Synthesis of the new 2-[6-Carboxy-2-Benzothiazolylazo]-4-nitro phenol organic Reagent to spectrophotometric determination of aluminium (III)

تحضير الكاشف العضوي الجديد 2-[6-كاربوكسي 2-بنزوثيازوليل آزو]-4-نايترو فينول لأجل التقدير الطيفي لأيون ألمنيوم(III)

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Abstract

A new 2-[6-Carboxy-2-benzothiazolylazo]-4-nitro phenol (CBTANP) organic reagent was synthesized. A sensitive and selective spectrophotometric method was proposed for the rapid determination of Al(III) using (CBTANP) reagent .The reaction between Al(III) and (CBTANP) reagent is instantaneous at pH=8.0 and the absorbance remains stable for over 24 hrs.

The Method allows for the determination of Al(III) between the range (0.02-2.5) $\mu g.ml^{-1}$,with molar absorptivity of ($9.76 \times 10^{+3}$)$l.mol^{-1}.cm^{-1}$ and a detection limit of 0.015 $\mu g.ml^{-1}$.Recovery and relative error values of precision and accuracy of method were found to be R.S.D=1.4% , Re=98.0% , and Erel =-2.0 % . The properties of complex was studied and show;(M:R) ratio was 1:2 at pH=8.0 ,and the stability constant of $1.228 \times 10^{+10}$ $L^2.mol^{-2}$. The interferences was studied of ions (Ni^{2+} , Ag^{+}, CrO_4^{2-} , Fe^{+3},Ca^{2+} , pb^{2+},Cu^{+2},WO_4^{-2},MO_4^{-2}, Hg^{+2},Co^{2+} , Mg^{2+} , Cd^{2+}, Ba^{2+} , Bi^{3+}, Zn^{+2},Mn^{+2}) and masking agents effect on absorbance were studied .

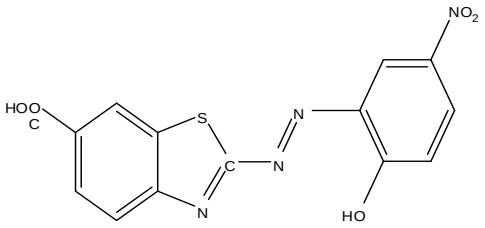
الخلاصة:

تم تحضير الكاشف العضوي الجديد 2-[6-كاربوكسي-2-بنزوثيازوليل آزو]-4-نايترو فينول , وأستعمل في طريقة تقدير طيفي حساسة و إنتقائية لأيونات الالمنيوم(III) . التفاعل بين الكاشف و آيون الالمنيوم(III) يتم عند دالة حامضية = 8 و إمتصاصية المحلول تبقى ثابتة لأكثر من 24 ساعة.

الطريقة تسمح لتقدير آيون الالمنيوم (III) ضمن مدى تركيز (0.02- 2.5) مايكرو غرام لكل مليلتر و بمعامل إمتصاص مولاري ($9.76 \times 10^{+3}$) لتر.مول$^{-1}$.سم$^{-1}$. و بحد كشف 0.015 مايكرو غرام لكل مليلتر.

تم حساب دقة الطريقة التحليلية و ضبطها فكانت R.S.D=1.4 % و Re = 98.0 % و Erel = - 2.0%.

درست طبيعة المعقد الذائب فكانت نسبة (الكاشف: الفلز) = 1:2 عند دالة حامضية = 8 و كان ثابت إستقرارية المعقد الذائب = $1.228 \times 10^{+10}$ لتر^2.مول$^{-2}$. وكما درست تداخلات الآيونات (Ni^{2+} , Ag^{+}, CrO_4^{2-} , Fe^{+3},Ca^{2+} , pb^{2+},Cu^{+2},WO_4^{-2},MO_4^{-2}, Hg^{+2},Co^{2+} , Mg^{2+} , Cd^{2+}, Ba^{2+} , Bi^{3+}, Zn^{+2},Mn^{+2}) و تأثير عوامل الحجب المختلفة على الإمتصاصية المدروسة.



(CBTANP) reagent

Introduction

Aluminium (Al) is widespread throughout nature, air, water, plants and consequently in all the food chain [(1)]. Food is the main source of aluminium intake for human body [(2)]. One of the possible routes through which Al can enter human body could be foods packed in Al containers, e.g. Al cans [(3)]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS)[(4)], electrothermal atomic absorption spectrometry (ETAAS) [(1,5)] and inductively coupled plasma-optical emission spectrometry (ICP-OES) [(6-7)] devoted to low-level metals determination, however, their present very high acquisition and operational costs. Spectrophotometry is a well-established analytical technique that provides low cost, simplicity and wide range of applications for aluminium determination in some food samples [(8-10)].

Some chromogenic reagents have been used in spectrophotometric methods of determination of aluminium(III) such as,Diacetylmonoxime IsonicotinoylHydrazone [(11)], 8-hydroxyquinoline[(12)], Xylenol Orange[(13)], 5-Bromo-2-hydroxy-3-methoxy benzaldehyde-P-hydroxybenzoic hydrazine[(14)], 2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazine[(15)], pyrocatechol violet (PCV)[(16)], and 5-[4-nitrophenyl azo] salicylic acid[(17)].

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 because they are relatively easy to synthesize and purify[(18)] .

In this work ,a new (CBTANP) chromogenic reagent was synthesized ,and used in simple method involving spectrophotometric determination of Al(III) .

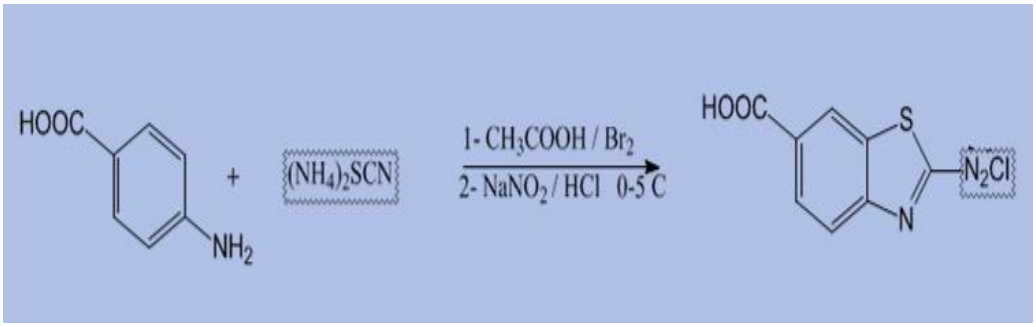
Reagents;

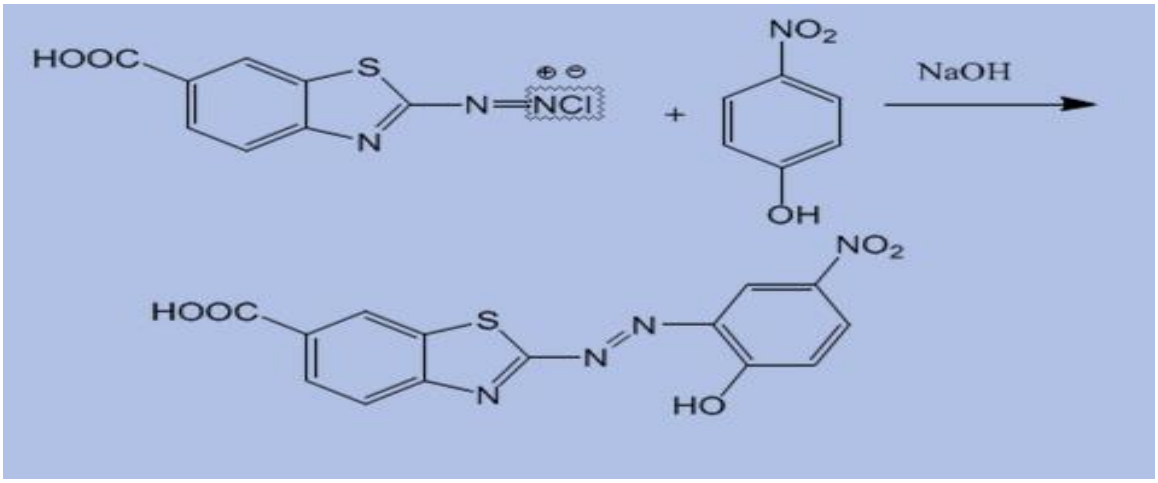
All reagents were of analytical grade. Freshly distilled and deionized water was used for solutions preparations .

Preparation of reagent[(19)]

To a mixture of {(4.29 gm of para amino benzoic acid and 3.8gm of ammonium thiacyanate) in 70 ml glacial acetic acid }, was added drop by drop from burette (1.2 ml Br_2 + 15ml glacial acetic acid) keeping at temperature >10 Cº.

After 15 minutes alkaline solution was added to precipitate the thiazole derivative , 1.144 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 0-5 Cº to diazonium salt , then (0.1.392 gm of para nitro phenol + 50 ml ethanol)is added to diazonium salt and 2-[6-carboxy-2-benzothiazolyl azo]-4- nitro phenol (CBTANP)organic reagent was formed .





Standard solutions:

stock Al (III) solution ; A solution of Al (III) (100 μg.ml^{-1}) was prepared by dissolving (0.1972) gm of aluminium nitrate in (250ml) distilled water . Other standard solutions of Al(III) were prepared by dilution of stock solution with distilled water.

-1x10^{-3} M (CBTANP)standard solution was prepared by dissolving (0.088)g in 250 ml of absolute ethanol .

-Buffer solution [20](pH=8.0) was prepared by mixing 19.45ml of (0.2)M Na_2HPO_4 (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 , and FT-IR Spectrophotometer shimadzo., Japan .,Were used in this work .

Procedure;

To an aliquot containing < 10μg .ml $^{-1}$ of Al(III) in a 10-ml volumetric flask ,was added 2 ml of buffer solution , and 4.0 ml of (2 x 10^{-4}M) of (CBTANP) solution as optimum volume.The solution was diluted to the mark with distilled water , and absorbance was measured at 25C^{o} and wave length of 606 nm against the reagent solution as a blank solution prepared under the same conditions.

Results and Discussion;

1-FT-IR spectrum of reagent (CBTANP)

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

Wave number (cm^{-1})	Groups
3300-3400	υ O-H , H_2OCrys.
1345	$(C – H)_{bending.}$ aromatic
1630	υ C =N
1512	υ N=N
1448-1602	υ C =C Ar.
1139	υ C – S
1274	υ C – O phenolic
1695	υ C = O carboxylic
1355	υ C – N

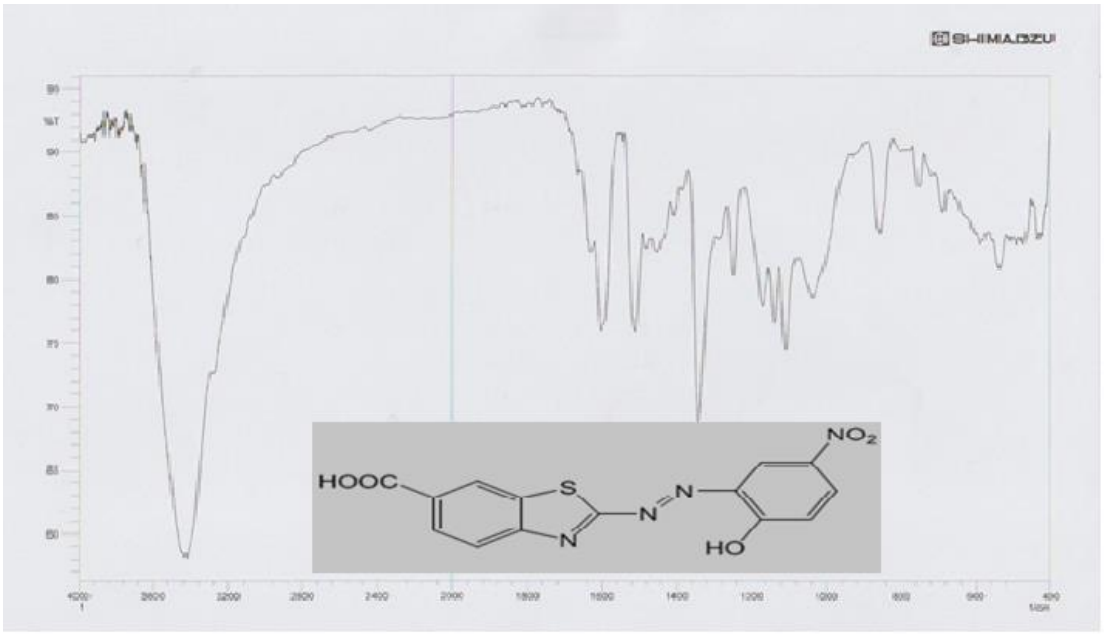
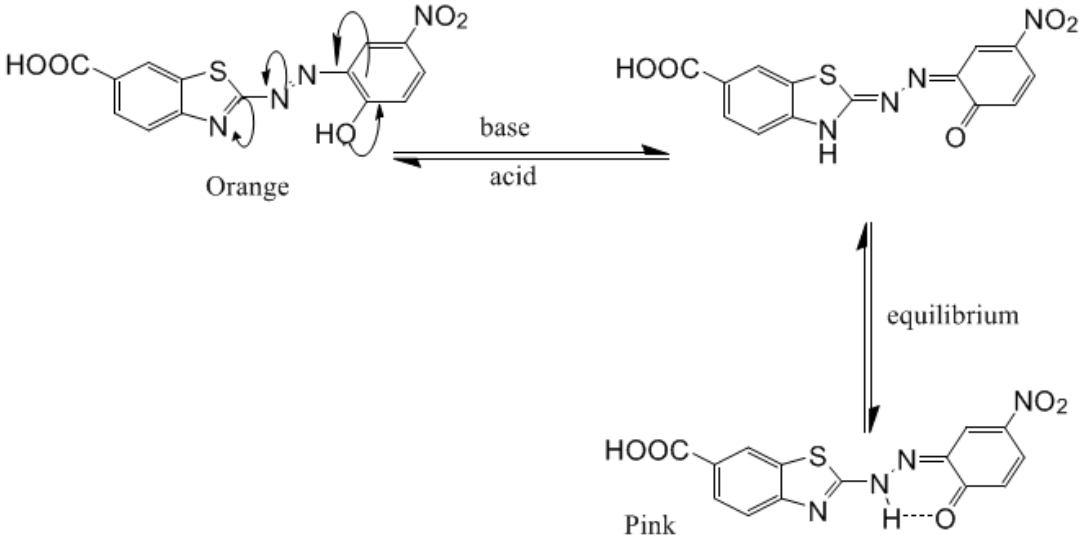


Fig.1: FT-IR spectrum of reagent (CBTANP)

2-Properties of the (CBTANP)

(CBTANP) 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;



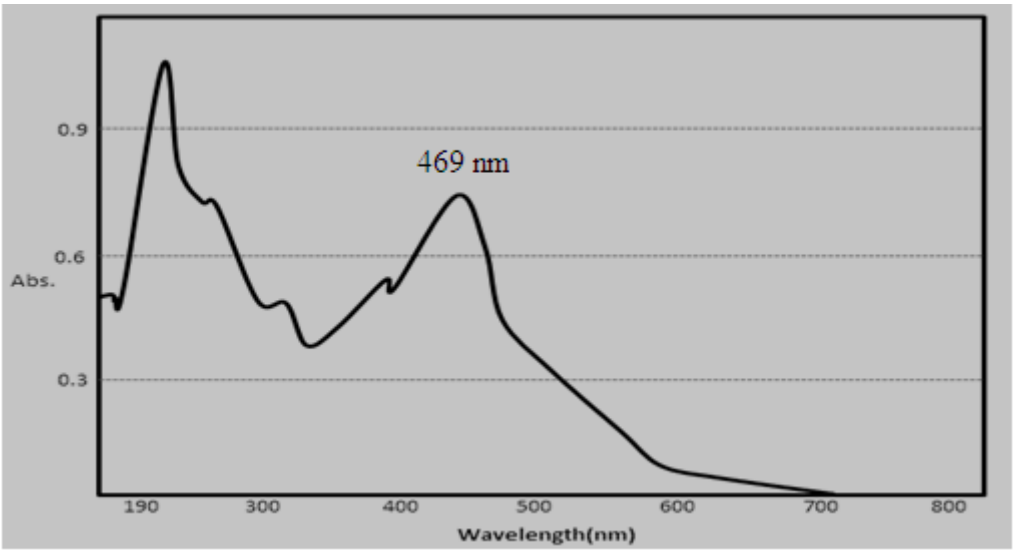


Fig.2: Uv-Visible spectrum of (CBTANP) reagent

Study of Al(III) –(CBTANP)complex

Absorption spectra

a-Ultra violet –visible absorption spectra of (CBTANP)reagent ,and Al(III) -(CBTANP)complex solution are shown in fig (3).The reagent showed an absorption maximum at 469 nm,and the complex at 606 nm.

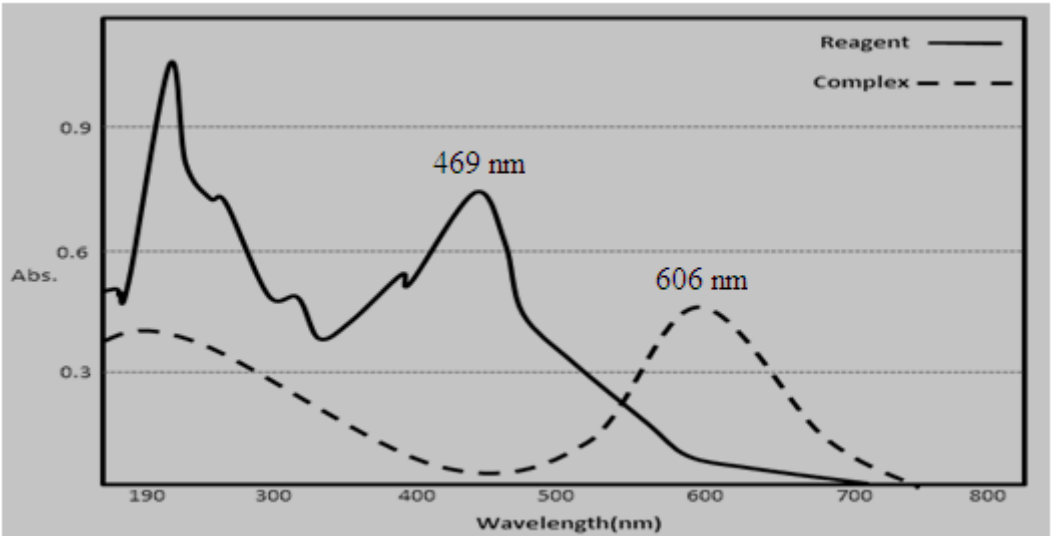


Fig.3: Uv-Visible spectrum of Al(III)-(CBTANP) complex

FT-IR spectrum of Al(III)- (CBTANP) complex:

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

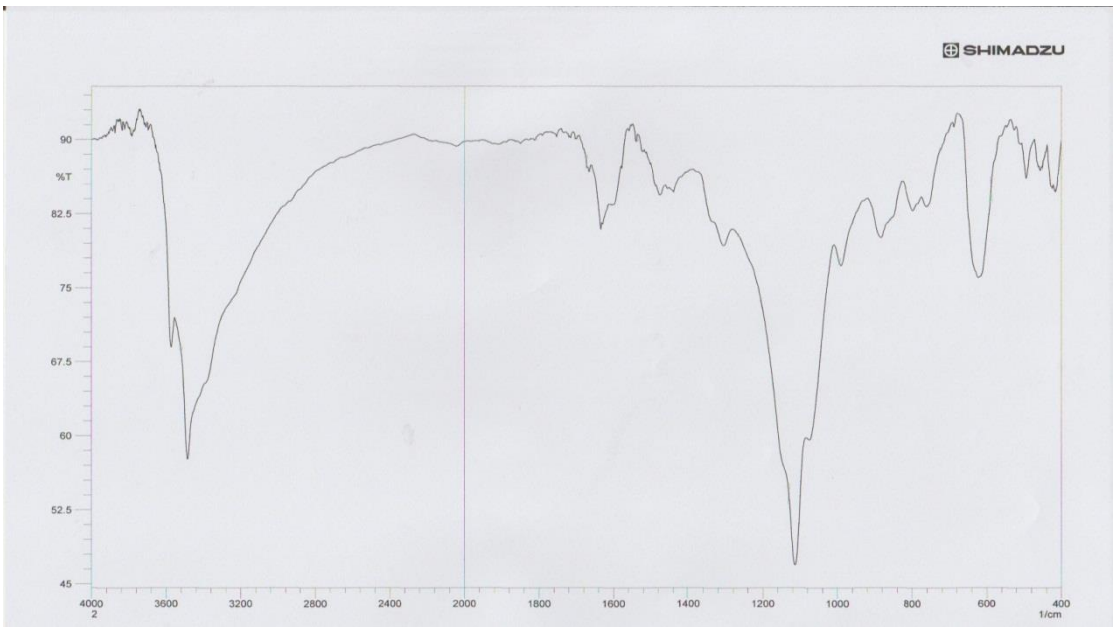
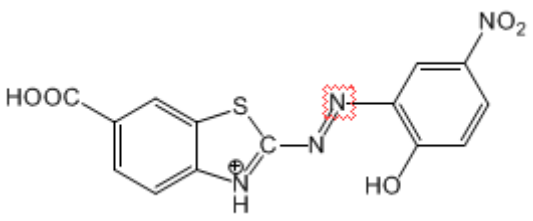


Fig.4: FT-IR spectrum of Al(III) –(CBTANP)complex.

Effect of pH

The effect of pH was studied over the rang (2-10) adjusted by means of dilute HCl and NaOH solution. figure (5)shows the relationship between absorbance and pH ,where the maximum absorbance obtained in the range of pH =(6.0-8.5) .
At 8.5 < pH< 6.0 a decrease in absorbance that attributable to formation of azonium ion in acidic medium lead to decreasing in reagent reactivity, and in basic medium the hydroxide ion may be compete the reagent to react with aluminiun ion . Therefore, the optimum pH was 8.0, where the absorbance was maximum and constant.



Azonium ion

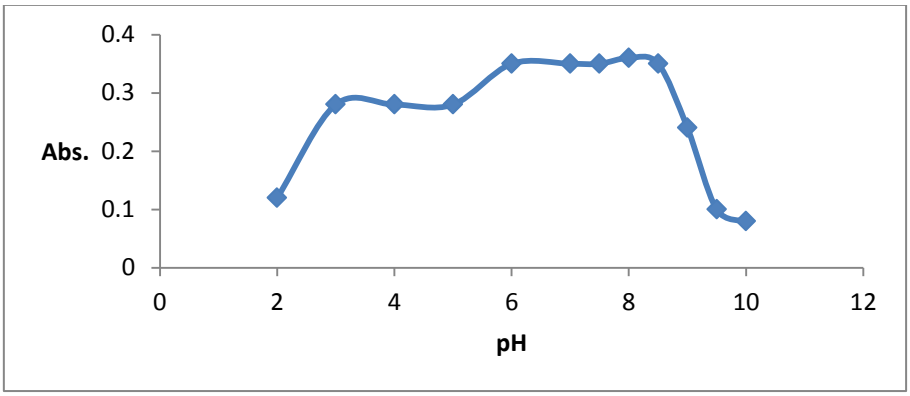


Fig (5); Effect of pH on absorbance Al(III) –(CBTANP)complex.

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 reached at 10 minutes figure (6) after that the absorbance remains constant .

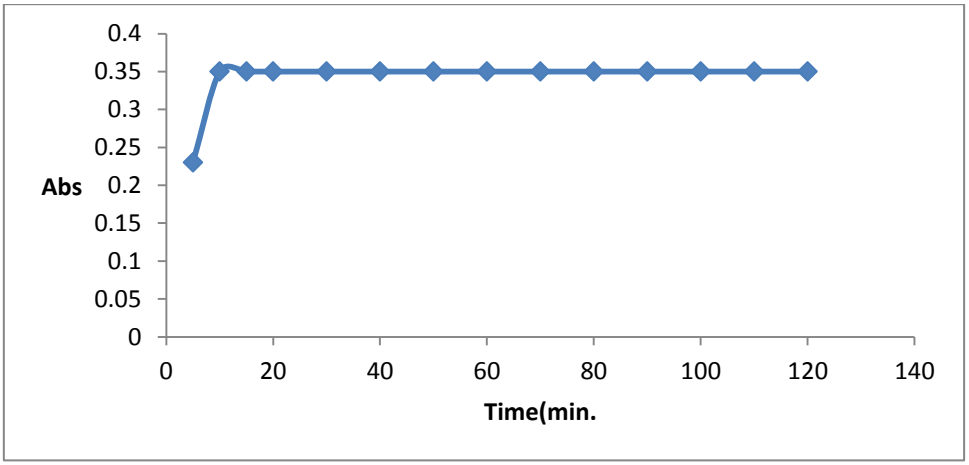


Fig (6); Effect of time on the stability of Al(III) –(CBTANP)complex.

Effect of temperature

The effect of temperature on absorbance of complex was studied ; the study was performed at temperature between (5 – 80)ºC .Fig (7)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 .

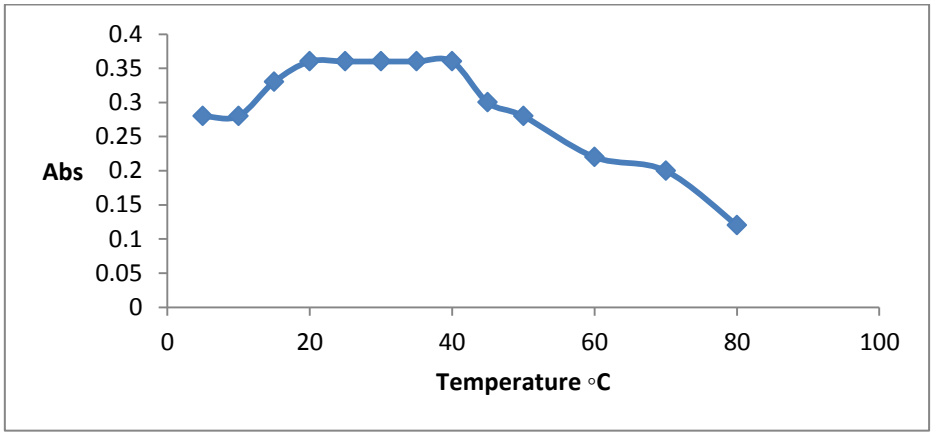


Fig (7); Effect of temperature on the stability of Al(III) –(CBTANP)complex.

Determination of stoichiometry and formation constant

The composing of complex was studied by jobs method of continuous variations and mole ratio method [21] . Fig (8,9) both methods indicate that the ratio of metal ion to reagent molecules (M:L) was (1:2) at pH = 8.0 .

The formation constant calculated by applied procedure , was found to be (1.228 x 10^{+10}) L^2. mol^{-2}

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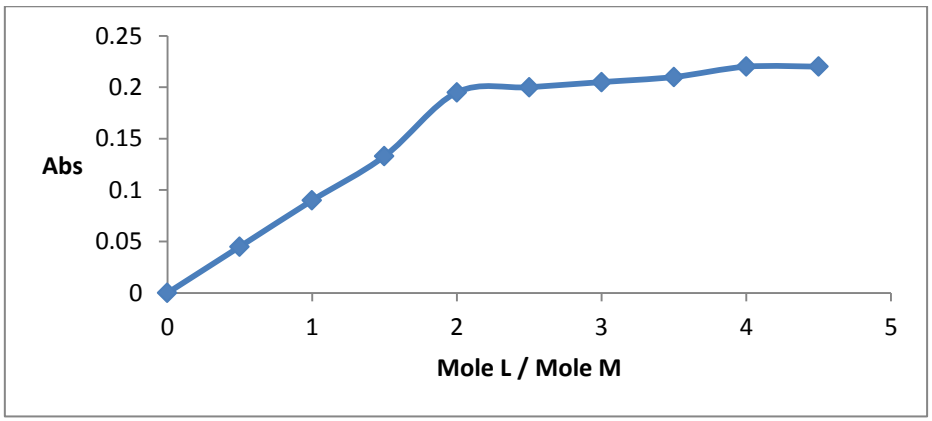
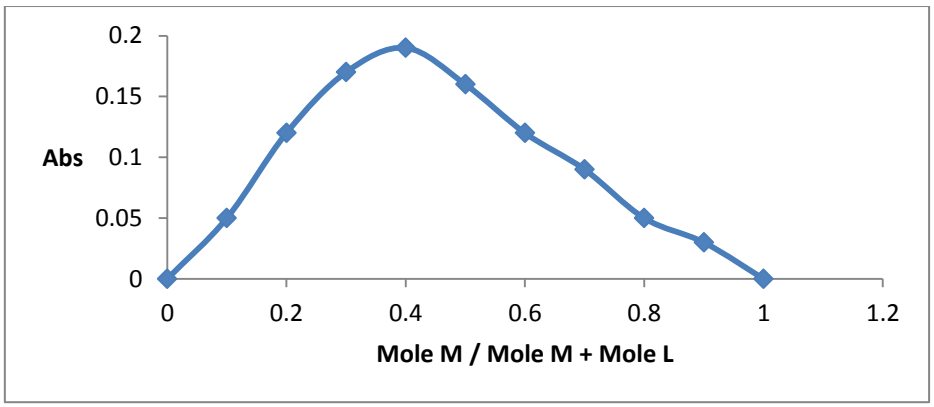


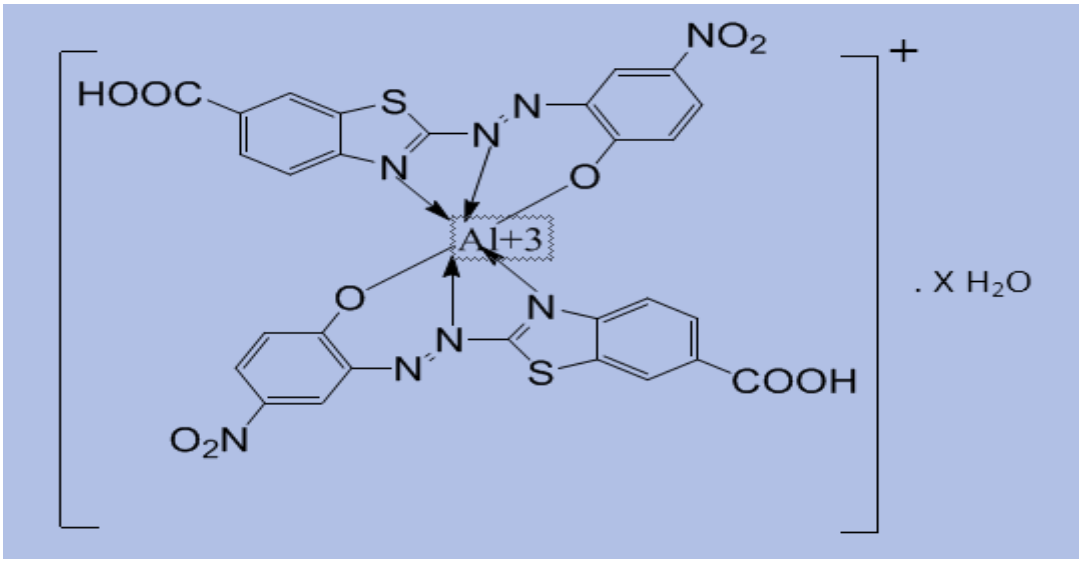
Fig(8);Mole ratio plot ,pH =8.0



Fig(9);Jobs plot , pH=8.0

Suggestion of structural formula of Al(III) –(CBTANP) complex

From the obtained results of metal to reagent ratio, and depending on thiazolyl azo Compounds 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 (0.02 – 2.5) µg . ml $^{-1}$ of Al (III) . The average molar absorptivity was found to be (9.76 x 10 $^{+3}$) l . mol^{-1} .Cm $^{-1}$.
The sandells sensitivity $^{(22)}$ was (0.0027) µg of Al(III).Cm^{-2} , and correlation coefficient (r) was 0.9984.

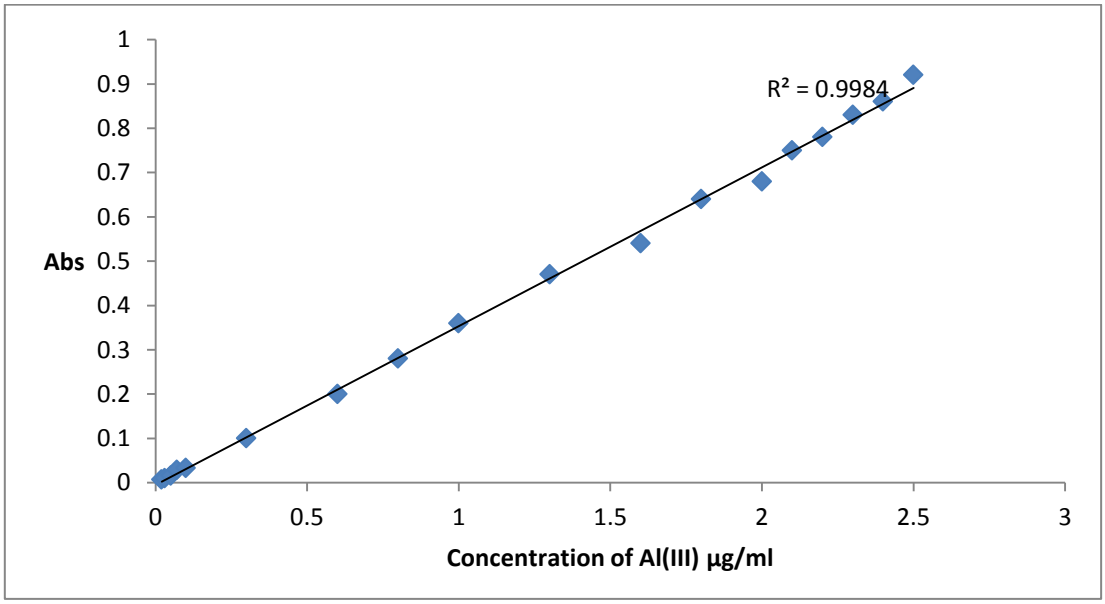


Fig (10): calibration curve of Al(III) –(CBTANP) complex

Precision and accuracy

The relative standard deviation (R.S.D %) , evaluated from seven independent determination of 1.0 µg . ml $^{-1}$ of Al(III) was 1.4 % , this result show that this method is highly precise . Also the accuracy of this method was determined by calculated the Erel % for 1.0 µg . ml $^{-1}$ standard solution of Al(III) which was found to be (– 2.0) and Re% = 98.0 .

Interferences

The effect of the ions (Ni^{2+} , Ag^{+}, CrO_4^{2-} , Fe^{+3},Ca^{2+} , pb^{2+},Cu^{+2},WO_4^{-2},MO_4^{-2}, Hg^{+2},Co^{2+} , Mg^{2+} , Cd^{2+}, Ba^{2+} , Bi^{3+}, Zn^{+2},Mn^{+2}) which form complex with the reagent during its reaction with Al(III) were studied . On the other hand , suitable masking agents examined for eliminating the effect of the seventeen ions , where the mixture of KCl , NaF , $Na_2S_2O_3$, and NH_3 were found to be a suitable masking agents.

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