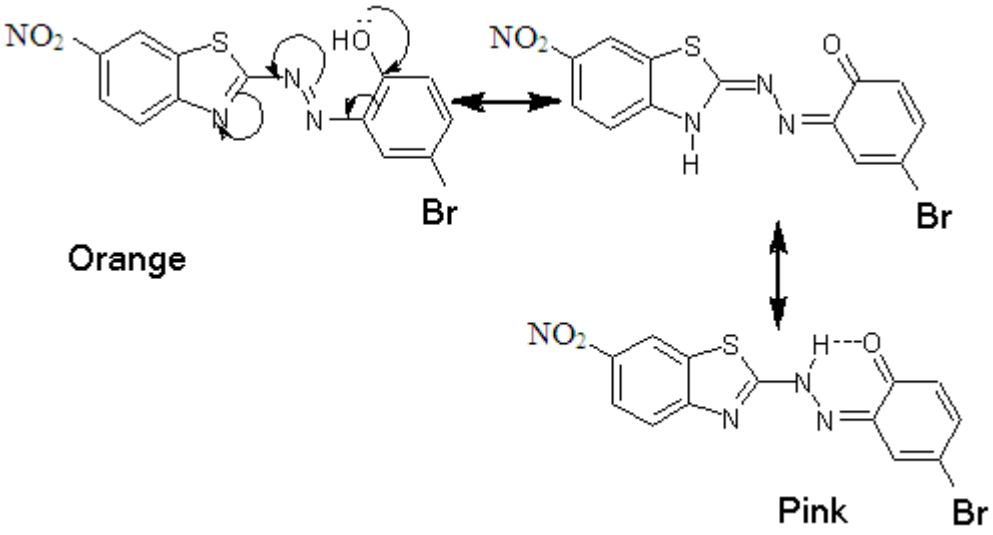
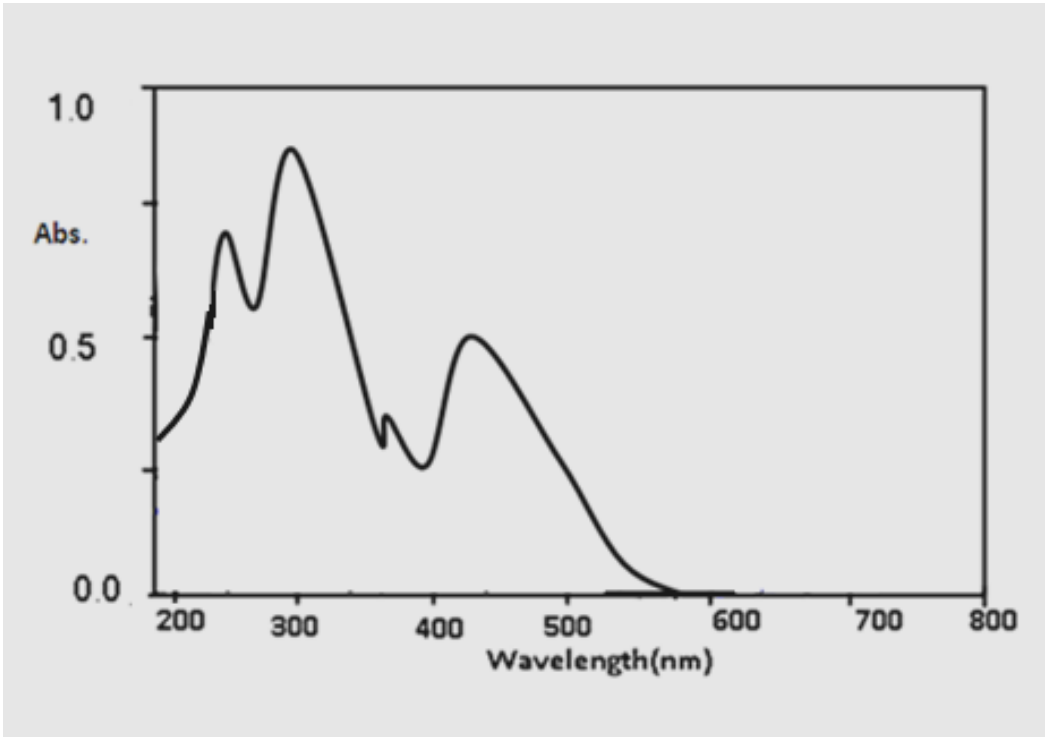



Fig (1); FT-IR spectrum of reagent ($NO_2$BTABrP)

**2-Properties of the ($NO_2$BTABrP)**

($NO_2$BTABrP) reagent is slightly soluble in water ,red powder , orange and stable solution for suitable period time , but in basic medium pH≥8.0 the solution being pink .Such behavior may be interpretated by the following equilibria;



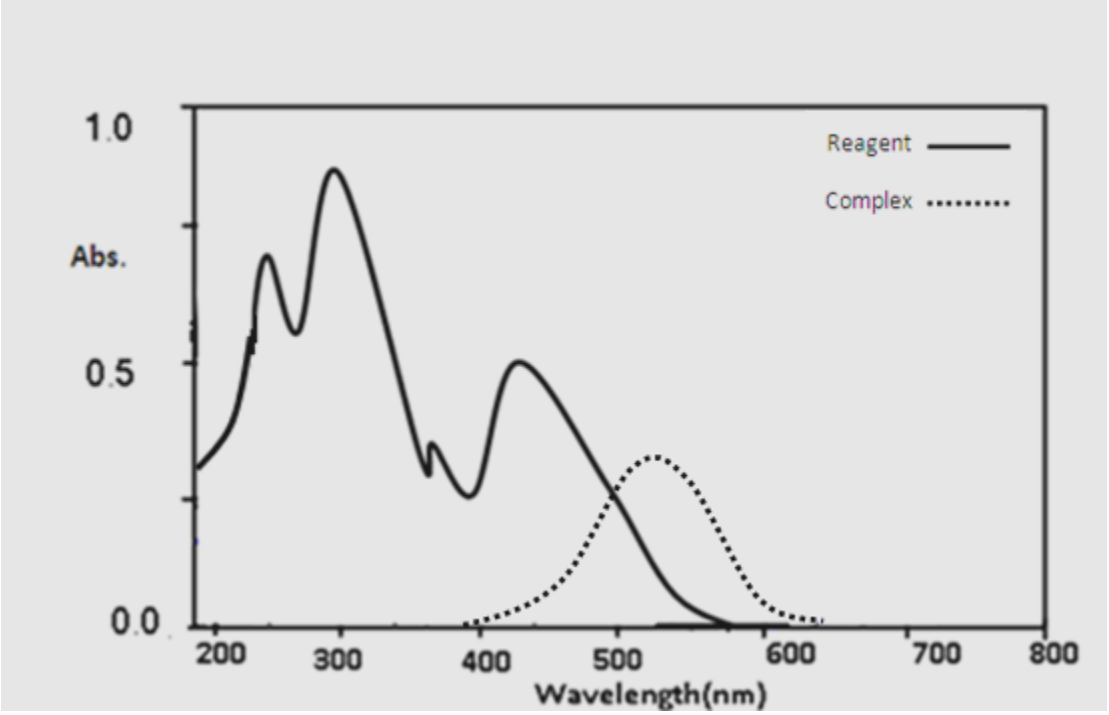



**Fig(2);** UV-Visible spectrum of reagent ($NO_2$BTABrP)

**Study of Zn(II) –($NO_2$BTABrP) complex**

**Absorption spectra**

a-Ultra violet –visible absorption spectra of ($NO_2$BTABrP) reagent ,and Zn(II) -($NO_2$BTABrP) complex solution are shown in fig (3).The reagent showed an absorption maximum at 443 nm,and the complex at 515 nm.




**Fig(3);** UV-Visible spectrum of Zn(II) -($NO_2$BTABrP) complex

**Effect of pH**

The effect of pH was studied over the rang (2-9) adjusted by means of dilute HCl and NaOH solution. figure (4)shows the relationship between absorbance and pH ,where the maximum absorbance obtained in the range of pH =(4.0-7.0) .At 7.0 < pH < 4.0 a decrease in absorbance. Therefore, the optimum pH was 6.0, where the absorbance was maximum and constant.

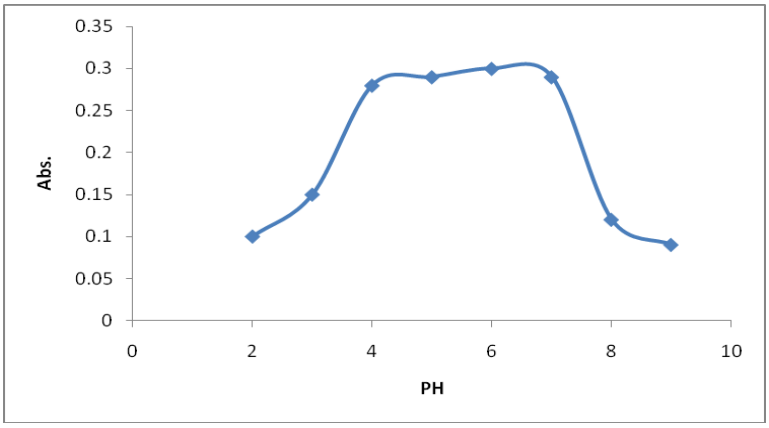



Fig (4); Effect of pH on absorbance of Zn(II)- ($NO_2$BTABrP) Complex.

**Effect of time**

The stability of complex was studied from ( 0 – 120 ) min. with 5 minutes. intervals up to 24 hrs. the maximum absorbance was dttend at 10 minutes figure (5) after that the absorbance remains constant .

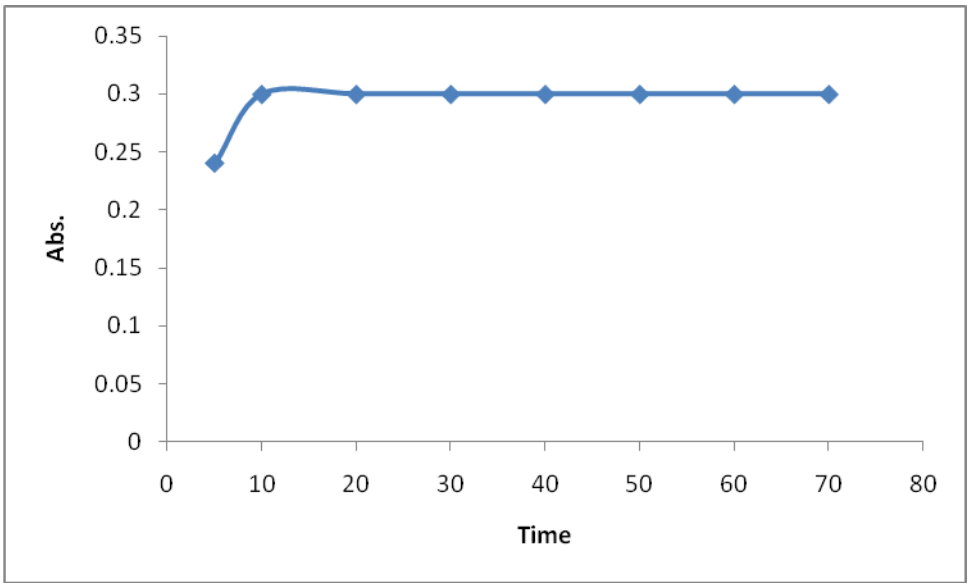



Fig (5); Effect of time on the stability of Zn(II)- ($NO_2$BTABrP) Complex.

**Effect of temperature**

The effect of temperature on absorbance of complex was studied ; the study was performed at temperature between ( 5 – 80 )ºC .Fig (6)show the maximum absorbance obtained at temperature range ( 20 -40 ) ºC which was regarded as a proper

temperature of complex formation . At temperatures higher than 40 ºC the absorbance decrease due to dissociation of complex gradually .

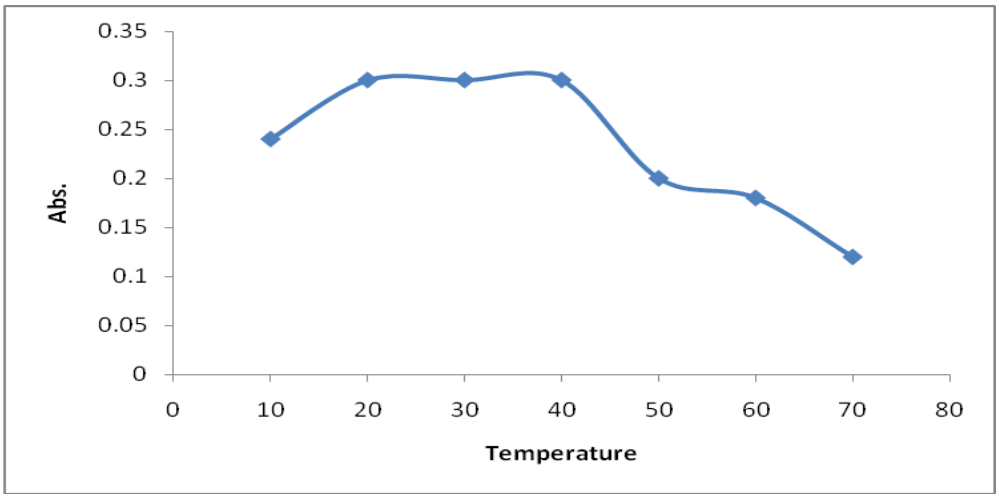
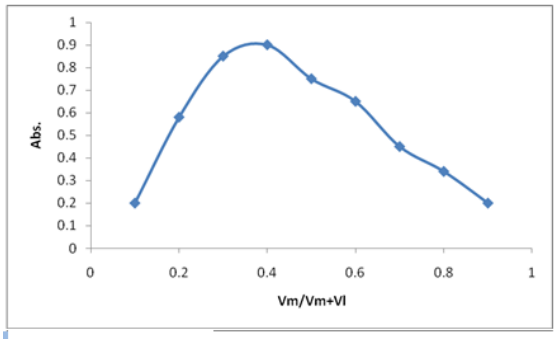



Fig (6); Effect of temperature on the stability of Zn(II)- (No2BTABrP) Complex.

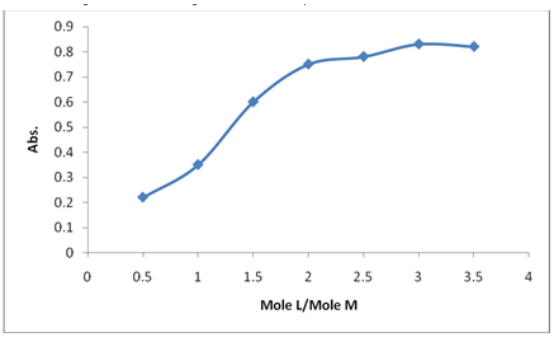
**Determination of stoichiometry and formation constant**

The composing of complex was studied by jobs method of continuous variations and mole ratio method [11] . Fig (7,8) both methods indicate that the ratio of metal ion to reagent molecules ( M:L) was (1:2) at pH = 6.0 .

The formation constant calculated by applied procedure , was found to be ( 0.823 x $10^{+10}$ ) $l^2$. $mol^{-2}$ .



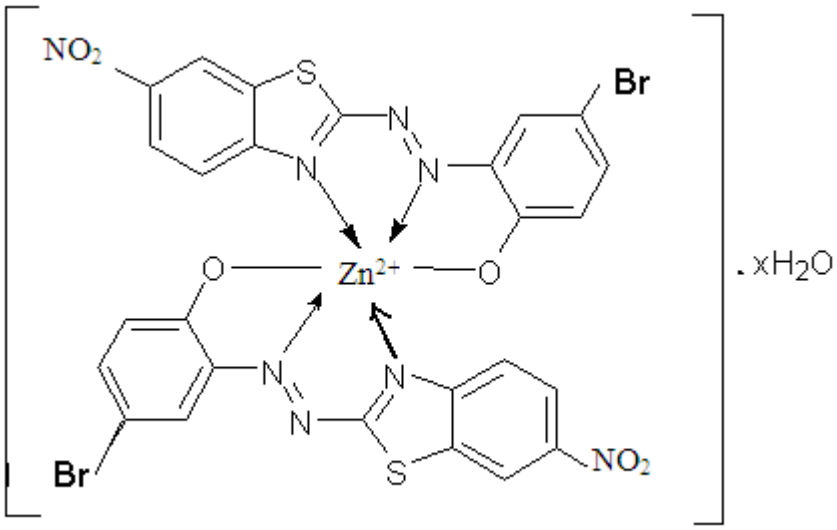

Fig(7);Jobs plot , pH=6.0




Fig(8);Mole ratio plot ,pH =6.0

**Suggestion of structural formula of Zn(II) –($NO_2$BTABrP) complex**

From the obtained results of metal to reagent ratio, and depending on thiazolyl azo compound properties ; the following structure can be suggested ;

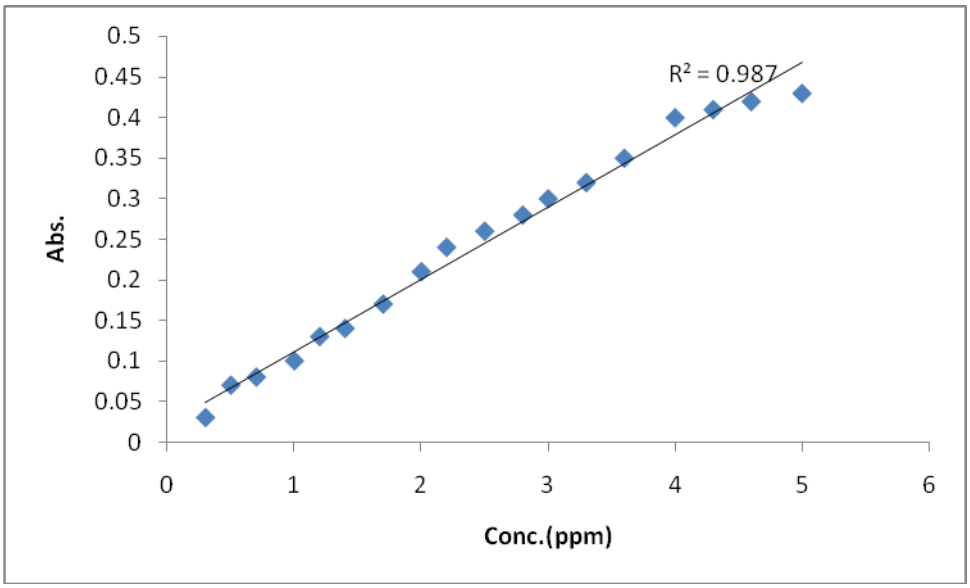



**Analytical characteristics**

**Calibration curve**

Linear calibration graph through the origin was obtained which obeyed Beers law over the range ( 0.3 – 4.0 ) µg . ml $^{-1}$ of Zn (II) . The average molar absorptivity was found to be (6.221 x 10 $^{+3}$ ) l . mol$^{-1}$ .Cm $^{-1}$ .

The sandells sensitivity [12] was ( 0.0174 ) µg of Zn(II).Cm$^{-2}$ , and correlation coefficient (r) was 0.9870 .




**Fig(10);**Calibration curve of Zn(II)- ($NO_2$BTABrP) Complex.

**Precision and accuracy**

The relative standard deviation ( R.S.D %) , evaluated from seven independent determination of 3.0 µg . ml $^{-1}$of Zn(II) was 1.6% , this result show that this method is highly precise . Also the accuracy of this method was determined by calculated the Erel % for 3.0 µg . ml $^{-1}$ standard solution of Zn(II) which was found to be (– 1.16 ) and Re% = 98.84 .

**Interferences**

The effect of the ions ($Cu^{+2}$ , $CrO^{-2}$ , $Ca^{+2}$ , $pb^{+2}$ , $Co^{+2}$ , $Mg^{+2}$ , $Cd^{+2}$, $Ba^{+2}$ , $Bi^{+3}$) which form complex with the reagent during its reaction with Zn(II) were studied . On the other hand , suitable masking agents examined for eliminating the effect of the nine ions , where the mixture of 1,10-phenanthroline ,ammonia , sodium floride ,and sodium acetate were found to be a suitable masking agents.

**References**

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**تحضير الكاشف العضوي 2-[(6-نايترو -2-بنزوثيازوليل)آزو]-4-برومو فينول لأجل التقدير الطيفي لأيون الخارصين الثنائي.**

**عقيل مهدي جريو**

**جامعة الكوفة –كلية العلوم –قسم الكيمياء.**

**الخلاصة**

تم تحضير الكاشف العضوي 2-[(6-نايترو -2-بنزوثيازوليل)آزو]-4-برومو فينول. و استخدم في التقدير الطيفي لأيون الخارصين (II)،التفاعل بين الكاشف و أيون الخارصين (II) يتم عند دالة حامضية =6.0 وامتصاصية المحلول تبقى ثابتة لأكثر من 24 ساعة.

الطريقة تسمح لتقدير أيونات الخارصين (II) ضمن مدى بين(0.3-4.0) ميكرو غرام.مل$^{-1}$،و بمعامل امتصاص مولا ري ($6.221 \times 10^{3}$) لتر.مول$^{-1}$.سم$^{-1}$، و بحد كشف (0.147) ميكروغرام.مل$^{-1}$.

تم حساب دقة الطريقة التحليلية و ضبطها فكانت قيم (R.S.D= 1.6 % ) و (Re%=98.84) و (Erel=- 1.16% ).

درست طبيعة المعقد الذائب فكانت نسبة الفلز إلى الكاشف (2:1) عند دالة حامضية=6.0، و ثابت الأستقرارية ($8.23 \times 10^{9}$)لتر$^{2}$.مول$^{-2}$،وكانت تداخلات الأيونات , $Mg^{2+}$ , $Co^{2+}$ , $pb^{2+}$ , $Ca^{2+}$ , $CrO^{2-}$ , $Cu^{2+}$ ($Cd^{2+}$, $Ba^{2+}$ , $Bi^{3+}$) و تأثير عوامل الحجب المختلفة على الامتصاصية المدروسة.