Synthesis and Spectrophotometric study of 4- (6- Nitro-2-benzothiazolylazo) resorcinol as an analytical reagent for the determination of zinc.

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Abstract :

4-(6-Nitro-2-benzothiazolyl azo)resorcinol (6-Nitro BTAR) has been synthesized , and was used as a reagent for the spectrophotometric determination of microgram amounts of zinc ions. This method sensitive, selective and rapid for reaction between Zn^{2+} and (6-Nitro BTAR), to form a brown complex having a molar ratio of 1:2 (Zn - 6-Nitro BTAR) at pH 6. The molar absorptivity of the complex is (5846 .7 $L.mol^{-1}.cm^{-1}$) at λ_{max} 462.5 nm .Beer's law is obeyed in the range of 0.2 –3 $\mu g.ml^{-1}$ and the stability constant was found to be $1x10^8$ $L^2.mole^{2-}$.

The relative standard deviation, recovery and relative error values of this method was found to be R.S.D% = 1.6, Re % = 98.84,and Erel % = -1.16. The most important interference were due to Hg^{2+},Cd^{2+},CrO_4^{2-}, Ag^+, Ni^{2+} and Co^{2+} , and suitable masking agents were used. The method was applied successfully for the determination of zinc in clay of shaat Al-Hilla.

الخلاصة

تم تحضير الكاشف العضوي 4- (6– نايترو – بنزوثيازوليل ازو) ريزورسينول واستخدم في تقدير كميـات مايكرو غرامية من ايون الزنك II بطريقة تحليلية طبقية سهلة وسريعة وحساسة. تم قياس المعقد المعقـد المتكـون (البني اللون) من تفاعل الكاشف مع ايون الزنك II عند pH = 6 بنسبة 1:2 من الايون الفلزي الى الكاشف عند الطول الموجي 462.5nm وكان معامل الامتصاص المولاري هو 5846.7 لتر. مول $^{-1}$.سم$^{-1}$ حيث كانت التراكيـز التـي تطاوع قانون بير مساوية الى (0.2-3) مايكرو غرام زنك II / مليلتر ، وبلغت قيمة ثابت الاستقرارية $1x10^8$ لتـر^2 .مول$^{-2}$ ، وحدد دقة وضبط الطريقة التحليلية المتبعة بأستخدام محاول قياسي من ايون الزنك فكانت قيمة R.S.D % , Re % , Erel % هي 1.16 , 98.84 , 1.6 على التوالي. كذلك تم دراسة تأثير ايونـات Hg^{2+},Cd^{2+},CrO_4^{2-}, Ag^+, Ni^{2+},Co^{2+} على التوالي والتي تتداخل عند تفاعل الكاشف BTAR مع ايون الزنك II وتم حجـب تاثيرهـا باستخدام عوامل حجب قياسية ، طبقت الطريقة التحليلية لتقدير الزنك في طين شط الحلة.

Introduction

The determination of trace – or ultra trace amounts of zinc become more and more important in different fields such as environmental, biological, and material sciences [(1)]. Zinc ions is one of the essential elements for animals, and often exist in food, drink and grains [(2)].

Many methods are used in the determination of Zn^{2+} ions, for example separation, preconcetration or by inductively coupled plasma atomic emission spectroscopy (ICP–AES)[(3)]. Another example is the simultaneous determination of Zn in cow liver by differential pulse polarographly [(4)] .

A spectrophotomctric determination of zinc was described using the 2- (3,5–dibromo –2 – pyridylazo)–5-diethyl amino phenol [(5)] . Beer's law was obeyed up to 0.36 $\mu g.ml^{-1}$, molar absorptivity of 12,000 $L.mol^{-1}.cm^{-1}$, and the ratio of zinc to reagent was 1:2.

Mohmmod et al[(6)] used 1-(2-benzothiozolylazo)-3-(4-hydroxy dibenzo furan) for the determination of zinc at λ_{max} 603 nm , the optimum pH was 4.8 and the molar absorptivity

was 10820 L.mole^{-1}.cm $^{-1}$. Hnilickova et al[7] used thiazolylazo resoreinol for determinetion of zinc at λ_{max} 510 nm, at optimum pH 4.8 and molar absorpitivity of 32000 L.mol^{-1}.cm^{-1} .

In this work , the reagent of (6-Nitro BTAR) which was prepared by Ghali [8] was prepared again and was used for the determination of zinc in aqueous solution and clay of shaat Al-Hilla. The present proposed method was found sensitive and selective for the spectrophotometric determination of Zn^{2+} at room temperature .

Experimental

Apparatus

Absorption spectra were recorded with Cintra5-GBC scientific Equipment, while absorption measurement were carried out by using Pye Unicam UV. Visible SP8–100 double–beam spectrophotometer both with matched 1 cm quartz cells. pH of the solutions was measured using Philips PW 9421 PH meter (PH $\pm$ 0.001).

FTIR spectra were recorded with FTIR – 8000 schimadzu, single beam , using KBr disks .

- Atomic absorption spectrophotometer 5000 , Perkin – Elmer , U.S.A

Reagents

- All chemical used were of analytical – reagent grade unless stated other wise .
- All solutions were prepared with de – ionized water .

Preparation of the Reagent [9]

Prepared by dissolve (3.45gm of para nitro aniline and 3.8gm amounium thiocyanate) in 70 ml dissolving glacial acetic acid , after that , add dropwise from a burette (1.2 ml Br_2 + 15 ml glacial acetic acid) and the reaction was kept at 10˚C. After 15 min add alkaline solution to precipitate the thiazole compound. dissolve 1.95 gm of thiazole in 50 ml of glacial acetic acid then add (5ml conc. HCl + 25ml water to this solution . After that add drop by drop from a burette a solution of (0.69 gm $NaNO_2$ + 5 ml H_2O)with stirring at 10˚C to form diazonium salt , then add a solution of (1.1 gm resorcinol in 50 ml ethanol) to the diazonium salt to form the 4-(6- Nitro-2- benzothiazolylazo) resorcinol (6-Nitro BTAR).

Standard Zinc Solution

1000 ppm prepared by dissolving (0.208)gm of $ZnCl_2$ in 100 ml of distilled water, working solutions were freshly prepared by appropriate dilution of the stock solution.

6- Nitro BTAR Solution

1×10^{-3} M prepared by dissolving 0.079gm in 250ml ethanol.

Procedure

Introduce 3 ml of reagent (BTAR) to 1 ml from solution containing $\leq$ 3 mg. ml^{-1} of Zn^{2+} in 10 ml calibrated flask and the solution was diluted to the mark with water after the adjustment to a pH 7. Measure the absorbance of the resultant solution after 10-15 min. at λmax 462.5 nm at 25˚ C against blank solution prepared under the same conditions but containg no zinc.

Results and Discussion

FTIR Spectra of Reagent

The FTIR spectra of reagent fig.(1) showed absorption band of (O-H) at 3454.3 cm^{-1} which refers to hydroxy group of resorcinol , absorption band of (C-H) at 2947.0 cm^{-1} which refers to (C-H) of aromatic ring, absorption band of (C-H) at 1649.0 cm^{-1} , absorption band of (C = C) thiazol ring at 1494.7 cm^{-1}, absorption band of (N=N) at 1529.4 cm^{-1} , and absorption band at 1328.9 cm^{-1} which refers to (NO_2)[10,11].

FTIR Spectra of complex

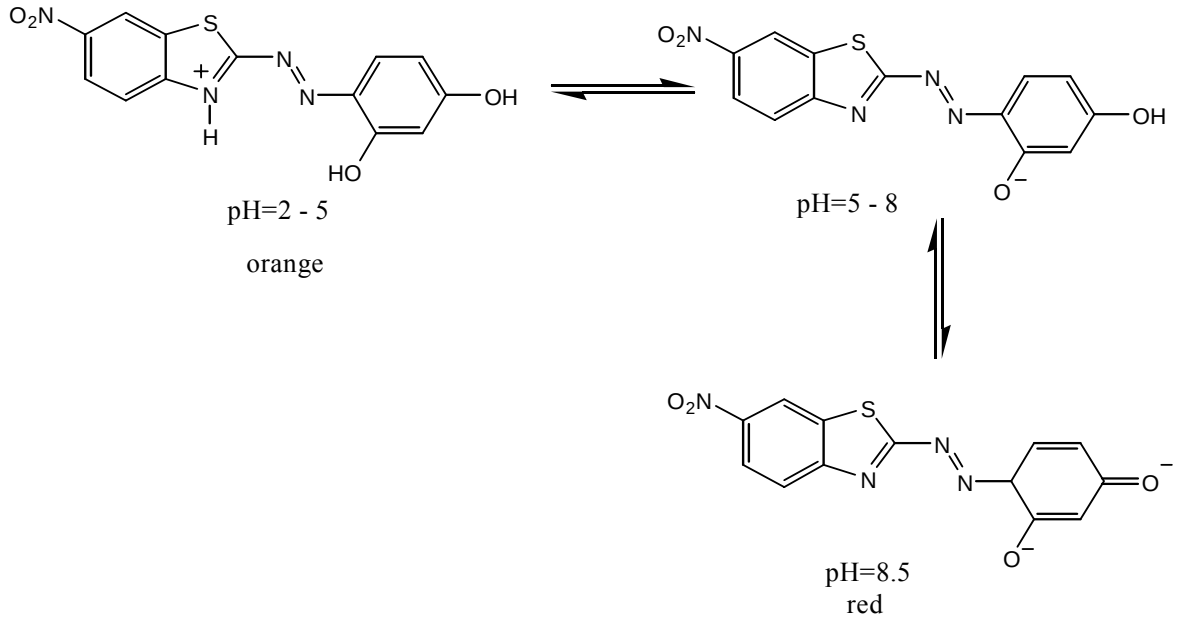
The FTIR spectra of complex Fig. (2) showed absorption band at 3300-2089.8 cm^{-1} which refers to the (OH) found in para position of resorcinol or to the found H_2O in the complex.

Absorption band appeared at 1647.1 cm^{-1} refer to (C=N) of thiazole ring which differ from this band in the reagent because it was shifted to lower vibrational, that mean a coordination of metal with nitrogen thiazole ring.

In addition to that absorption band spilted in 1529.4 cm^{-1} which refers to (N = N) , and that means coordination with metal from nitrogen azo group. In this complex, a new band at 553.5 cm^{-1} is appeared which refers to (M-O).

Properties of 6- Nitro BTAR:

6- Nitro BTAR, is orange colored stable in ethanol , but at pH ≥ 8.5 its solution is deep red where this situation may be interpretated by the following equilibrium :



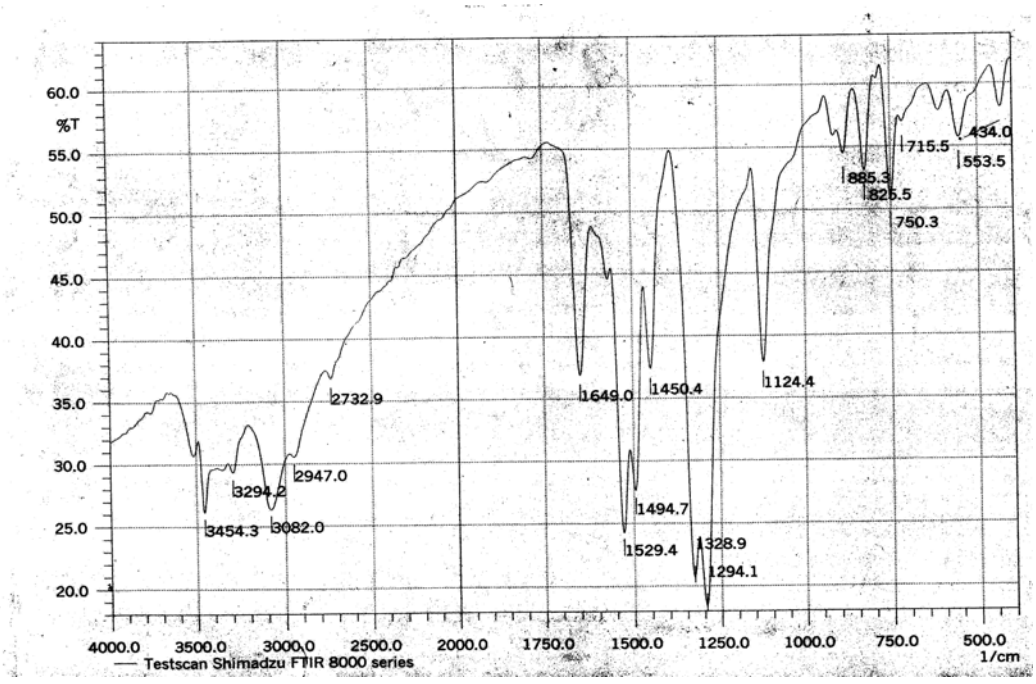


Fig.(1) FTIR spectra of reagent.

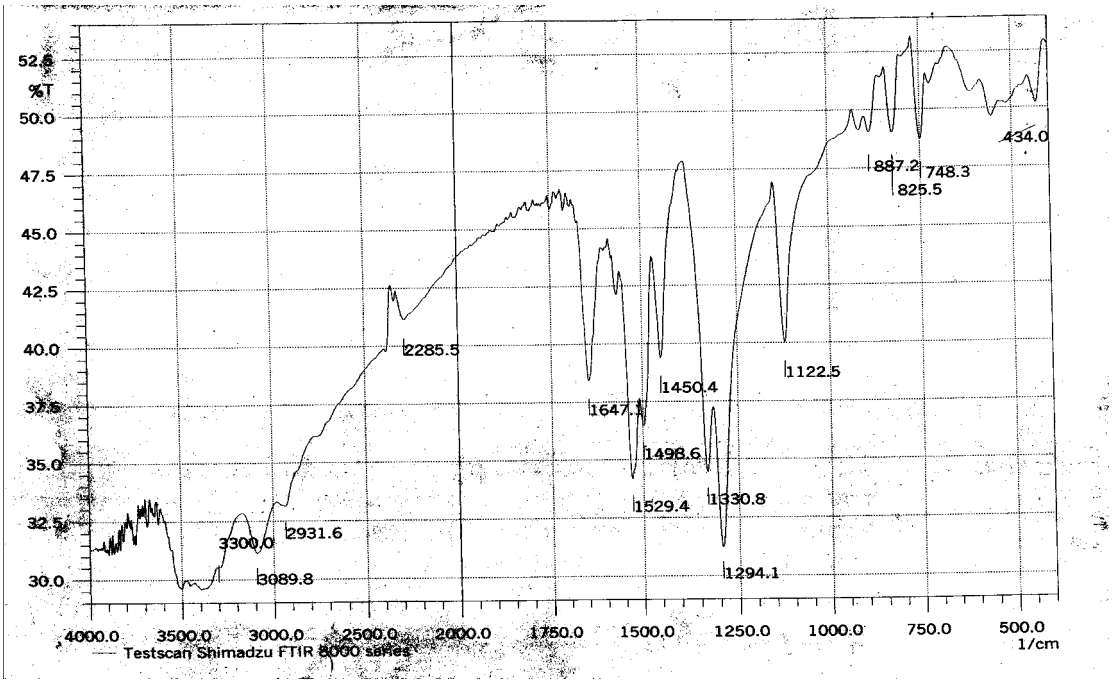


Fig.(2) FTIR spectra of complex.

Study of the [Zinc– 6 Nitro BTAR complex]

Absorption spectra :

UV- visible absorption spectra of solutions containing the reagent and its Zinc complex are shown in Fig.(3). The free Zinc showed an absorption maxima at 231 nm, the reagent at 414 nm, and the complex at 462.5 nm.

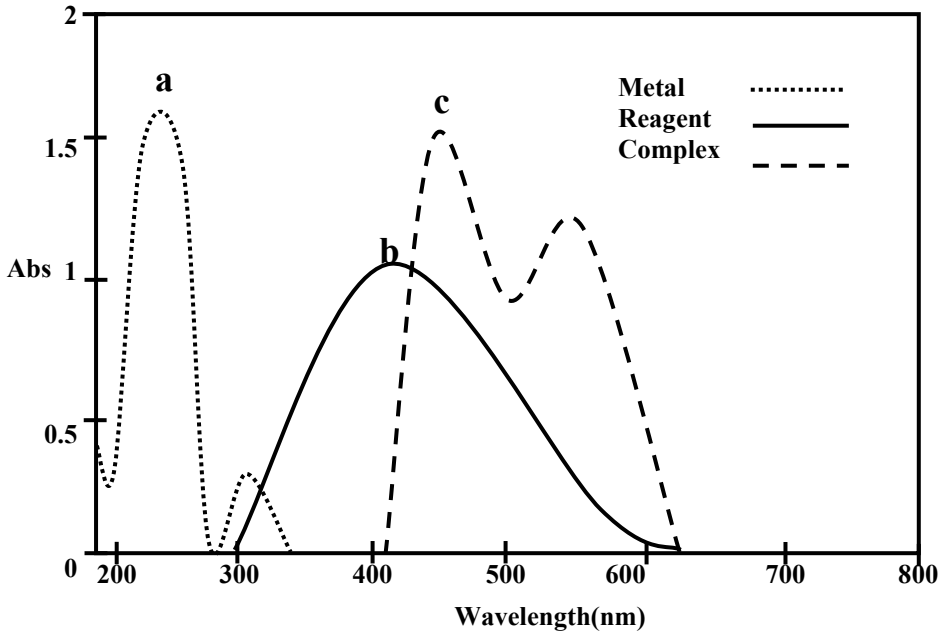


Fig.(3) Absorption spectra of (a) Zn , (b) 6- Nitro BTAR, (c) Zn- BTAR complex. at pH= 6.

Effect of Reagent concentration:

The amount of reagent added to an aliquot of solution containing 1 mg of Zn^{2+} , was varied from (0.5-4.0) ml, and the maximum absorbance was observed on the addition of 3 ml of BTAR at pH= 6.

Effect of pH:

The influence of pH was studied over the range (2-9.5) , adjusted by means of dilute HCl and NaOH solution , Fig.(4) shows the relation ship between absorbance and pH, where the maximum absorbance obtained in the range of pH (5.5- 8) . At pH > 8 a decreases in absorbance because the precipitation of Zinc complex, and also before pH < 5.5 a decrease in absorbance may be due to form a zolium cationresult from the reaction between hydrogen ion and lone pair of electron found in a nitrogen atom in the thiazole ring.

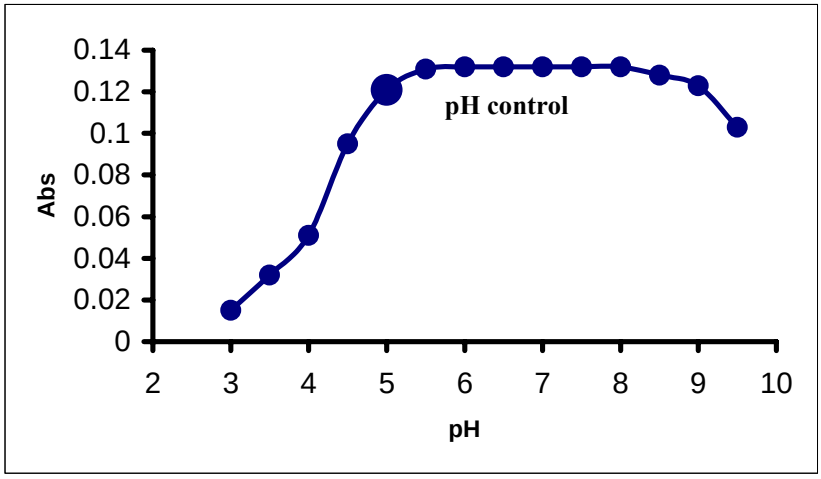


Fig.(4) Effect of pH on the absorbance of Zinc complex, Zn^{2+}1 µg.ml^{-1}.

Effect of time and temperature:-

The stability of the absorbance of the complex was studied from 1 to 10 min (intervals 1 min) till 24 h. (Fig.5) . The maximum absorbance was reached at the 10 min . The absorbance after this optimal time was, almost stable until 24 hrs.

The effect of temp. on the absorbance of the Zn-6- Nitro BTAR complex was studied. The study was performed at temp. between 10^{o}c and 60^{o}c (Fig. 6)

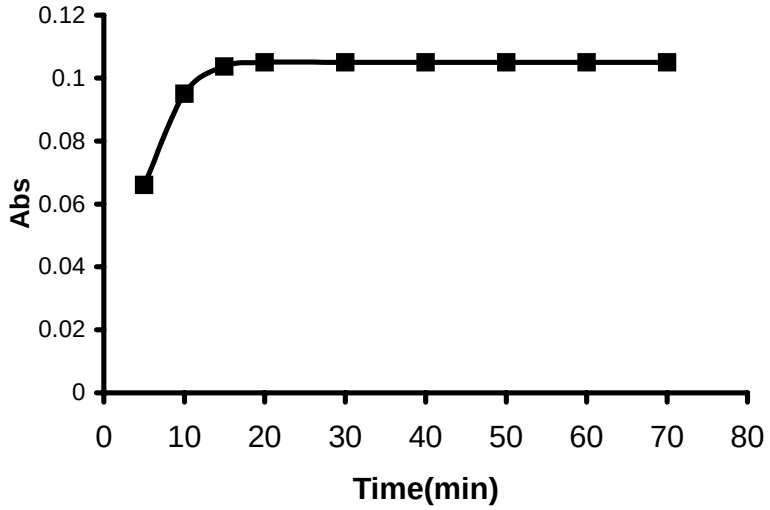


Fig.(5): Effect of time on the absorbance of Zinc complex Zn^{2+}1 µg.ml^{-1}.

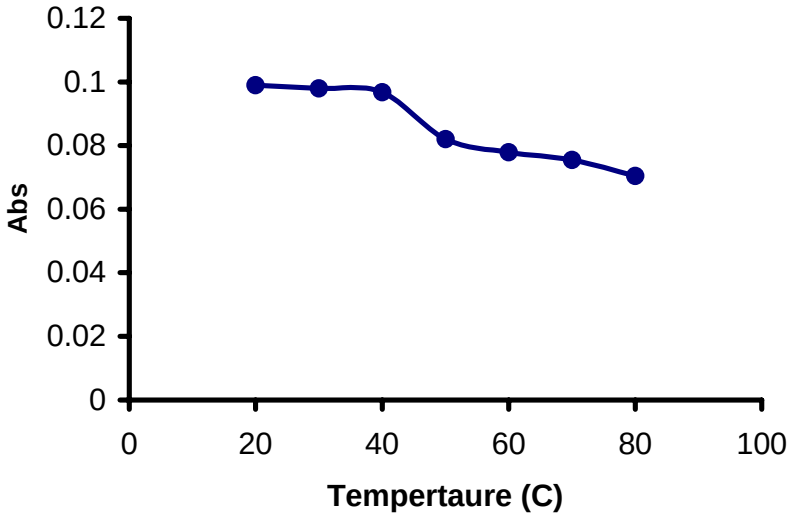


Fig.(6)Effect of temp on the absorbance of Zinc complex Zn^{2+}1 µg.ml^{-1}.

The maximum absorption was obtained when the temp.range between 20C^{o} , and 40C^{o} , at temp. higher than 40 C^{o} the absorbance gradually decreased with increasing temp. until it reaches 80C^{o} , which may be due to dissociation of the complex.

The Stiocheiometry of the complex [12]

The composition of the complex was studied by Job's method (Fig.6,7). Both methods indicated that the ratio of metal ion to ligand molecules was 1:2 at pH 5.5-8. The stability constant , calculated by applied procedure, was found to be 1 x 10^{8} L^{2}. $mole^{-2}$.

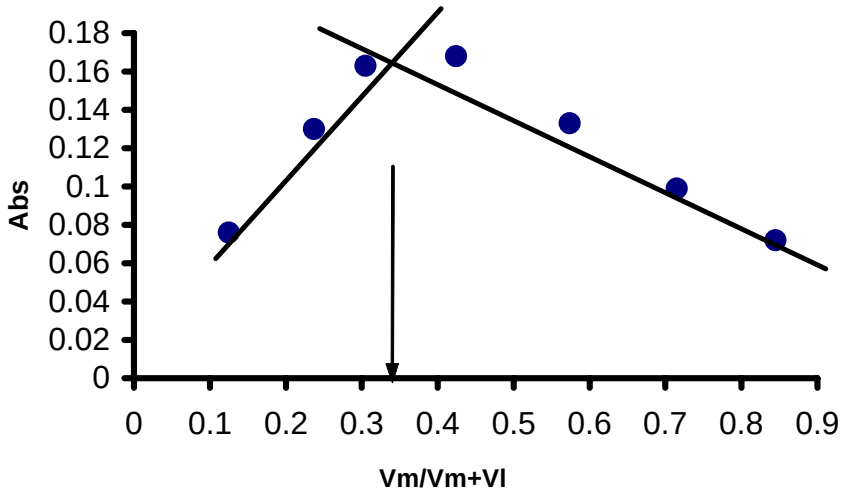


Fig.(6): Job plots (BTAR) = [Zn^{+2}]=1x10^{-3}, pH=5.5-8.

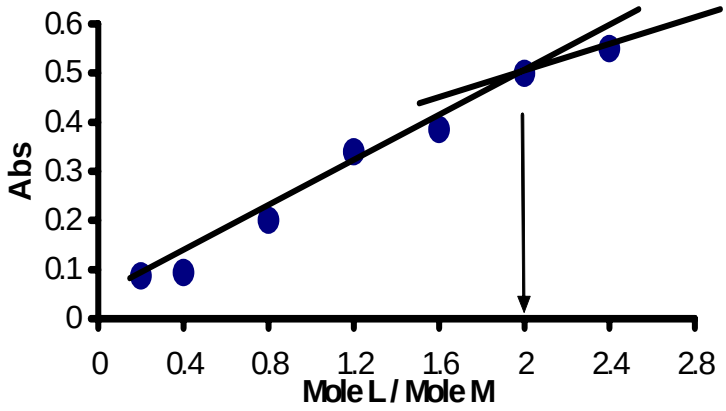


Fig.(7): Mole- ratio plots (BTAR)= [Zn^{+2}]=1x10^{-3}, pH=5.5-8.

Analytical characteristics:

Linearity range:-

Linear calibration graph through the origin was obtained and showed that the complex obeyed Beer's law over the range (0.2-3) µg/ml of Zn^{2+}. The average molar absorptivity was found to be 5846.7 L.$mole^{-1}$.cm^{-1} , the Saudell's sensitivity was 0.0011 µg.cm^{-2} and the correlation coefficient (r) was 0.9984. The high value of (r) indicate the good linearity and correspondence to Beer's law.

Precision and accuracy

The relative standard deviation, evaluated for seven independent of 3 µg/ml of Zn^{2+} was 1.6%, while the recovery and relative error for the complex solution containing (1.5) ppm of Zinc was 98.84, - 1.16% respectively. This result show that this method is highly precise and of very good accuracy.

Interferences:

The effect of the ions (Hg^{2+}, Cd^{2+}, Ag^{+},CrO_4^{2-},Ni^{2+},Co^{2+}) which form complex with the reagent 6- nitro BTAR during its reaction with Zn^{2+}were studied. On the other hand, suitable masking agents were examined for eliminating the effect of the interfering six ions as shown in table (1).

Table 1: Effect of Masking reagents on the absorbance of Zinc complex

Zn^{2+}/ ppm	Masking agent (2) ml,[0.01]*M*	Abs
3	-	0.234
3	Citric acid	0.242
3	Tartaric acid	0.235
3	Ascorbic acid	0.361
3	Oxalic acid	0.276
3	5-sulphosalcylic acid	0.082
3	1,10 phenoanthroline	0.143
3	NaF	0.197

From this table it appered that citric acid, tartaric acid, and oxalic acid had no effect on the absorbance, therefore a mixture of these reagents was made and the absorbance of the zinc was calculated.

Analytical Application:

Seeking for applicability of the method proposed by this work the method is used to determine zinc in a clay sample taken from Shett Al-Hilla which is previously determined by Al- Tace[13]. A sample of clay was dried in a porcelain crucible at 105 C° for 48 hours then cooled, and 1gm of this dried sample was taken 20 ml of conc. Nitric acid is add to it with stirring then 30 ml of deionized water was add after that the mixture is filtrated using Whatman filter paper, the filtrate is subdivided into two parts, the first is analyzed using flame atomic absorption (standard addition method) and the zinc concentration is found to be 132 $\mu g.gm^{-1}$. The second part is analyzed using the preposed method of this research after using the optimized conditions for analysis and it was found to be 124 $\mu g.gm^{-1}$.

The two methods showd no great difference between them and it is concluded that the proposed method of this research can be used for the determination of zinc in different matrices.

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