A Sensitive Spectrohotometric Assay for the Determination of Manganese (II) Using Antipyrine azo as New Reagent

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الخلاصة

تم تطوير طريقة بسيطة وحساسة وأنتقائية لتقدير الكميات الضئيلة لمنغنيز(II) اعتمدت الطريقة على عملية التعقيد بين ايون المنغيز والكاشف الجديد ٤-(٤̀-امينو انتيبايرين أزو) ريزورسينول وتكوين معقد ذائب ملون له أعلى امتصاص عند الطول الموجي ٤٨٦نانو ميتر ومعامل امتصاص مولاري ١,٦٢x 10^4 لتر .مول$^{-١}$.سم$^{-١}$. وكانت العلاقة الخطية بين الامتصاص والتراكيز تتراوح بين (١.٢- 0.1) جزء في المليون عند الطول الموجي الاعظم . وكانت قيم الدقة والتكرارية للتراكيز المحضرة مختبرياً هي أفضل من 0.462 و0.2 % على التتالي .كما تم دراسة أنتقائية الطريقة عن طريق المتداخلات الايونية الموجبه والسالبة .أما ثابت استقرار المعقد فقد كانت قيمته$7.8x10^{٧}$ عند درجة حرارة المختبر .تم تطبيق الطريقة على نماذج عملية محضرة مختبرياً . وكذلك تم تطبيقها أيضا على نماذج ترابية متراكمة على جوانب البنايات والقريبة من الشوارع الرئيسية في محافظة الكوت في العراق لمعرفة تراكيز المنغنيز (II).

Abstract

A simple , sensitive and selective method has been developed for the determination of Manganese (II). The method is based on the chelation of metal ion with 4-(4- Amino antipyrine azo) resorcinol (APAR)to form an intense color soluble product , that is stable and has a maximum absorption at 486 nm , ε_{max} of $1.62x10^4$ $L.mol^{-1}.cm^{-1}$. A linear correlation (0.1-1.2 µg/ml) was found between absorbance at λ_{max} and concentration .The accuracy and reproducibility of the determination method for various known amounts of Manganese (II) were tested . The results obtained are both precise (%RSD was better than 0.462 %) and accurate (relative error was better than 0.2%) .The effect of diverse ions on the determination of Manganese (II) to investigate the selectivity of the method were also studied .The stability constant of the complex under optimized conditions and at room temperature was $7.8x10^7$ $L.mole^{-1}$ .The method was applied to the determination of Mn(II) ion in some standard practical samples and the determination of the content of Mn (II) in fallen dust particles upon AL- Kut governerate in Iraq .The fallen dust particles were collected form the buildings roof .

Introduction

Manganese is an important element for industry and biological systems [(1,2)] .Many sensitive instrument ,such as flow injection ,[(3,4)]atomic absorption spectrometry [(5-7)]and inductively coupled plasma [(8,9)]have been widely applied to the determination of manganese (II) .However ,the Spectrophotometric method has the advantages of being simple and not requiring .In our previous studies, some pyridyl azo ,azo pyrimidyl and antipyriyl azo were reported for the determination of metal ions [(10-13)].pyrozolon azo has a higher sensitivity than pyridyl azo and pyrimidyl reagents because of its larger conjugated system .To select a more sensitive reagent ,we synthesized 4-(4̀-pyrozolon azo) resorcinol (APAR) and thoroughly studied the color reaction of APAR with manganese (II) .This work reports on a simple and sensitive method involving spectrophotometric determination of manganese (II).

Experimental

All chemical used were of analytical grade.

preparation of reagent (APAR): The reagent was prepared by coupling of4 – amino antipyrine diazotate in alkaline solution A diazonium solution was prepared by taking 0.004 mol, 1.0 gm of 4 –amino antipyrine in 15 ml of ethanol and 6 ml concentrated HCl with 15ml of distilled water ,and adding sodium nitrite solution drop wise at 0 – 5C°,resorcine 0.011 mole ,1.2 gm was dissolved in 50 ml of ethanol , and 50 ml of (0.1ml) NaOH and 25ml of NaHCO3 were added at (0 – 5C°).The mixture was allowed to stand and added 10 % HCl solution . The precipitate was filtered off and recrystallized .from ethanol, scheme (1) .

Preparation of complex: The complex was prepared by stoichiometric amount from ligand in 50 ml of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 for copper salt in 25 ml hot distilled water. The solid product thus formed off , washed with ethanol and dried**.**

Apparatus: Spectrophotometric measurements were made with shimadzu UV Visible -1700 double beam spectrometric using 1.0 cm glass cells .The pH measurements were performed with AWTW PH –meter 720 . Vibration spectrawere carried out on testscan Shimadzu FT. IR 8000 series. Electric molarconductivity measurements were curried out at room temperature using an Alpha digital conductivity model -800 . Atomic absorption USA was used for comparative metal ion determination**.**

Reagents: All chemicals used were of analytical reagent grade .

Manganese (II) stock solution (200 µg/ml): Dissolve 0.307 gm of $MnSO_4.H_2O$ in 500ml of distilled water ,working standard Mn(II) solution were prepared by dilution of the appropriate volume of standard Mn(II) solution (100 µg/ml) with distilled water .

4-(4̀- antipyriyl azo) resorcinol (1x10^{-3}M): 0.081 gm of ragent (APAR) was dissolved in250ml of ethanol . working(APRA)solution was prepared by simple dilution of appropriate volume of the reagent solution (1x10^{-3}M) with ethanol.

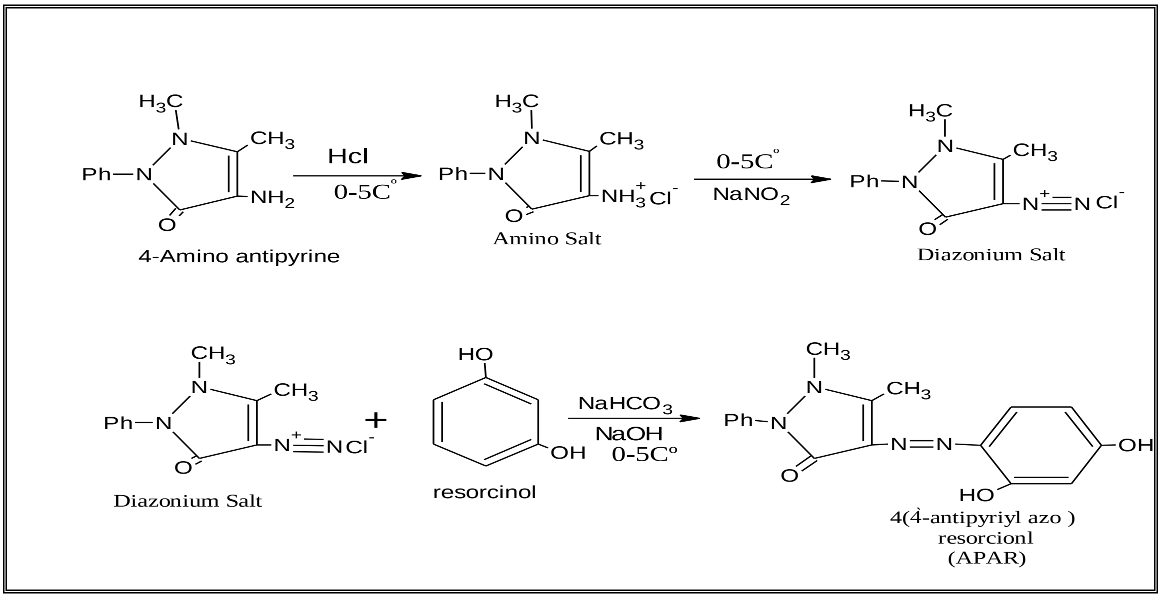
Foreign ion solution (100µg.ml^{-1}): These solution were prepared by dissolving an amount of the compound in distilled water completing in distilled water completing the volume in a volumetric flask .

Procedure for determination of manganese (II): Into a series of 10 ml calibrated flask , transfer in creasing volume of Manganese (II)solution (10µg/ml) to cover the reagent of the calibration graph and 3 ml of 1x10^{-3}M (APAR) solution and the pH was adjusted by 0.05N HCl or NaOH ,dilute the solution to the mark with distilled water and allow the reaction mixture to stand for 5 min .Measure the absorbance at 486 nm against reagent blank, prepared in the same way but containing no Manganese (II) using 1 cm glass cells.

Results and Discussion

The result of this investigation indicated that the reaction between Manganese (II) and APAR at pH 6 yield highly soluble product which can be utilized as a suitable assay procedure for Manganese (II) this product has a maximum absorption at 486 nm , at which the blank at this wavelength shows zero absorbance Fig.1 was adopted in all subsequent experiments .

The mechanism of reagent reaction: The reaction sequence in procedure of reagent involves two steps. In the Firstly 4-amino antipyrine react with nirite to form diazoniuum ion , the second including the diazanium ion coupling with resorcinol to form dark red azo dye ;



Scheme .1 Preparation of reagent APAR

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized .

Effect of pH: To establish the optimum condition (stability of the product from the reaction of Manganese (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (2-10) was studied . The pH 8.0 was found to be optimum .Neutral and alkaline results in low sensitivity and was not stable. pH change on the electronic absorption spectra of the complex was studied by adding a small amount of 0.1M HCl and NaOH. The UV-Visible spectra of Mn (II) complex gives the band centered at 486 nm (14) . The bands appearing in the range of 290-420 nm are attributed to π→π* transition. The other band observed in the region of 477 nm is attributed to n→π* electronic transition(15,16)Fig.2.Table.1.

Effect of (APAR) concentration: Various concentrations of 4- (4̀-antipyriyl azo)resorcinol was added to fixed concentration of Copper 3.0 ml of $1x10^{-3}$ M (APAR) solution was sufficient and gave minimum blank value, under 2.0 ml, the absorbance of blank value was increased causing a decrease in the absorbance of the sample. Therefore 2.0ml of $1x10^{-3}$ M of APAR was used in all subsequent experiments Fig.3.

Order of addition of reagents: To obtain the optimum results, the order of addition of materials should be followed as give by the procedure , otherwise , a loss in stability are observed.

Calibration graph: Employing the conditions described under procedure a linear calibration graph of Manganese (Π) is obtained which shows that Beer's law is obeyed over the concentration range of (١-1٢ µg per 10 ml 0.1 -1.2ppm)with correlation coefficient of 0.9989 and an intercept of ٠,٠١٣٣. The molar absorptivity of the product with reference to Manganese was1.62x10^{4} L. mole^{-1}.cm^{-1}.Table.1.

Table 1: Analytical characteristics of Mn(II)-APAR complex .

Characteristic	***Mn(II)***
Absorption maxima (nm)	486nm
Berr's low range (ppm)	(0.2-1.2)
pH range	(7.5-9.5)
Sandell 'S sensitivity µg.cm^{-2}	٠,٠٠٣٣
Molar absorptivity (L.mole^{-1}.cm^{-1})	1.62x10^{4}
Ethanol	٥,١
DMSO	١٠,٨٦
Stability constant (L.mole $^{-1}$)	7.8 x10^{7}
Formation constant	0.8x10^{3}
Free energy (KJ.mol^{-1})	-12273

Accuracy and precision: To determine the accuracy and precision of the method, Manganese was determined at two different concentrations. The results are shown in table 2, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table 2 :- Accuracy and precision of the proposed method .

Amount taken Mn(II) ppm	***Recovery**%***	***R.S.D %***
0.5	0.2	0.893
0.8	0.2	0.642

***For five determinations .**

Conductivity measurements: The solubility of the complexes in ethanol and DMSO permitted of the molar conductivity of 1x10^{-3}M solution at 25C$^{\circ}$ and by comparison ,the electrolytic nature for complex .The low values of molar conductance data listed in Table 3, indicate that the complex is non electrolyte .

Table 3: Effect of Conductivity measurement

Conductivity measurements		***Complex***
DMSO	***Ethanol***	
10.68	5.1	$Mn(APAR)_2$

Interferences: The effect of diverse ions on determination of Manganese (II) was studied .To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. The metal ion can be determined in the presence of a 10 or more fold excess of cation and anion. Table 4.

Table 4: Effect of foreign ions

Foreign ion	***Concentration ppm***	***Relative error***
Fe^{+3}	$FeCl_3$	١٠٠,٣٩
Cr^{+3}	$CrCl_3.6H_2O$	٩٨,١٦
Ni^{+2}	$NiCl_2.6H_2O$	٧٨,٧٠
Mn^{+2}	$MnCl_2.H_2O$	٤٠,٧٩
Pb^{+2}	$PbCl_2$	-٧,٧٦
Zn^{+2}	$ZnCl_2$	٢١,٥٨
Sr^{+2}	$SrCl_2$	٥,٦٦
Co^{+2}	$CoCl_2$	٣٧,٩٧
Pt^{+2}	K_2PtCl_4	١٥,٨٨
Cs^{+}	$CsCl$	-٧,٥٨
Ag^{+}	$AgCl$	-٤,٤
Hg^{+2}	$HgCl_2$	٧,٩٤٥
Cd^{+2}	$CdCl_2$	42.69
NO_2^{-}	$NaNO_2$	26.35
NO_3^{-}	$NaNO_3$	37.18
CO_3^{-2}	Na_2CO_3	30.68

SO_4^{-2}	Na_2SO_4	37.90
Cl^-	KCl	30.32

The stoichiometry of the reaction between manganese (Π) and (APAR) was investigated using the mole ratio method(17).The results obtained Fig.4, show a 1:2 complex formed between Manganese (Π) and (APAR) at 486 nm . The apparent stability constant was calculated by comparing the absorbance of a solution containing stoichiometric amount of Manganese and APAR with of a solution containing a five – fold excess of (APAR) reagent. The average conditional stability constant of complex in water ,under the described experimental conditions is $7.8x10^7$ L. $mole^{-1}$.

IR Spectra of the reagent and it`s Complex: A detailed interpretation of the IR Spectra of HL and the effect of binding with Mn^{++}. On the vibrational frequencies of the free H_2L ligand are discussed . The IR Spectra of the free ligand and it̀s metal chelate were carried out in the 4000-400 cm^{-1} range Table 5.The IR Spectrum of the ligand shows abraod band at 3425 cm^{-1},which can be attributed to the phenolic OH group. This band is still broad in nickel complex , which renders it difficult to attribute to the involvement of phenolic OH group in coordination . The involvement of the deprotonated phenolic OH group in chelation is confirmed by the blue-shift of the ν (C-O) stretching band , observed at 1120 cm^{-1} in the free ligand ,to the extent of 1157 cm^{-1} in the complex. However ,the ν (N=N) stretching band in the free ligand is observed at 1580 cm^{-1} .This band is shifted to lower with low intensity 1512 cm^{-1} frequency values upon complexation suggesting chelation via the (M-N) (18-21) .The IR Spectrum of the ligand reveled a sharp band at 16 cm^{-1} due to ν (C=N)of the N pyrozol azo nitrogen .This band is shifted to lower (20-35cm^{-1}) frequencies in the complex indication to that it has been affected upon chelation to the metal ion(22). The bonding of oxygen to the metal ion is provided by the occurrence of bands at 540 cm^{-1} as the result of ν (M-O)(23) .

Table 5: Selected IR data of (APAR) and its complex with Mn (II) .

Compound	ν(C=N)	(0H)ν	ν(C-H)Arom	(N=N)ν	(C-O)ν	(M-O)ν	(M-N)azo ν
H_2L	١٦٣٠s	345m	3050 m	١٥٨٠m	١١٢٠s	------	-----
$[Mn(HL)_2]$	١٥٨١m	3348m	3062 m	١٥١٢m	١١٥٧s	540w	٤٥٥w

S: sharp, m: medium ,w: weak

On the basis of the IR , and a stoichiometric data the structure of complex can be suggested as follows Fig 5:

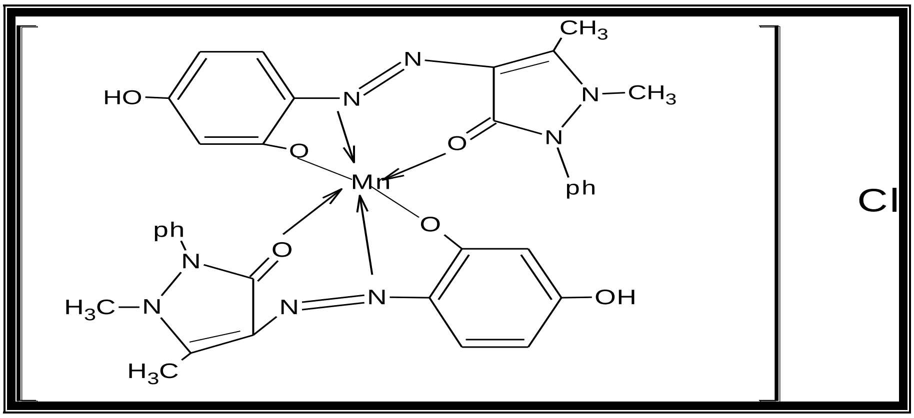


Figure 5: The proposed structural formula of Mn(II)complex with APAR

Formation constant of the complex and free energy: The formation constant of the reaction product was calculated according to the equation(24). Also the free energy changes (G) were calculated according to the following equation; $\Delta G = -2.303RT \log Kf$

R=gas constant =8.3 J/degree. mole, T= absolute temperature = ºC + 273

Using the above equation ΔG was found to be -12273 KJ.mole^{-1}. The negative value of ΔG indicates that the reaction is spontaneous.

Analytical application: A 1.0g of fallen dust from building at high 4 meter and 6 meter upon Al-Kut governorate in Iraq put in 150 ml beaker and dried for 3 hrs at 180 Cº, after that digested in 5 ml of concentrated nitric acid with heating for 15 min and filtrated. The filtrate was made up to 100 ml in a volumetric flask with double distilled water and 1ml of the solution was analyzed by the standard addition method. The results are given in table 6.

Table 6: Determination of Mn^{++}in fallen dust

Samples fallen dust	***Mn(II) µg.g^{-1}Atomic absorption***	****Mn(II) µg.g^{-1}(n=5 Amount found)***
Building at high 4m	5.7	5.5
Building at high 6m	7.6	7.5

***This work**

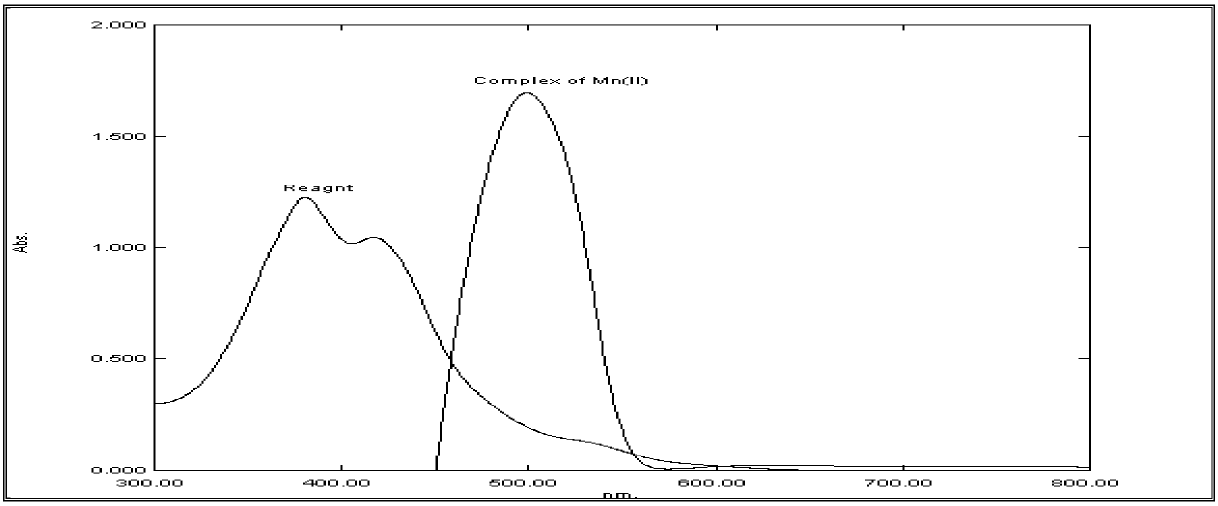


Fig 1 :- Absorption spectra of (Mn(*II)* + APAR) treated as described under procedure and against a reagent blank and reagent blank against ethanol .

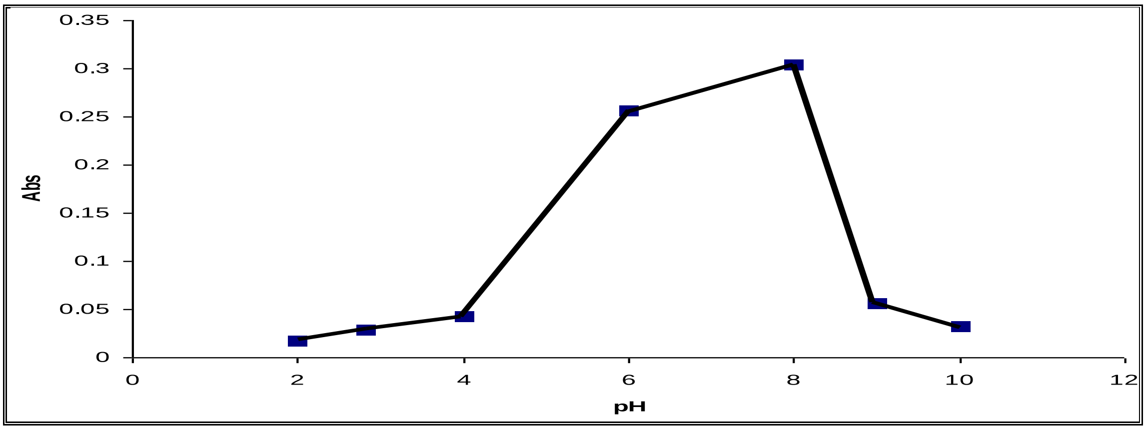


Fig 2:- Effect of the pH on The coloured products.

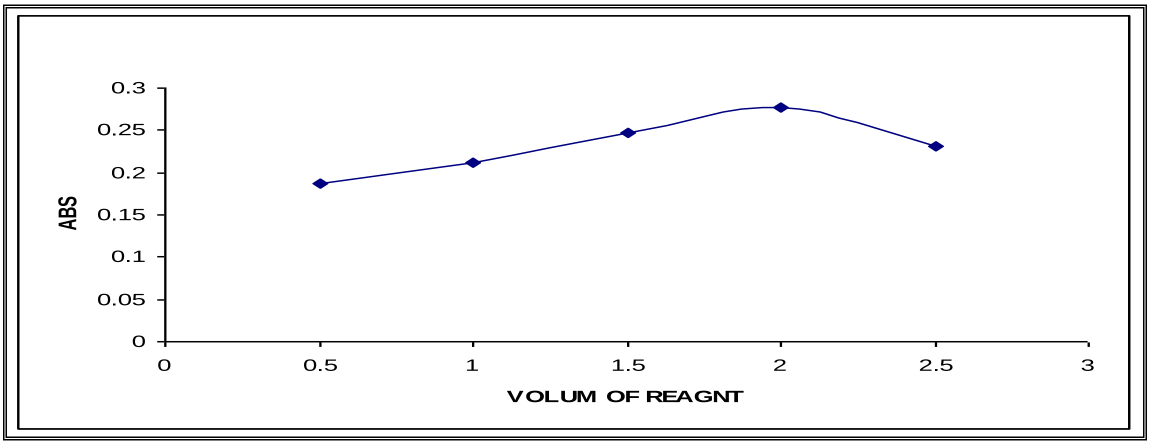


Fig 3:- Effect of the concentration of reaction on the coloured reaction.

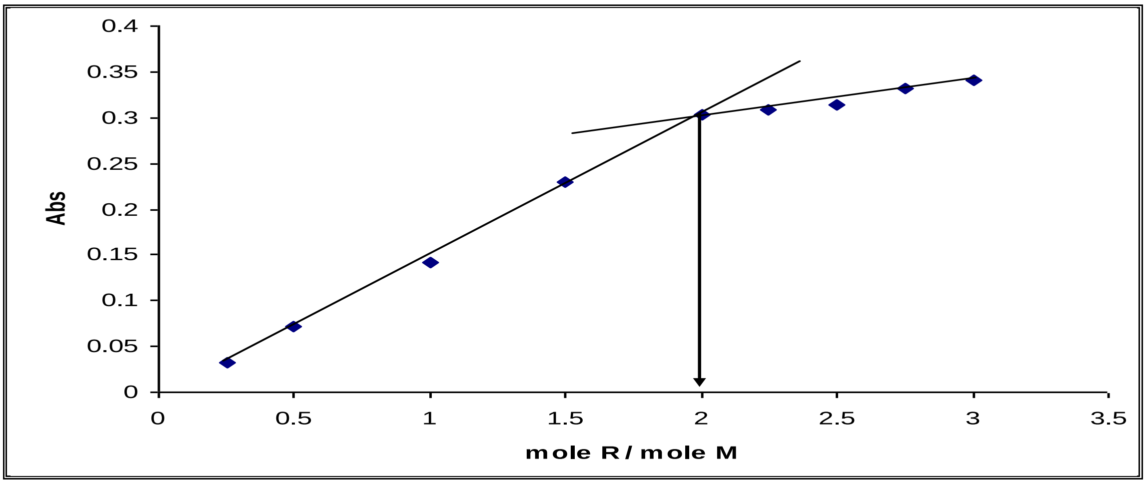


Fig 4:- Mole ratio of reagent to sample for the Mn(II) Complex .

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