

Spectrophotometric study and Characterization of Aurintricarboxylic acid as analytical reagent for Manganese (II) determination

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Abstract :

Aurintricarboxylic acid (ATA) has been synthesized , and prepared complex with Mn(II) was characterized by spectrophotometric methods UV-Visible, FT-IR and molar conductivity measurement. The octahedral geometry around Mn(II) ion can be suggested. The ligand used as a reagent for the spectrophotometer determination of micrograms of manganese ions. The reaction between Mn^{2+} and ATA form a pink complex having a molar ratio of 2:1 (M: L) at pH 7 and the stability constant was found to be $(1.62 \times 10^{10} L^2 \cdot mole^{-2})$. The molar absorptivity of the complex is $2.55 \times 10^4 L \cdot mole^{-1} \cdot cm^{-1}$ at λ_{max} 552 nm. This method sensitive and the complex formed high stable which can used a reagent ATA to spectrophotometric determination of the manganese (II).

الخلاصة :

تم تحضير الكاشف حامض أيرون ثلاثي الكربوكسيل (ATA) , حيث استخدم هذا الكاشف لتحضر معقد مع عنصر المنغنيز الثنائي, شخص المعقد بالطرق الطيفية مثل الأشعة مافوق البنفسجية والأشعة تحت الحمراء إضافة الى التوصيلية المولارية ومن خلال تلك القياسات تم اقتراح الصيغة الهندسية للمعقد المحضر بالصيغة الثماني السطوح. كما استخدم هذا الكاشف لتقدير كميات قليلة من ايون المنغنيز الثنائي الشحنة بالطرق المطياف الضوئي. إن التفاعل السريع بين ايون الفلز و الكاشف يكون معقد ذو لون احمر غامق, وكانت نسبة (الليكند:فلز) هي (2:1) للمعقد المحضر عند الدالة الحامضية (7), معامل الامتصاص المولاري للمعقد $(2.55 \times 10^4 L \cdot mole^{-1} \cdot cm^{-1})$ عند الطول الموجي الأعظم 552nm , وثابت استقرارية $1.62 \times 10^{10} L^2 \cdot mole^{-2}$. هذه الطريقة حساسة لتقدير Mn^{2+} كما إن المعقد المتكون ذو استقرارية عالية مما يسمح باستخدام الكاشف ATA في تقدير ايون المنغنيز الثنائي.

Introduction :

Aurintricarboxylic acid (ATA) was used as an analytical reagent in the estimation of copper (II) by using silica gel as a support medium to form bidentate complex ⁽¹⁾. The binding of metal ion-ligand complexes with protein is important for preparation of different biosensors ⁽²⁾. ATA could bond to the different polymers including modeled aminopropyl silica gel ⁽¹⁾. A selective interaction of ATA with RNA, unlike DNA via phosphoric-ether bond (P-O-C), which was absent in the case of DNA-ATA complex ⁽³⁾. This property can be tested for the protein molecules, which are polymers, to have the ability to interact with ATA complexes in the present work. ATA selectively prevented the binding of specific monoclonal antibody (mAb) to the CD4 cell receptor for human immunodeficiency virus type 1 (HIV-1). Thus, ATA is a selective marker molecule for the CD4 receptor. ATA also interfered with the staining of membrane-associated HIV-1 glycoprotein by a mAb against it ^(4,5). (ATA) is a polymeric carboxylated triphenylmethane derivative ⁽⁶⁾. In cell free systems, ATA has been reported to be a nonspecific enzyme inhibitor by virtue of its polyanionic structure with effects on many systems ⁽⁶⁾. The bidentate ligands binds with metal ions by two atoms at same ligands molecule such as N, N' atoms as in ethylenediamine ^(7,8), N and O atoms ⁽⁹⁾, or by two O atoms ⁽⁹⁾. In this respect, carboxylic acids have an important because the binding occur by oxygen atoms and make a special banding. Pavel K. and co-worker ⁽¹⁰⁾ prepared some of metallic complexes by reaction of N,N'-salsilidin-o-vanilindiamine, abbreviated (Salen H₂), with 6-methyl - 2,4-pyridinedicarboxyl acid, abbreviated, (MidicarpH₂) where the carboxylic acid acts as a bridge

binding the two Fe(III) complexes. Tyagi and co-workers ⁽¹¹⁾ reported the synthesis of Mn⁺² complexes of the general formula [Mn(L)₂X₂] (where: L= p-methylacetophenone smicarbazone and X= Cl⁻, Br⁻, 1/2 SO₄⁻²). An octahedral geometry about Mn⁺² ion was assigned on the bases of the previous studies. Bernhardt and co-workers ⁽¹²⁾ reported the coordination chemistry of tridentate chelators di-2-pyridyl ketone isonicotinoyl hydrazone (HPKIH) and di-2-pyridyl ketone benzoyl hydrazone (HPKBH), with the divalent metal ions, Mn, Co, Ni, Cu, and Zn. In this work, synthesis and characterization of ligand (ATA) and it's Mn(II)-complex and study that as analytical reagent for manganese(II) determination .

Experimental

Apparatus and materials

IR spectra were recorded using KBr discs 4000-400 cm⁻¹ on FTIR Test scan Shimadzu model 8400S. Absorption spectra were recorded with UV-Visible spectrophotometer (Shimadzu 160A) double-beam length spectrophotometer both with matched 1 cm quartz cells. pH of the solution was measured using a Philips PW 9421 PH meter. While the conductivity measurement with Conductivity meter Model PCM 3 – (JENWAY) were used dimethylsulphoxide as the solvent at 25°C and concentration 1X10⁻³M . Melting point or decomposition temperature measurement by Richert-Jung Heizbank type WME .

All chemical were used of analytical – reagent grade unless stated other wise and solution were prepared with Absolute ethanol.

Preparation of Aurintricarboxylic acid ⁽¹³⁾

20 ml of concentrated phosphoric acid were mixed with 2.8 gm (28mmole) of solid potassium nitrate. When solution is complete, add 5.8 gm(56mmole) of salicylic acid with stirring. The mixture should then be light red to brown in color. It is surrounded by an ice-salt bath. Added 1.4 ml of formaldehyde is slowly with extremely vigorous stirring. A bout 30 gm of crushed ice is then added, the stirring should be vigorous during the addition. The content of the flask are stirred until the ATA has disintegrated into small pieces.

Preparation of the solid Complex manganese(II)-ATA

Weighted 2.11gm of ATA (5mmole) and mixed with 15ml of absolute ethanol ,then weighted 2.03gm (10mmole) of the solid salt MnCl₂.6H₂O that dissolved previously with a minimum amount of absolute ethanol in a 50ml beaker and mixed at room temperature for ten minutes. The complex then filtered and precipitated by adding a few amounts of diethyl ether as a precipitating agent. The precipitate after purification dried and stored in a tightly closed container until using it in the following experiments.The physical properties of the manganese(II)-ATA complex are; molecular weight =955.27g.mole⁻¹, melting point =>300°C, yield=71%. The complex have a pink color while it's insoluble in water, acetone and dichloromethane.While its soluble in dimethylsulphoxide and dimethylformamide.

Standard manganese Solution

A solution of Mn⁺² 1000 ppm was prepared by dissolving (0.208)gm of MnCl₂.6H₂O in 100 ml of Absolute ethanol, working solution were prepared freshly by appropriate dilution of the stock solution.

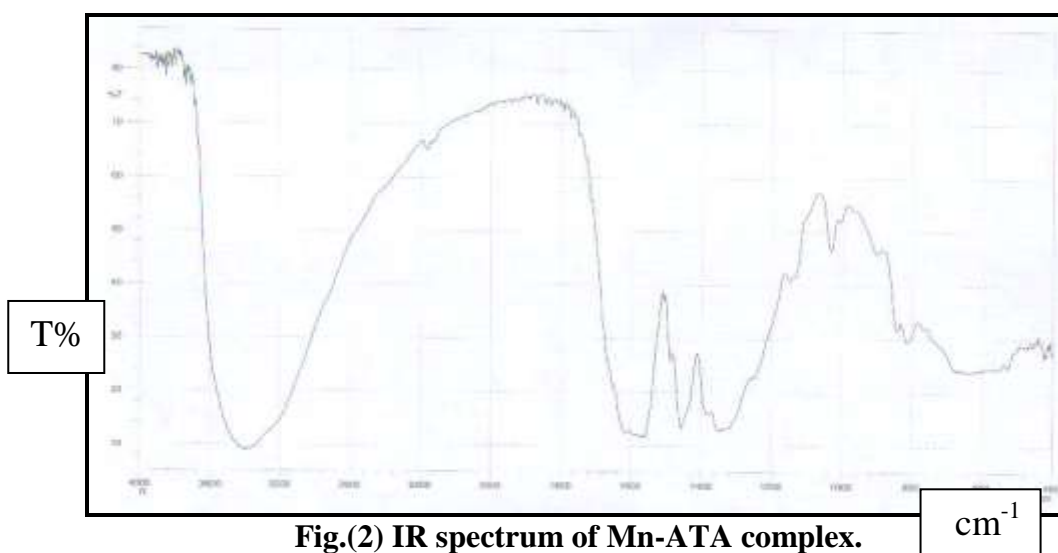
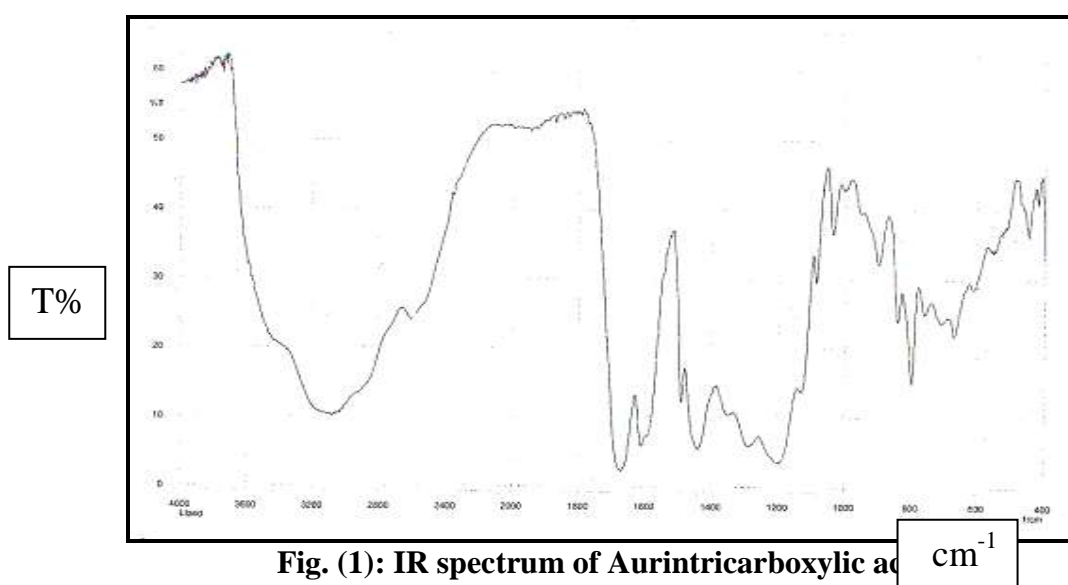
Results and Discussion

Characterization of Mn-ATA complex

FT-IR spectra study

The IR spectrum of the ligand ATA alone figure (1) showed a wide absorption peak in the range (2800-3500)cm⁻¹ due to the stretch of (-OH) bond and to the hydrogen bonding in carboxyl groups^(14,15). The spectrum also showed two absorption peaks at 1440 and 1490 cm⁻¹ due to the

symmetric stretch of (-COOH) groups and two absorption peaks at 1610 and 1670 cm^{-1} due to the asymmetric stretch of (-COOH) groups⁽¹⁵⁾. The FTIR spectra of complex figure(2) showed a change in the phenolic (-OH) bands. This band is narrowed in the complex as compared with its wide shape in the ATA alone spectrum. This fact give an evidence about the formation of coordination with the metal ion by covalent bonds via oxygen atom. Also the location of the stretch and asymmetric stretch of (-COOH) groups at 1670 was shifted to lower frequencies⁽¹⁶⁾. There is also a shifting noticed in the (C-O) group of phenol group from 1200 cm^{-1} toward 1240 cm^{-1} producing another evidence about involvement of phenol group in coordination with manganese ion via oxygen group⁽¹⁷⁾. The spectrum of complex revealed a splitting of carboxyl group band into two peaks at 1430 cm^{-1} and 1450 cm^{-1} formation of coordination bonds between Mn(II) ion and carboxyl groups. Two new peaks also noticed in the spectrum of the complex at (530 and 440) due to the presence of water coordination and Mn-O bond, respectively⁽¹⁸⁾. No (Mn-Cl) binds were noticed because the limitation of the IR spectrophotometer because they appear (if present) at peaks lower than (400 cm).



Absorption spectra study

When the pure solid complex dissolved in dimethylsulphoxide at a concentration (0.001M), the UV-Visible spectrum showed three obvious peaks at 258nm , 314nm and 552nm , the first and

second peaks are attributed to charge transfer while the third peak is assigned d-d transitions type (${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$) in octahedral structure about Mn^{+2} (19^+) according to figure (4)

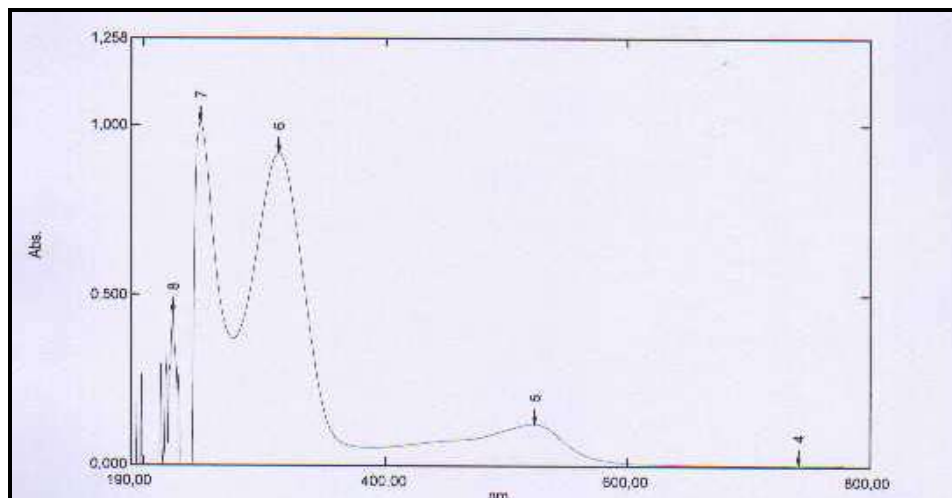


Fig.(3) Absorption spectra of ligand (ATA)

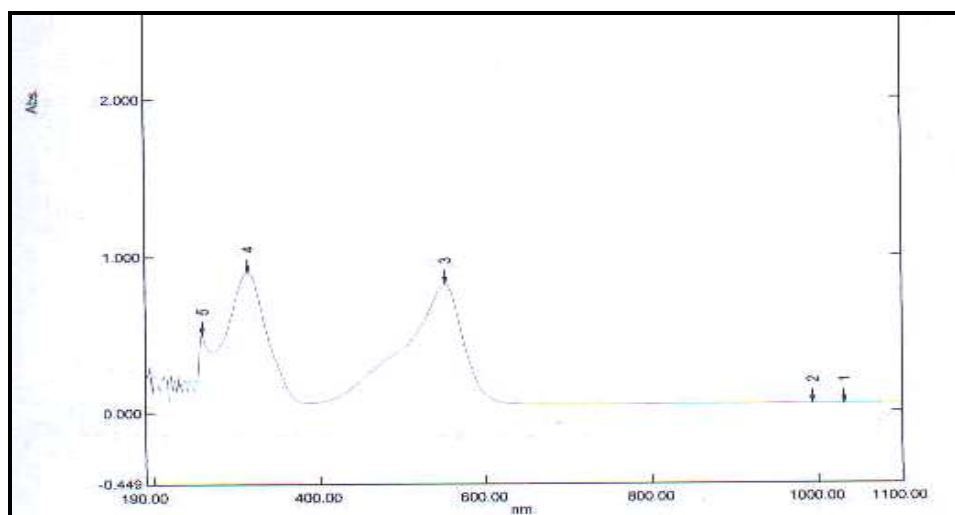


Fig.(4) Absorption spectra of Mn(II)- ATA complex

Molar conductivity result to the complex have ($8.8 \text{ S.cm}^2.\text{mol}^{-1}$) where used dimethylsulphoxide as a solvent at concentration (0.001M) that the complex is not conductive (neutral non-electrolyte substance).

Optimization Study of the Mn(II)– ATA complex:

Effect of time and temperature

Various temperature between 5°C and 40°C figure (5) on the absorbance of the Mn-ATA complex was studied. The maximum absorption was obtained when the temperature was varied at 20°C , at temp. higher than 20°C the absorbance gradually decreased with increasing temp. until it reaches 40°C , which may be due to dissociation of the complex. The stability of the absorbance of the complex was studies from 1 to 40 min (intervals 1 min) till 24 h. figure(6) . The maximum absorbance was obtained at the 15 min . The absorbance after this optimal time was, almost stable until 24 hrs.

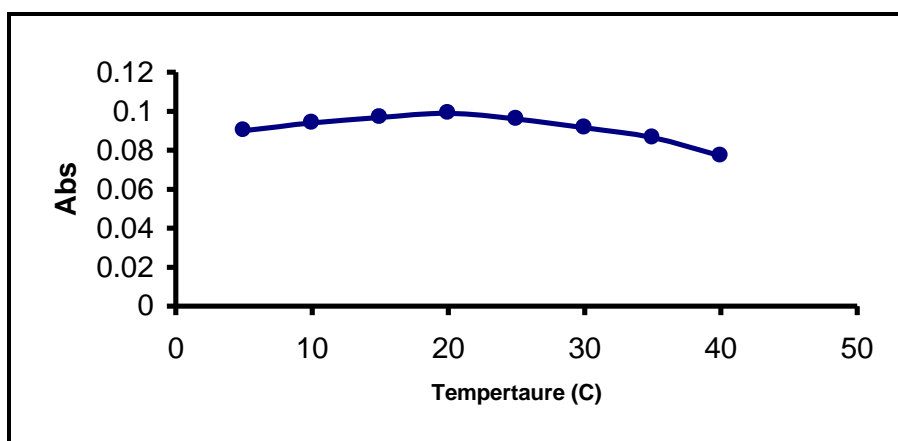


Fig.(5) Variation of temperature with the absorbance of Mn(II)-Complex

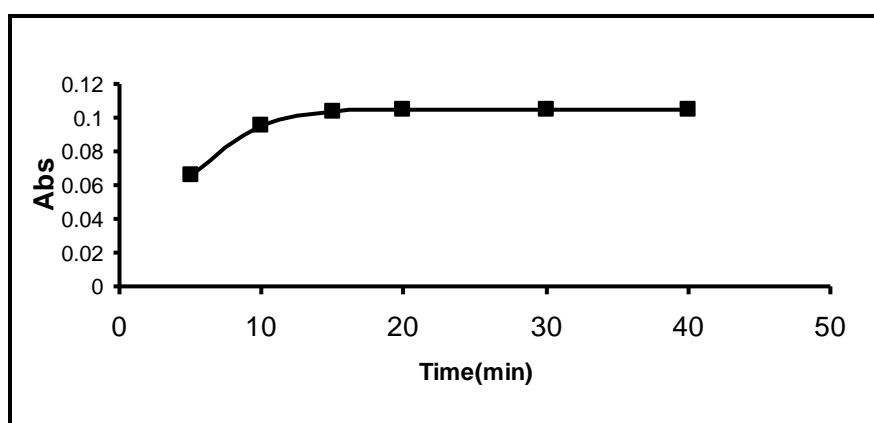


Fig.(6) Variation of time with the absorbance of Mn(II)-Complex

Effect of pH:

The pH was studied between the rang (3-9) figure (7), adjusted by means of dilute HCl and KOH solution , where the maximum absorbance obtained in the range of pH (5 - 8) . At pH > 7 a decreases in absorbance because the precipitation of manganese complex or form unstable ionic complexes ⁽¹⁸⁾ .

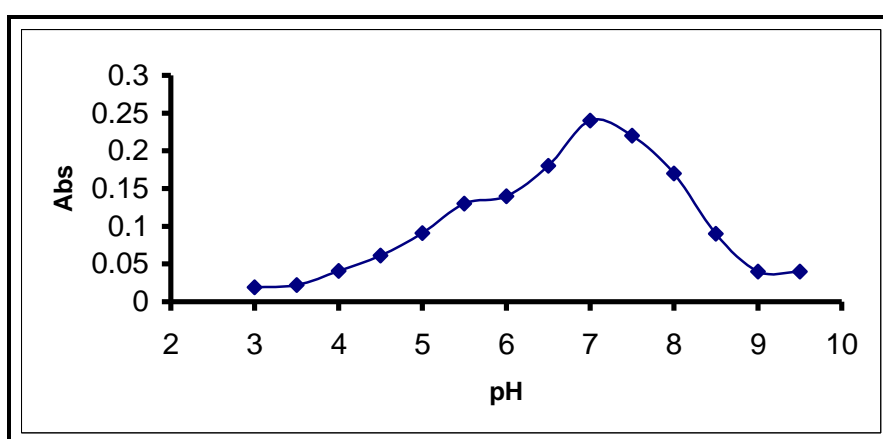


Fig.(7) Variation of pH with the absorbance of Mn(II)- complex

Determination Stiocheiometry and stability constant of the complex:

The composition of the complex was studied by Job's method figure (8) and mole ratio method figure (9). the results indicated from Both methods that the formation 2:1(M:L) to Mn(II)-ATA complex at pH 7.

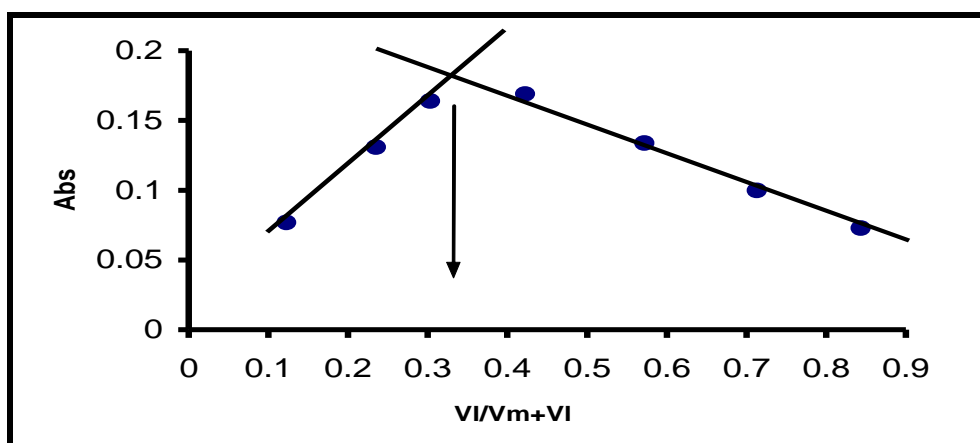


Fig.(8) Job method [ATA] = [Mn⁺²]=1x10⁻⁴, pH=7.

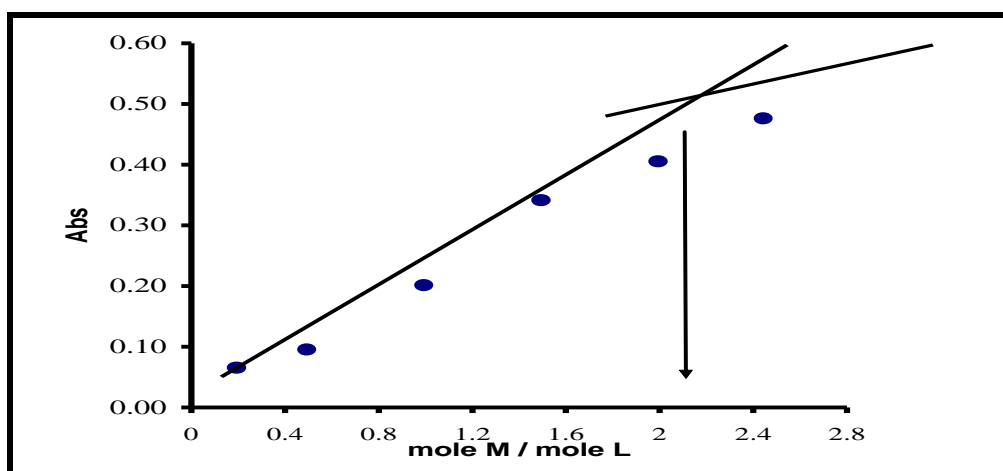


Fig.(9) Mole ratio method [ATA] = [Mn⁺²]=1x10⁻⁴, pH=7.

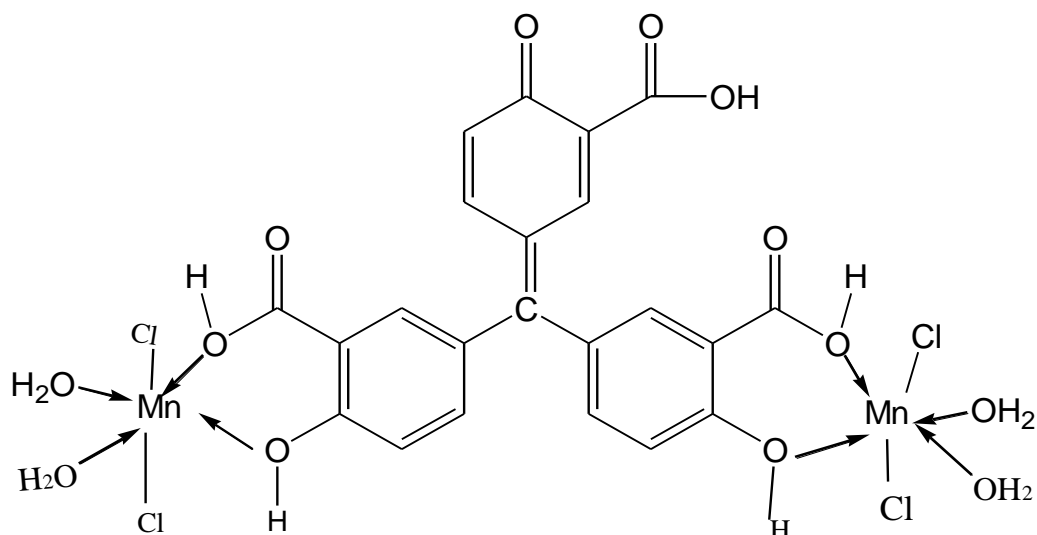
As applied to the molar ratio method , stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength λ_{max} and pH values. The degree of formation of the complexes is obtained according to the relationship⁽²⁰⁾, $\beta = (1 - \alpha) / (4\alpha^3c^2)$, and $\alpha = (A_m - A_s)/A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The calculated β values for the prepared complexes are recorded in Table(1)that appear the complex highly stability which can used a reagent ATA to spectrometric determination of the manganese(II)

Table (1) The stability constant value of the Mn-ATA complex

Metal ion determined	As Value	Am Value	α	β
Mn ⁺²	0.40	0.450	0.111	1.624x 10 ¹⁰ L ² .mole ⁻²

Suggestion of structural formula of Mn(II) –ATA complex:

According to these results from FT-IR spectrum ,Absorption spectra study and conductivity measurement while the composition of the complex was studied by Job's method and mole ratio method. Both methods indicated that the ratio of metal ion to ligand molecules was 2:1(M:L). The octahedral geometry around Mn(II) ion can be suggested, as follow



Beer 's Law and Precision

Linear calibration figure (10) and table (2) show that the complex obey Beer's law over the range (15-100) μg of Mn^{2+} in final volume of 25 ml ,the average molar absorptivity was found to be $2.55 \times 10^4 \text{L.mole}^{-1}.\text{cm}^{-1}$ and the Sandell's sensitivity was $0.014 \mu\text{g}.\text{ml}^{-2}$ and the correlation coefficient (r) was 0.9968 The high value of (r) indicate the good linearity and correspondence to Beer's law. The relative standard deviation for five determinations of $35 \mu\text{g}$ in 25ml of manganese was 2.9%.

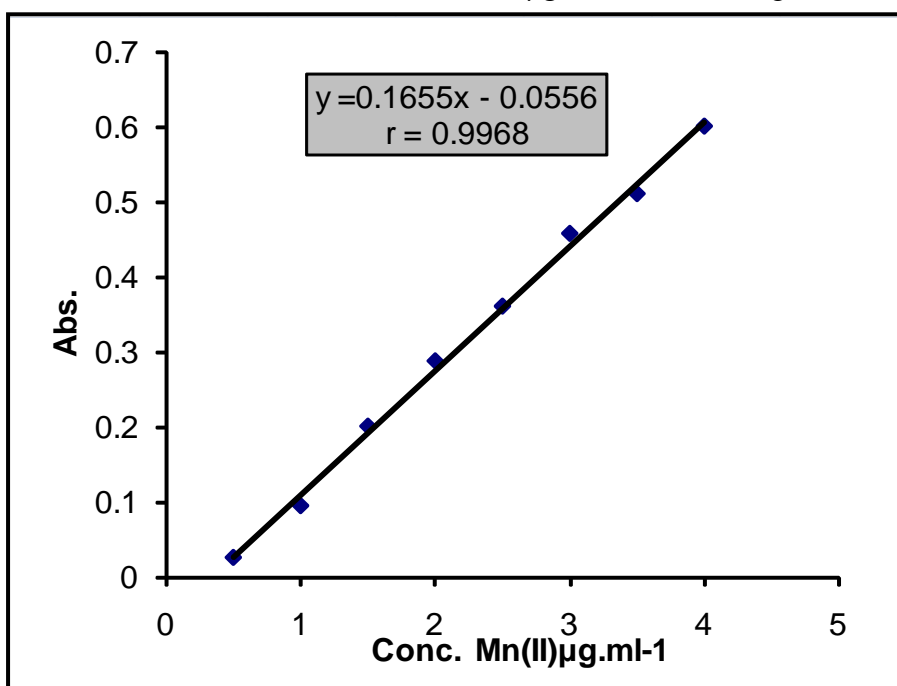


Fig.(10) Linear calibration to determination of Mn^{2+} by ATA reagent

Table(2)Analytical parameter obtained from calibration curve

Parameter	Value
Correlation Coffecient(r)	0.9968
Linearty($r^2\%$)	99.16
Slope(b) $\text{ml}.\mu\text{g}^{-1}$	0.1655
Intercept(a)	-0.0556
Equation	$y = 0.1655x - 0.0556$
Molar absorptivity (ϵ) $\text{L.mole}^{-1}.\text{cm}^{-1}$	2.55×10^4
Sandell Sensitivity $\mu\text{g}.\text{ml}^{-2}$	0.014

Effect of foreign ions:

Mn(II)- ATA complex (28µg Mn/ 10ml),data led to conclusion that up to Li⁺ , Na⁺ , K⁺ , Ti⁺ , Ba²⁺ ,Mg²⁺ , Cl⁻ , NO₃⁻ , ClO₄⁻ , SO₄²⁻ ,formate, acetate ,and succinate ions do not interfere ; while Ag⁺ , Hg²⁺ , V⁴⁺ , Zr⁴⁺ , Al³⁺ ,Zn²⁺ ,Co²⁺ ,Ni²⁺ ,UO₂²⁺ , EDTA, citrate, phosphate and oxalate interfere.

Analytical application

A validity of the method was checked by preparation solution 35µg in 25ml of manganese was determine at the optimum conditions of the method , this method show a low difference of manganese concentration by using the calibration carve , the recovery and relative error for the complex solution of Manganese are 98.84, 0.76% respectively .

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