

**Synthesis of The new 2-[6-Nitro-2-benzothiazolylazo]-4-Amino benzoic acid Organic Reagent for Spectrophotometric Determination of Lead (II)**

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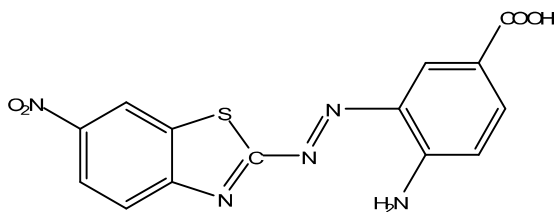
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**Abstract:-**

A new 2-[6-Nitro-2-benzothiazolylazo]-4-amino benzoic acid (NO<sub>2</sub>BTAAB) organic reagent was synthesized. A sensitive and selective spectrophotometric method was proposed for the rapid determination of Pb(II) using (NO<sub>2</sub>BTAAB) reagent .The reaction between Pb(II) and (NO<sub>2</sub>BTAAB) reagent is instantaneous at pH=8.0 and the absorbance remains stable for over 24 hrs.

The Method allows for the determination of Pb(II) over the range (0.1-5.5) µg.ml<sup>-1</sup> ,with molar absorptivity of (2.248 x 10<sup>+4</sup>)L.mol<sup>-1</sup>.cm<sup>-1</sup> and a detection limit of 0.012 µg.ml<sup>-1</sup>.Recovery and relative error values of precision and accuracy of method were found to be R.S.D=2.6% , Re=103 % , and Erel = 3 % . The properties of complex was studied and show;(M:R) ratio was 1:2 at pH=8.0 ,and the stability constant of 1.254 x 10<sup>+10</sup> L<sup>2</sup>.mol<sup>-2</sup> . The interferences of ions (NH<sub>4</sub><sup>+</sup>,Ni<sup>2+</sup> , CrO<sub>4</sub><sup>2-</sup> , Ag<sup>+</sup> , Cu<sup>2+</sup>, Hg<sup>+2</sup> ,WO<sub>4</sub><sup>-2</sup> , Zn<sup>+2</sup> , Co<sup>2+</sup> , Mg<sup>2+</sup> , Cd<sup>2+</sup> , Ba<sup>2+</sup> , Bi<sup>3+</sup>) and masking agents effect on absorbance were studied .



Figure(1): (NO<sub>2</sub>BTAAB) reagent

**Key word: (NO<sub>2</sub>BTAAB),lead, Spectrophotometric Determination**

**Chemistry classification:QD71-142**

**Introduction**

analysis of Pb(II) include methods based on atomic absorption spectrometry , atomic emission spectrometry , inductively coupled plasma mass spectrometry, anodic stripping voltammety and reversed – phase high performance liquid chromatography coupled with UV-Vis or fluorescence detection<sup>(12-17)</sup> .

Spectrophotometry is a relatively sensitive method for lead (II) as it is of low cost, simple and within the reach of even ordinary laboratories, which is based

Lead is cumulative poison<sup>(1)</sup> that enters the body from lead water pipes, and lead based paints. Lead pollution is a serious danger to the environment and human health<sup>(2-3)</sup> . Lead intake causes many fatal diseases including disfunction of renal, blood and neurological systems. Lead (II) easily deposits in blood, kidney, reproductive system, nervous system and brain and cause lead poisoning<sup>(4-8)</sup> . Even low levels of lead in children cause brain and neurodevelopmental deseases<sup>(9-11)</sup> . Several methods developed for the

ditizonate<sup>(26)</sup>, and Cetyltrimethyl ammoniumbromide<sup>(27)</sup>.

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<sup>(28)</sup>.

In this paper, a new (NO<sub>2</sub>BTAAB)chromogenic reagent was synthesized for spectrophotometric determination of Pb(II).

**Experimental:**

**Reagents;**

for solutions preparations .

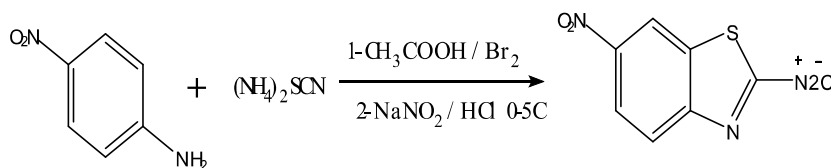
**Preparation of reagent<sup>(29)</sup>**

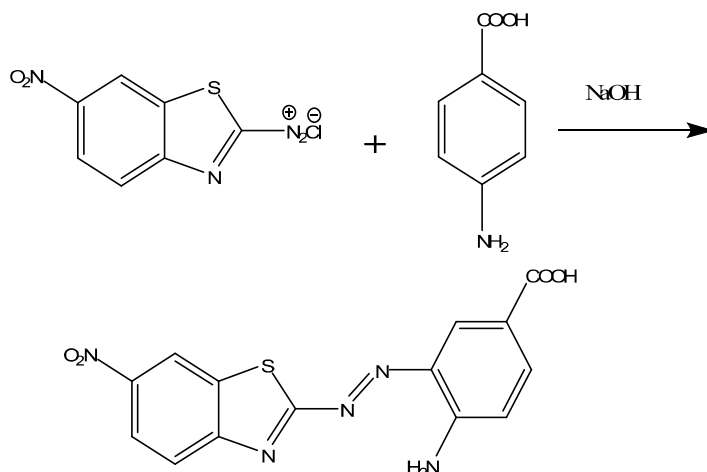
ml water ) to the solution . After that drop by drop from burette a solution ( 0.690 gm NaNO<sub>2</sub> + 50 ml H<sub>2</sub>O ) with stirring at 0-5 C° to diazonium salt , then ( 0.1.387 gm of para amino benzoic acid + 50 ml ethanol ) added to diazonium salt and 2-[6-nitro-2-benzothiazolyl azo]-4- amino benzoic acid (NO<sub>2</sub>BTAAB) organic reagent was formed then recrystalized and purified by absolute ethanol.

on reaction between lead and chromogenic reagents. Some chromogenic reagents have been used in spectrophotometric methods of determination of lead such as; Phenanthraquinone monophenyl thiosemicarbazone (PPT)<sup>(18)</sup>, diphenylthiocarbazone<sup>(19)</sup>, malachite green<sup>(20)</sup>, Purpurin (1,2,4-Trihydroxyanthraquinone)<sup>(21)</sup>, dibromo-*p*-methyl-bromosulfonazo (DBMBSA)<sup>(22)</sup>, 5-bromo-2-hydroxyl -3-Methoxybenzaldehyde -4-hydroxy benzoic hydrazone<sup>(23)</sup>, 3,5-Dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone (DMHBIH)<sup>(24)</sup>, isonitroso-*pi*sopropyl acetophenone phenyl hydrazine<sup>(25)</sup>,

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

To a mixture of {4.3 gm of para nitro aniline and 3.8gm of ammonium thiocyanate } in 70 ml glacial acetic acid }, was added drop by drop from burette (1.2 ml Br<sub>2</sub> + 15 ml glacial acetic acid ) keeping at temperature >10 C°. After 15 minutes alkaline solution was added to precipitate the thiazole derivative , 1.145 gm of thiazole in 50 ml glacial acetic acid then add ( 5 ml conc. HCl + 25





**Standard solutions:**

and FT-IR Spectrophotometer shimadzo., Japan .,Were used in this work .

**Procedure;**

To an aliquot containing < 10µg .ml<sup>-1</sup> of Pb(II) in a 10-ml volumetric flask ,was added 2 ml of buffer solution , and 3.0 ml of (1 x 10<sup>-4</sup>M ) of (NO<sub>2</sub>BTAAB) solution .The solution was diluted to the mark with distilled water , and absorbance was measured at 25C° and wave length of 621 nm against the reagent solution as a blank solution prepared under the same conditions.

**Results and Discussion;**

**1-FT-IR spectrum of reagent (NO<sub>2</sub>BTAAB)**

The following table shows the main vibration frequencies of main absorption bands

characteristic of reagent

table(1): shows the main vibration frequencies of main absorption bands

characteristic of reagent

stock Pb (II) solution ; A solution of Pb (II) ( 100 µg.ml<sup>-1</sup>) was prepared by dissolving ( 15.99) mg of Pb(NO<sub>3</sub>)<sub>2</sub> in (100ml) distilled water . Other standard solutions of Pb(II) were prepared by dilution of stock solution with distilled water.

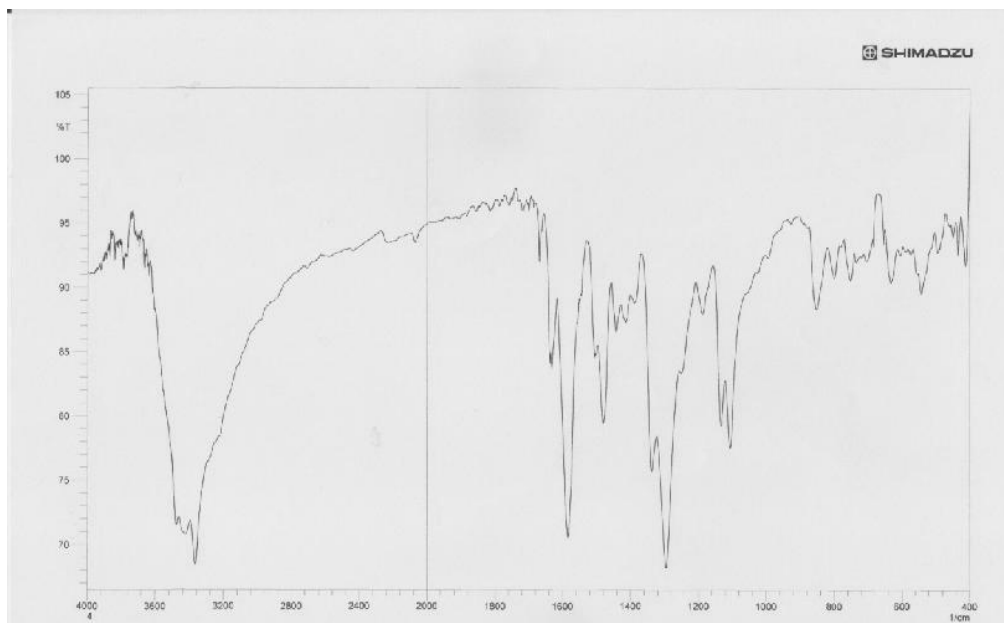
-1x10<sup>-3</sup> M (NO<sub>2</sub>BTAAB)standard solution was prepared by dissolving (0.0878)g in 250 ml of absolute ethanol .

-Buffer solution <sup>(30)</sup>(pH=8.0) was prepared by mixing 19.45 ml of (0.2)M Na<sub>2</sub>HPO<sub>4</sub> (which was prepared by dissolving 2.83 gm in 100 ml distilled water) and 0.55 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 ,

Wave number (Cm <sup>-1</sup> )	Groups
3300-3500	ν NH, ν O-H
1413	δ(C - H) <sub>bending</sub> , Aromatic
1633	ν C =N
1577	ν N=N
1480	ν C =C
1132	ν C - S
1692	ν C = O carboxylic
1332	ν C - N
1554	ν N-O

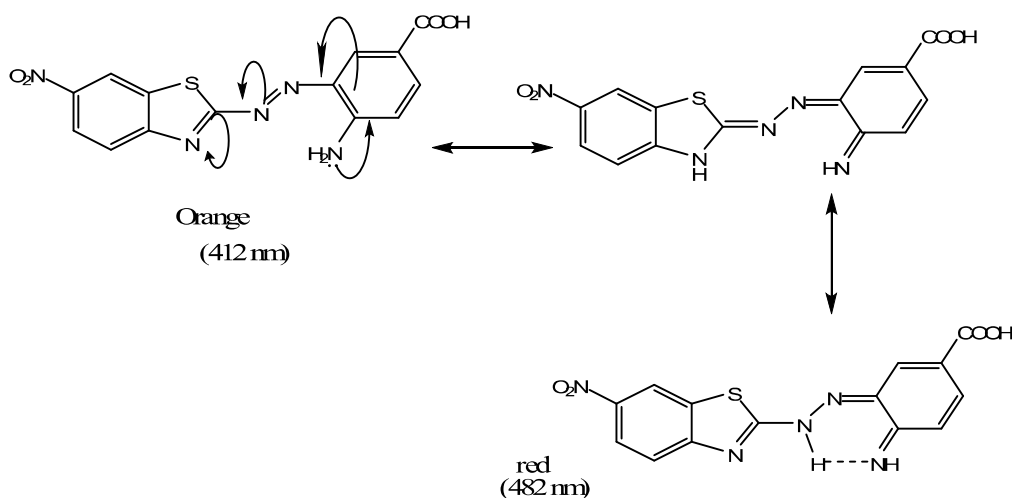


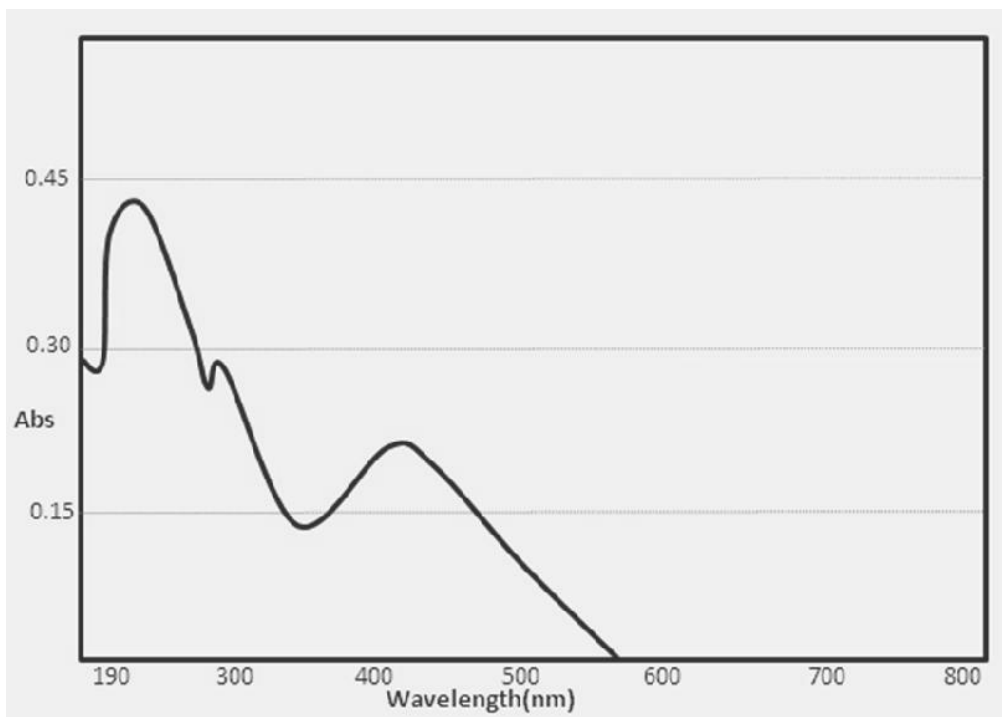
**Fig.2: FT-IR spectrum of reagent (NO<sub>2</sub>BTAAB)**

**2-Properties of the (NO<sub>2</sub>BTAAB)**

red .Such behavior may be interpreted by the following equilibria;

(NO<sub>2</sub>BTAAB)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



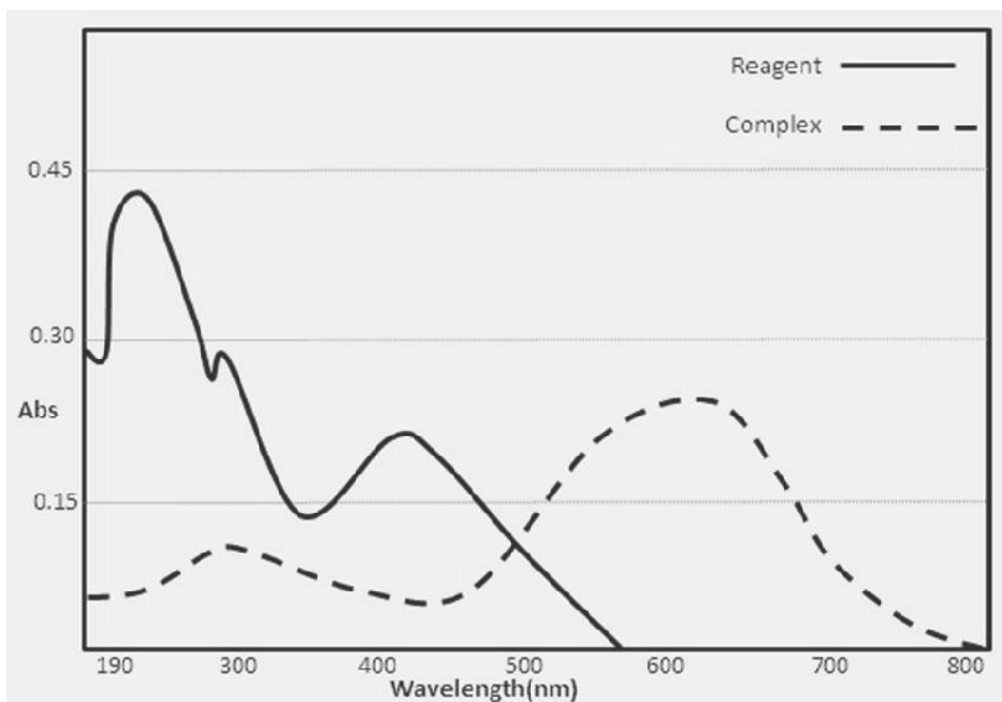


**Fig.3: UV-Visible spectrum of (NO<sub>2</sub>BTAAB) reagent**

Study of Pb(II)–(NO<sub>2</sub>BTAAB) complex solution are shown in fig (4).The reagent showed an absorption maximum at 412 nm,and the complex at 621 nm.

**Absorption spectra**

a-Ultra violet –visible absorption spectra of ( $1 \times 10^{-4}$  M)(NO<sub>2</sub>BTAAB)reagent ,and ( $2 \times 10^{-5}$  M ) Pb(II) - (NO<sub>2</sub>BTAAB)



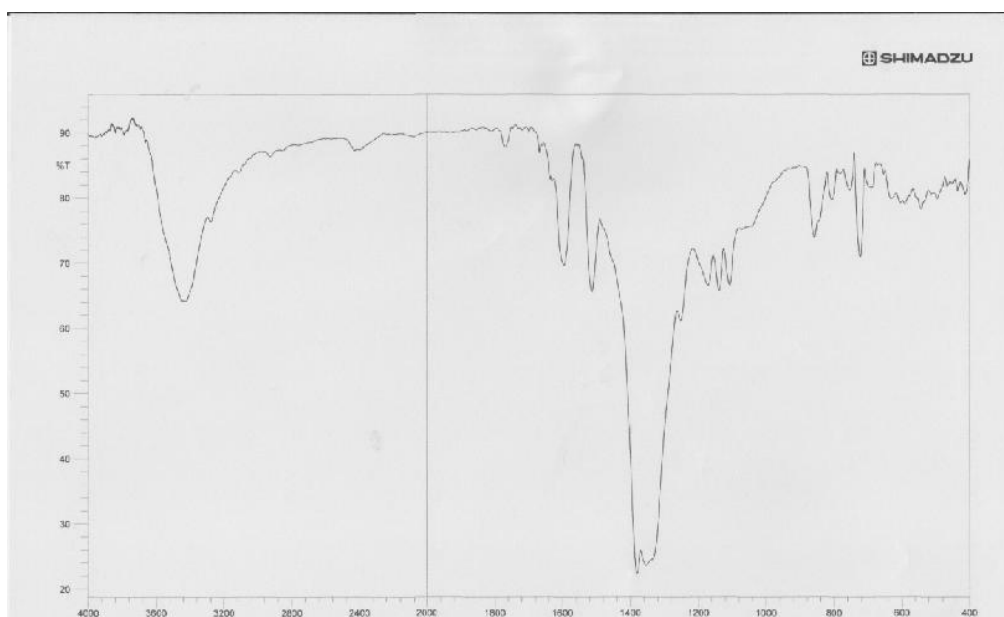
**Fig.4: Uv-Visible spectrum of Pb(II)-(NO<sub>2</sub>BTAAB) complex**

**-FT-IR spectrum of Pb- (NO<sub>2</sub>BTAAB) complex:**

table(2): shows the main vibration frequencies of main absorption bands characteristic of Pb- (NO<sub>2</sub>BTAAB) complex

Changing in intensities , shift in peaks positions , and fission in azo peak were seen which indicate to formation of complex as in figure(5).

Wave number (Cm <sup>-1</sup> )	Groups
3300 – 3500	$\nu$ NH, $\nu$ O-H
1440	$\delta$ (C – H) <sub>bending</sub> , Aromatic
1696	$\nu$ C =N
1486	$\nu$ N=N
1427	$\nu$ C =C
1123	$\nu$ C – S
1680	$\nu$ C = O carboxylic
1344	$\nu$ C – N
1651	$\nu$ N-O
720	$\delta$ Pb-N

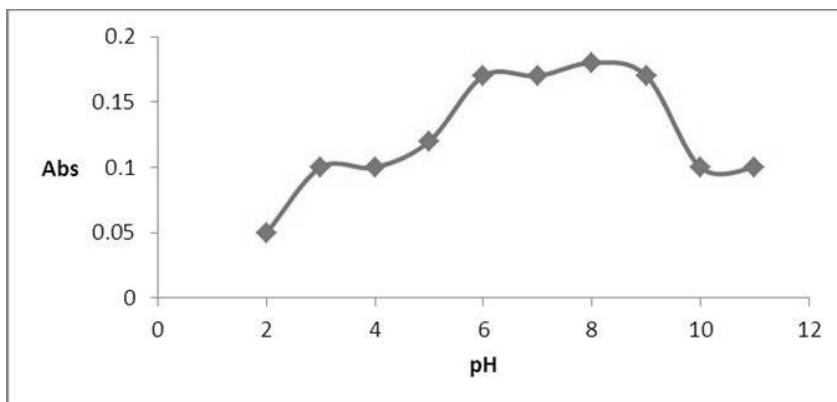


**Fig.5: FT-IR spectrum of Pb(II) –(NO<sub>2</sub>BTAAB)complex.**

**Effect of pH**

a decrease in absorbance. Therefore, the optimum pH was 8.0, where the absorbance was maximum and constant, 2 ppm of lead(II) was used.

The effect of pH was studied over the rang (2-11) adjusted by means of dilute HCl and NaOH solution. figure (6)shows the relationship between absorbance and pH ,where the maximum absorbance obtained in the range of pH =(6-9) .At 9< pH< 6

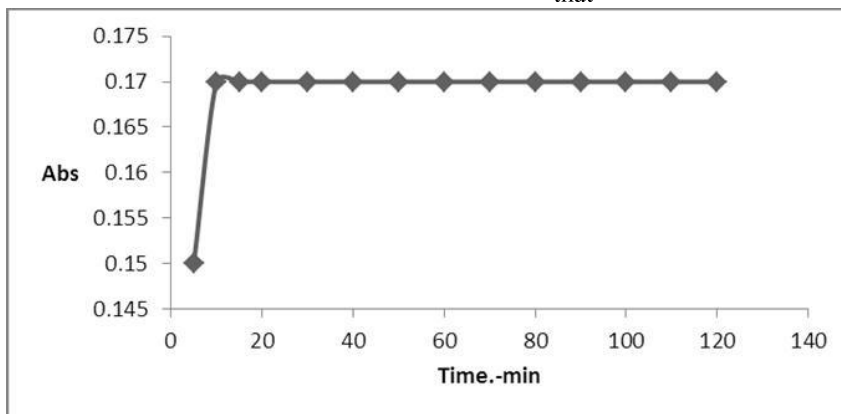


**Fig (6); Effect of pH on absorbance Pb(II)-(NO<sub>2</sub>BTAAB)complex.**

**Effect of time**

the absorbance remains constant , 2 ppm of lead(II) was used.

The stability of complex was studied from ( 0 – 120 ) min. with 5 minutes. intervals up to 24 hrs. the maximum absorbance was reached at 10 minutes figure (7) after that

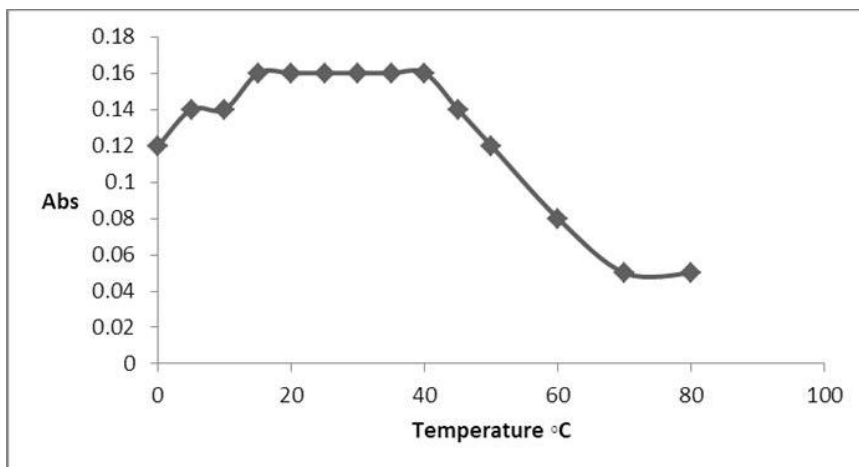


**Fig (7); Effect of time on the stability of Pb(II)-(NO<sub>2</sub>BTAAB)complex.**

**Effect of temperature**

temperature of complex formation . At temperatures higher than 45 °C the absorbance decrease due to dissociation of complex gradually , 2 ppm of lead(II) was used.

The effect of temperature on absorbance of complex was studied ; the study was performed at temperature between ( 5 – 80 )°C .Fig (8)show the maximum absorbance obtained at temperature range ( 20 - 45 ) °C which was regarded as a proper

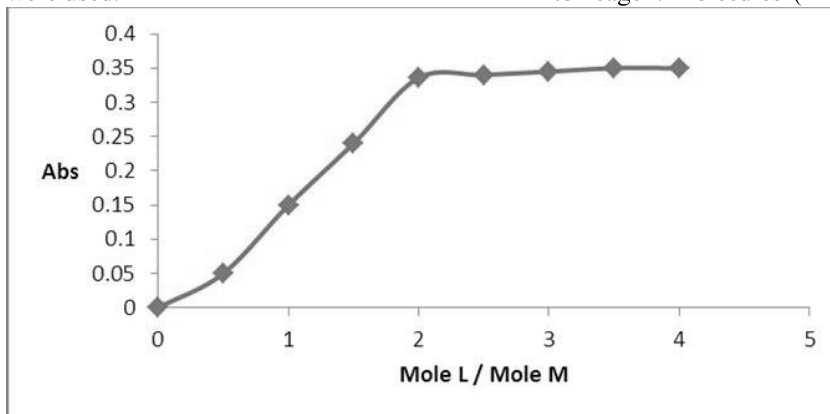


**Fig (8); Effect of temperature on the stability of Pb(II)-(NO<sub>2</sub>BTAAB) complex.**

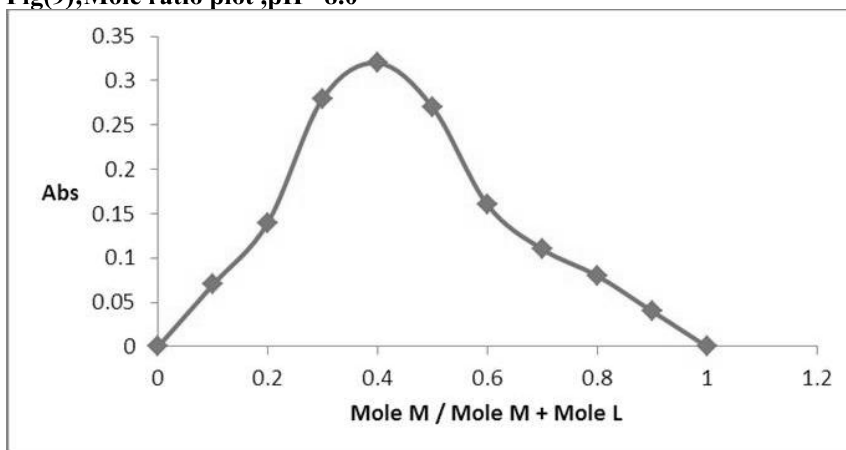
**Determination of stoichiometry and formation constant**

pH = 8.0 .The formation constant calculated by applied procedure , was found to be  $(1.254 \times 10^{+10}) \text{ L}^2 \cdot \text{mol}^{-2}$ , ( $1.5 \times 10^{-5} \text{ M}$ ) of both lead(II) and reagent were used.

The composing of complex was studied by jobs method of continuous variations and mole ratio method <sup>(31)</sup> . Fig (9,10) both methods indicate that the ratio of metal ion to reagent molecules ( M:L) was (1:2) at



**Fig(9);Mole ratio plot ,pH=8.0**



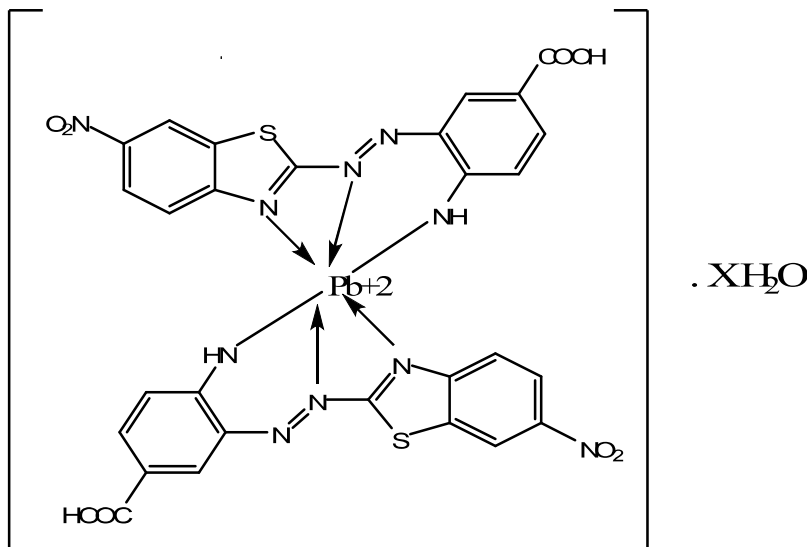
**Fig(10);Jobs plot , pH=8.0**

**Suggestion of structural formula of Pb(II)-(NO<sub>2</sub>BTAAB) complex**



Compounds properties ; the following structure can be suggested ;

From the obtained results of metal to reagent ratio, and depending on thiazolyl azo

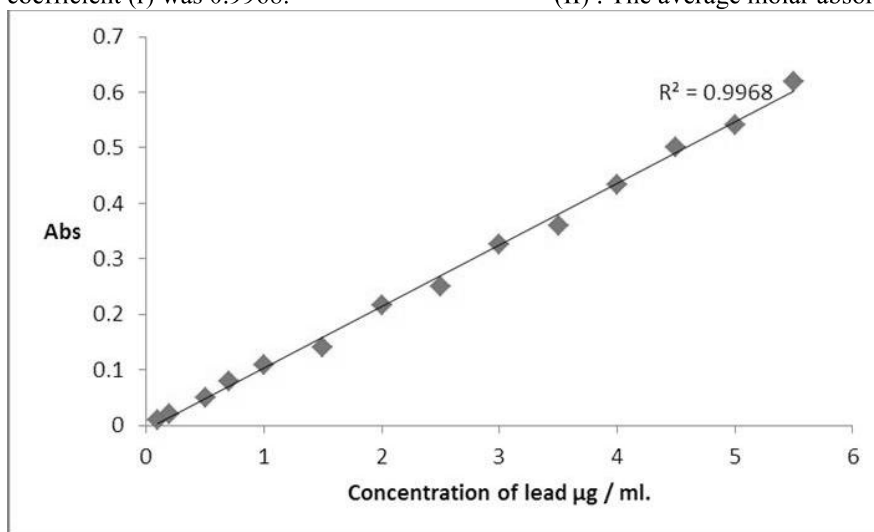


**Analytical characteristics**

**Calibration curve**

found to be  $(2.248 \times 10^{-4}) l \cdot mol^{-1} \cdot cm^{-1}$ . The sandells sensitivity<sup>(32)</sup> was  $(0.0092) \mu g$  of Pb(II). $cm^{-2}$ , and correlation coefficient (r) was 0.9968.

Linear calibration graph through the origin was obtained which obeyed Beers law over the range  $(0.1 - 5.5) \mu g \cdot ml^{-1}$  of Pb (II). The average molar absorptivity was



**Fig (11): calibration pbrve of Pb(II) –(NO2)BTAAAB complex**

**Precision and accuracy**

is highly precise . Also the accuracy of this method was determined by calculated the Erel % for  $1.0 \mu g \cdot ml^{-1}$  standard solution of Pb(II) which was found to be (3) and Re% = 103 .

The relative standard deviation ( R.S.D %) , evaluated from seven independent determination of  $1.0 \mu g \cdot ml^{-1}$  of Pb(II) was 2.6 % , this result show that this method

**Interferences**

$Cd^{2+}$ ,  $Ba^{2+}$ ,  $Bi^{3+}$  which form complex with the reagent during its reaction with

The effect of the ions  $(NH_4^+, Ni^{2+}, CrO_4^{2-}, Ag^+, Cu^{2+}, Hg^{+2}, WO_4^{-2}, Zn^{+2}, Co^{2+}, Mg^{2+},$

where the mixture of KCN , NaF , NH<sub>3</sub>, and thiourea were found to be a suitable masking agents.

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Pb(II) were studied . On the other hand , suitable masking agents examined for eliminating the effect of the thirteen ions ,

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**تحضير الكاشف العضوي الجديد 2- [6-نايترو-2-بنزوثيريازوليل آزو]-4-أمينو حامض البنزويك  
لأجل التقدير الطيفي لأيون الرصاص (II)**

تاريخ القبول: 2015/4/26

تاريخ الاستلام: 2015/2/18

عقيل مهدي جريو  
جامعة الكوفة – كلية العلوم – قسم الكيمياء

**الخلاصة:**

تم تحضير الكاشف العضوي الجديد 2- [6-نايترو-2-بنزوثيريازوليل آزو]-4-أمينو حامض البنزويك , وأستعمل في طريقة تقدير طيفي حساسة و إنتقائية لأيونات الرصاص(II) . التفاعل بين الكاشف و أيون الرصاص (II) يتم عند دالة حامضية = 8 و إمتصاصية المحلول تبقى ثابتة لأكثر من 24 ساعة. الطريقة تسمح لتقدير أيون الرصاص (II) ضمن مدى تركيز (0.1- 5.5) مايكرو غرام لكل مليلتر و بمعامل إمتصاص مولاري (x 10<sup>+4</sup> 2.248) لتر.مول<sup>-1</sup>.سم<sup>-1</sup>. و بحد كشف 0.012 مايكرو غرام لكل مليلتر. تم حساب دقة الطريقة التحليلية و ضبطها فكانت R.S.D=2.6 % و Re = 103 % و Erel = 3% . درست طبيعة المعقد الذائب فكانت نسبة (الكاشف: الفلز) = 1:2 عند دالة حامضية = 8 و كان ثابت إستقرارية المعقد الذائب = 1.254 x 10<sup>+10</sup> لتر.مول<sup>-2</sup>. وكما درست تداخلات الأيونات ( , Ag<sup>+</sup> , NH<sub>4</sub><sup>+</sup>, Ni<sup>2+</sup> , CrO<sub>4</sub><sup>2-</sup> , Bi<sup>3+</sup> , Ba<sup>2+</sup> , Cd<sup>2+</sup> , Mg<sup>2+</sup> , Co<sup>2+</sup> , Zn<sup>2+</sup> , WO<sub>4</sub><sup>2-</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>) و تأثير عوامل الحجب المختلفة على الإمتصاصية المدروسة.

**الكلمات المفتاحية:** التقدير الطيفي, الرصاص, - [6-نايترو-2-بنزوثيريازوليل آزو]-4-أمينو حامض البنزويك

Chemistry classification: QD71-142