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Spectrophotometric And Thermodynamic Determination Study of Manganese (II) By Using The Reagent 7-(6-Bromo-2-Benzothiazolylazo)-8-Hydroxyquinoline

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ABSTRACT

A thiazolylazo reagent, 7-(6-bromo-2-benzothiazolylazo)-8-hydroxyquinoline (7-(6-BrBTA8HQ)), was synthesized by di azo coupling of (2-amino-6-bromobenzothiazol derivative) with 8-hydroxy quinolone, and used for the spectrophotometric determination of Mn (II). This method was simple, rapid, sensitive, and selective for reaction between manganese and 7-(6-BrBTA8HQ) to form a pink complex with a molar ratio (1:2).The molar absorptivity of the complex was $(1.3695*10^{3} L.\ mol^{-1}.cm^{-1})$ *at* λ *max 562 nm. Beer's law obeyed in the range of (1-14) ppm of manganese, and the stability constant was equal to* $(3.688*10^{10} L.\ mol^{-1})$*.The relative standard deviation, recovery, and relative error were equal to (0.626%, 98.34%, 1.66%) respectively. The effect of temperature also studied and the thermodynamic parameters* (ΔG, ΔH *and* ΔS) *calculated and discussed. The ions (* Cr^{2+} ,V^{5+} , Cu^{2+} ,Cd^{2+} ,Fe^{2+} ,Ni^{2+} ,Co^{2+} ,Hg^{2+} *) were interferences when the reagent react with manganese ,and can be eliminated approximately using suitable masking agent.*

Keywords: 8-hydroxyquinoline, manganese (II), azo coupling, thermodynamic parameters.

INTRODUCTION

Manganese is one of transition element with the atomic number 25. It has atomic weight of 54.94.It has seven oxidation states (-1, 0, +2, +3, + 4, +6 and+7) of which +2 is the most common [1, 2].It is not found as free element but combined with other elements to form sulfates or oxides or others. Manganese is a metal with important industrial metal alloy uses, and used in dry cell batteries to prevent the formation of hydrogen, to remove the green color in glass that caused by the presence of iron contaminants, and as a drying agent in black paints[3].The most important methods, which are used, for determination of manganese are atomic absorption [4], inductivity coupled plasma –mass spectrometry (ICP-MS) [5], flow injection analysis (FIA) [6], kinetic methods[7], electrochemical methods[8]and spectrophotometry [9], which is one of essentially analysis technique based on formation colored complexes with organic and inorganic compounds.

In this work, a new heterocyclic azo dye reagent (7-(6-BrBTA8HQ) has been synthesized, and used for the spectrophotometric determination of manganese (II), this method is simple, sensitive, selective, and rapid. Different organic reagent are used to formation of color complexes with manganese, shown in table 1. This reagent (7-(6-BrBTA8HQ) was prepared by Azhar and prepared in this research and used to determination of manganese (II) [18].

Table 1. Different organic reagents are used to formation of color complexes with manganese

No.	*Organic reagents*	*λ max (nm)*	*Range ppm*	*ε L.mol^{-1}.cm-^{1}*	*Ref.*
1	*Benzohydroxamic acid*	*500*	*>10*	–	*10*
2	*Picolin aldehyde nicotinaylhydraone*	*385*	*0.02-1.5*	*4.6 *10^{4}*	*11*
3	*1,10-phenonethroline*	*560*	*0.05-5*	–	*12*
4	*1-(2-pyridyl azo)-2-naphthol*	*514*	–	*2.36 *10^{4}*	*13*
5	*2-hydroxy-4-methoxy acetophenone oxime*	*435*	*1-12*	*2.4 *10^{2}*	*14*
6	*Pyridine 2,6-dicarboxylic acid*	*500*	*50-225*	*9.89*10^{2}*	*15*
7	*2-amino acetophenone isonicotinayl hydrazone*	*435*	*0.1-2.7*	*1.49*10^{4}*	*16*
8	*O-nitrobenzol azo salicylic acid*	*400*	*1-22.5*	*1.36*10^{4}*	*17*

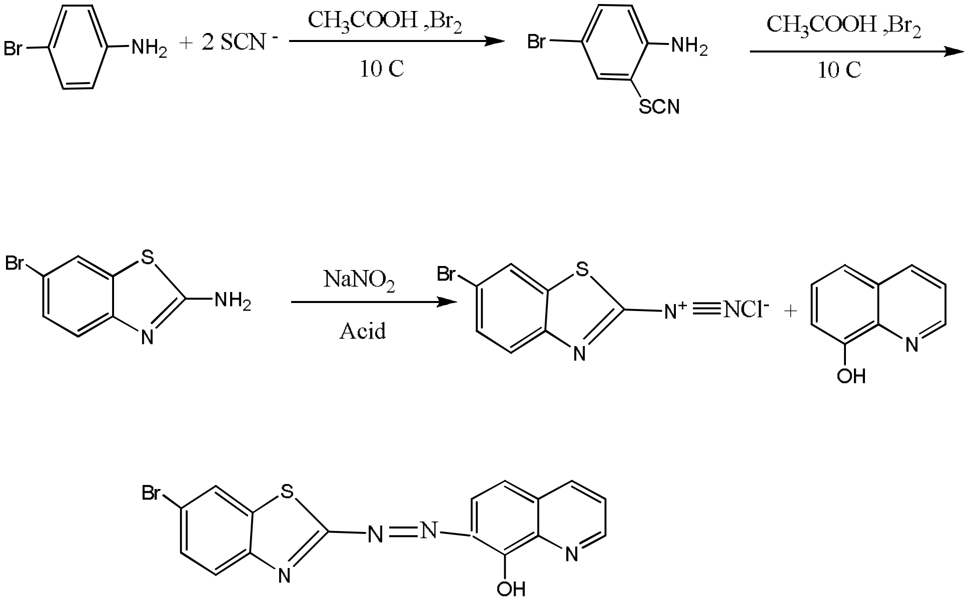
MATERIALS AND METHODS

Apparatus: A-FTIR spectra recorded as KBr discs using FTIR 8400 S Shimadzu in the range of 4000-200 cm-1. B- UV-1650 Shimadzu spectrophotometer were used to obtained electronic spectra.C-Sensitive balance Sartorius.D-pH meter WTW used to adjusted and measured pH of solutions.

Reagents: All chemicals were used of analytical grade − reagent unless otherwise stated. All solution was prepared using distilled water.

Synthesis of 2-Amino 6- BromoBenzothiazol (2-ABrBT) [19]: 2-ABrBT is prepared by a typical procedure (direct thiocyanogenation), it is described as follows:p-bromo aniline(1.7203 g) and ammonium thiocyanate (1.5224 g) were dissolved in (70mL) glacial acetic acid cooled in ice and stirred mechanically, While a solution of bromine (1.5 mL) in (50 mL) glacial acetic acid was slowly added drop by drop.

external cooling was applied throughout the reaction to keep the temperature below 10°C and the stirring was continued for (2 h) after all the bromine had been added. The product was obtained by pouring in distilled water (D.W), an amount of cold NaOH solution was added to separate the precipitate and filtering. Filtering, washing with D.W, and recrystalization with ethanol obtained a purified yellow solid.
Synthesis of reagent 7-(6-bromo-2-benzothiazolyl azo) 8-hydroxyquinoline 7-(6BrBTA8HQ) [20]: The synthesis of 7-(6-BrBTA8HQ) was accomplished according to general procedure described elsewhere’ with some modification. A 2-amino-6-bromobenzothiazole (2-ABrBT) (2.2909g) was dissolved in (25 mL) of distilled water and (5 mL) of concentrated hydrochloric acid and diazotized below 5ºC with (0.75 g) of sodium nitrite. The resulting diazonium chloride solution was added drop wise with cooling to solution of (1.4516 g) of 8-Hydroxyquinoline dissolved in 50 mL of alkaline ethanol and the mixture kept in the refrigerator overnight. The mixture was then neutralized with Sodium hydroxide .The solid product was filtered off, washed with cold water, crystallized twice from hot ethanol to give a dark red crystals of compound with melting point (190-194) c^{o}[21].



Standard stock solution of reagent (10^{-3}M): The reagent was prepared by dissolved (0.0385 g) in ethanol and complete to 100 ml ethanol to prepare solution 10^{-3} M.

Standard solution of Manganese (100 ppm): A solution of manganese 100 ppm was prepared by dissolving working solutions were prepared freshly by appropriate dilution of the stock solution.

7-(6-BrBTA8HQ) solution (1*10^{-4} M): 5 mL of (10^{-3} M) 7-(6-BrBTA8HQ) was transferred into a 50 mL calibrated flask and diluted up to the mark with absolute ethanol to prepare (1*10^{-4} M).

General procedure: Into a 5ml standard flask, transfer 1ml of solution containing (1-14) ppm of manganese (II) and 2mL of 1× 10^{-4} M 7-(6-BrBTA8HQ) solution, dilute to the mark with ethanol, mix well and after 5 min measure the absorbance of solution at 562 nm in a 1 cm quartz cells against a reagent blank prepared in the same condition.

RESULTS AND DISCUSSION

FTIR spectrum of reagent and complex: The FTIR spectrum of reagent in fig. (1) Show the absorption band at (3431cm^{-}) due to (O-H) group in 8-hydroxyquinoline ring. Absorption band at (3161cm^{-}) refer to (C-H) of aromatic ring, absorption band at (1645 cm^{-}) refer to (C=N) group, absorption band at (1546 cm^{-}) refer to (C=C) group, absorption band at (1404 cm^{-}) and (1305 cm^{-}) refer to (N=N) and (C-N) group respectively. Absorption band for (C-O) and (C-S) at (1118, 1016cm^{-}) respectively. Absorption bands at (742,799,925 cm^{-}) refer to (Ar-H) and absorption band at (642cm^{-}) for (C-Br) (22).

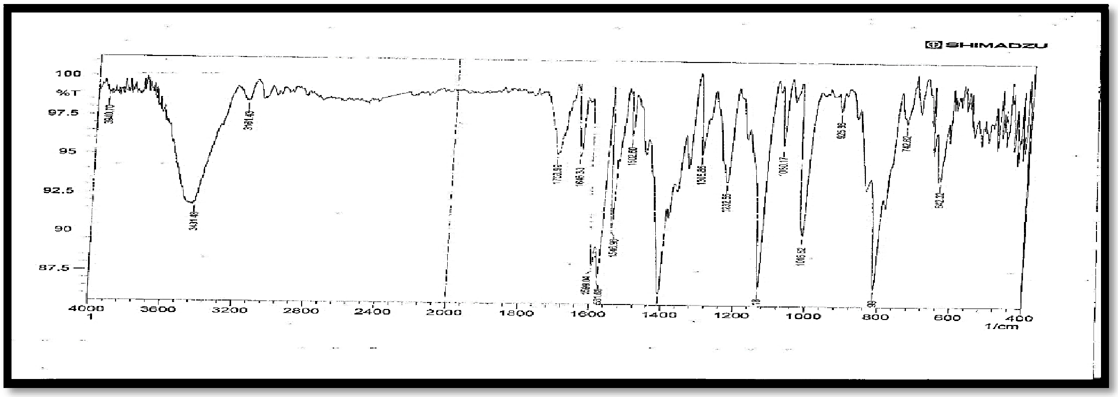


Fig. 1 FTIR Spectrum of the reagent

1645 Cm^{-1} which differ from bands in the reagent spectrum this difference is due to coordination metal ion with nitrogen ring. The coordination of metal ion with nitrogen of azo group gives an absorption band at 1581 Cm^{-1} that also differs from band in the reagent. A new band appears in this spectrum at (400-1000) Cm^{-1} which refers to metal-oxygen bond (M-O).

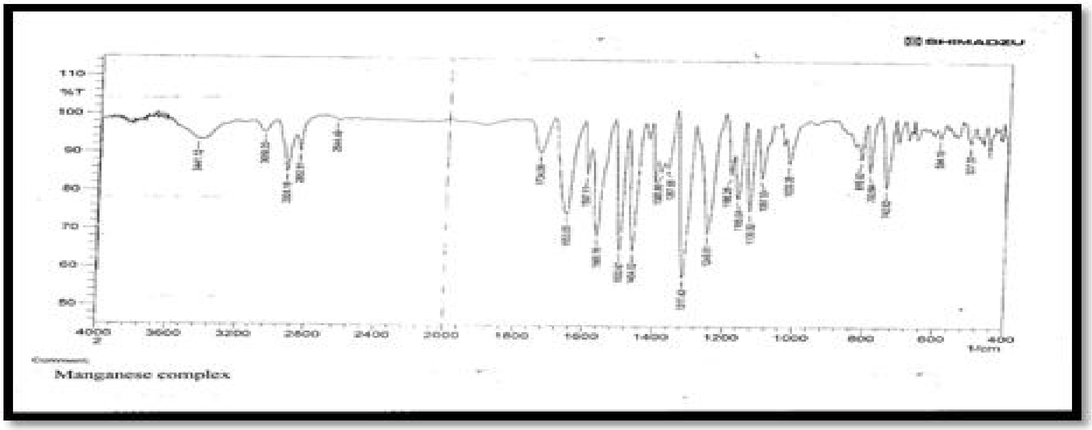


Fig. 2 FTIR Spectrum of the complex

Physical and chemical properties of 7-(6-BrBTA8HQ):7-(6-BrBTA8HQ) is reddish-orange powder which is insoluble in water, it is soluble in organic solvents, such as, DMSO, Acetone, DMF, ethanol. The reagent appears as orange color in acidic medium and violet in basic medium, absorption spectra of the reagent at different pH values as follows in fig. (3):

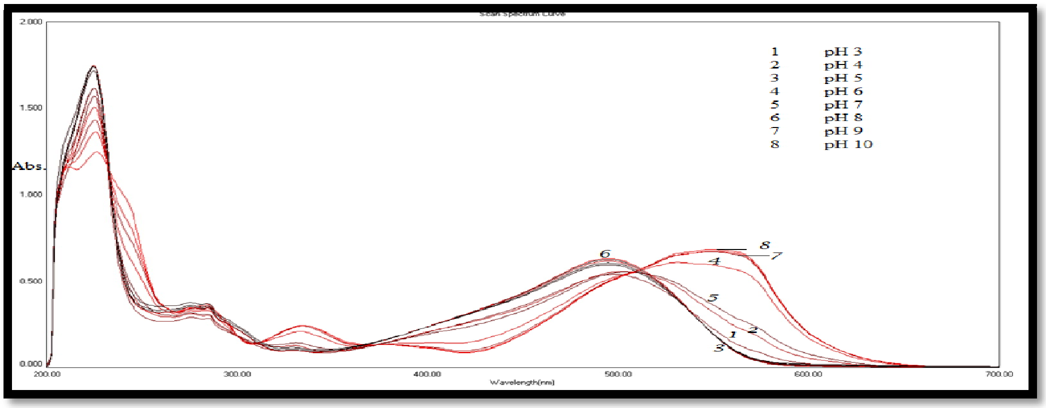


Fig. 3: Absorption spectra of the reagent at different pH values
This figure shows two isosbestic points the first at 370nm and the second at 512nm.

Absorption spectra of free reagent and complex: The absorption spectra of the reagent in the ethanol solvent and the complex spectra [Mn-7-(6-BrBTA8HQ)] shown in figure (4):

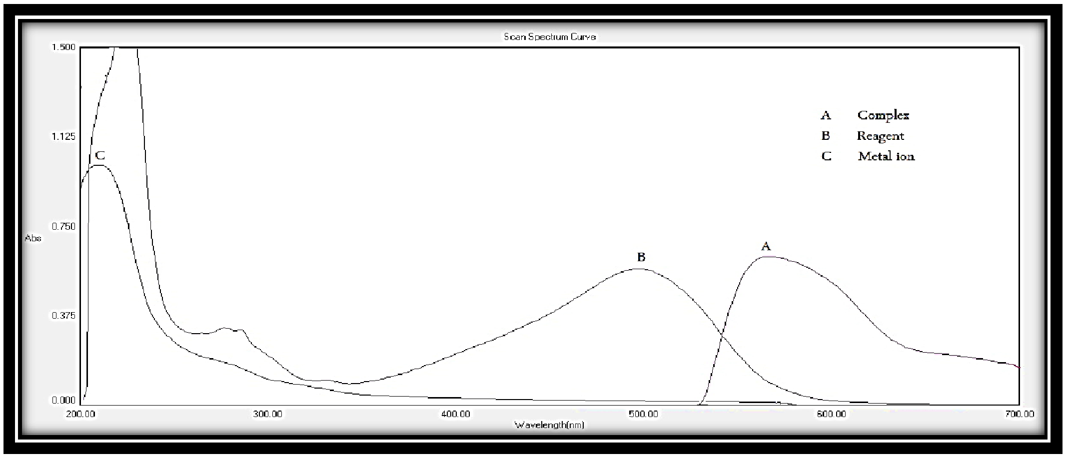


Fig. 4: Absorption spectra of A:Mn-7-(6-BrBTA8HQ) complex
B: 7-(6-BrBTA8HQ) reagent.C: Metal ion

The electronic spectrum of the reagent shows three characteristics bands, the two band at (226,268) nm is due to the (π -π*) transition of the phenolic ring, while the third band at (518) nm is due to the (n- π*) transition of the nonbonding electron pairs of the nitrogen atom. The complex of Mn (II) with this reagent appears the peak at 562 nm, this indicate the reaction happen between Mn and the reagent 7-(6-BrBTA8HQ).

Absorption spectra show that the λ max of absorption of reagent is apparent at 518 nm, while for Mn complex at 562 nm, this new λ max mean the red shift in λ max of complex.

Effect of reagent concentration: Keeping a constant concentration (20 ppm) of Mn (II) solution, the effect of reagent concentration (1 x10^{-4} M) on absorbance of the complex was studied by varying the amount of the volume of reagent (1-3) mL, it was obtained that the complex formation was complete and absorbance was maximum when the amount exceeds 3mL**.**

The effect of pH: The absorbance of the Mn-complex depends on the pH of the solution, the influence of pH was studied over the range (2-10) adjusted by addition of dil. NaOH(0.01M) and dil. HCl (0.01M), the optimum pH range was obtained between (7-8) of complex. Fig. (5,6)shows the relationship between absorbance of complex and pH, At pH <7 a decrease in absorbance may be due to form azolium cation result from the reaction between hydrogen ion and the ion pair of electron on the nitrogen atom for thiazol ring . In addition, when pH >8 a decrease in absorbance observed due to formation of manganese hydroxide.

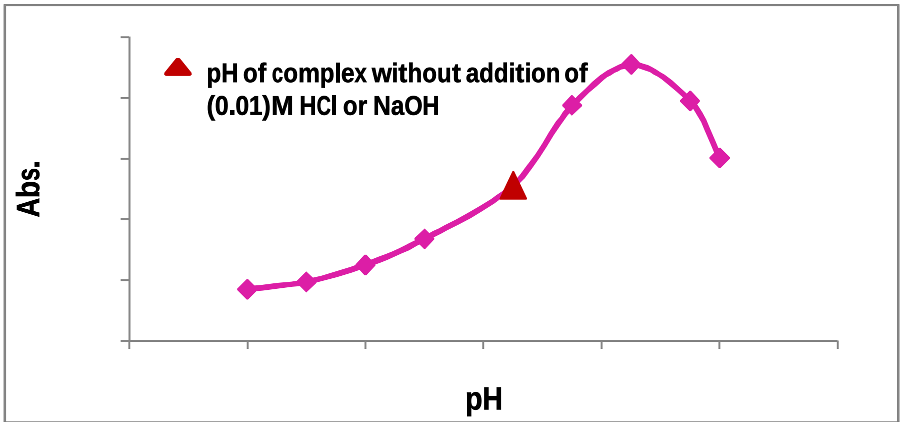


Fig. 5:-Effect of pH on the absorbance of manganese complex.

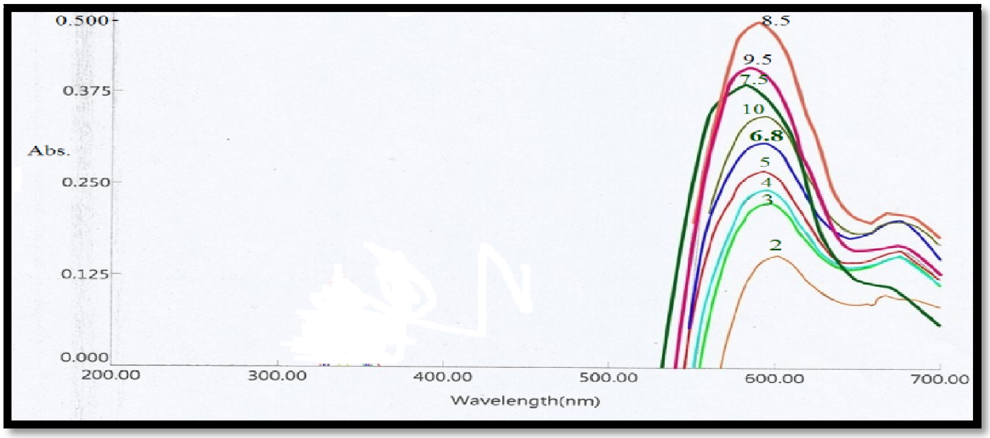


Fig. 6:-Effect of pH on the absorbance of manganese complex.

The stability of the complex at different times and different temperatures: The absorbance of the complex reaches a maximum value within 5 min and remains stable for 24 h. The absorbance of the - C, the maximum and c - C because the complex will be dissociated or evaporated in these temperatures.

Composition of complex and stability constant: The complex composition was determined by job's and mole-ratio methods [fig (7, 8)], both methods indicated that the complex has a molar ratio of (1:2) (M: L) at pH 7, and the stability constant ($K_{stab.}$) and (α) of complex was found to be ($3.688*10^{10}$L. mol^{-1}) and (0.0853) respectively by using the following equations [23]:

$$K_{stab.} = \frac{1}{K_{inst.}} \qquad \text{………… (1)}$$

$$K_{inst.} = \frac{(\alpha c).(n\alpha c)^{n}}{c(1-\alpha)} \qquad , \ \alpha = \frac{E_m - E_s}{E_m} \qquad \text{………… (2)}$$

Where:
α=degree of dissociation.
c =total concentration of the complex=1x10^{-4}M.
n =mole ratio = 2.
Em=absorbance of a solution containing reagent two times excess than the amount of manganese**.**
Es=absorbance of a solution containing a stoichiometric amounts [reagent] = [manganese] = 1x10 $^{-4}$M.

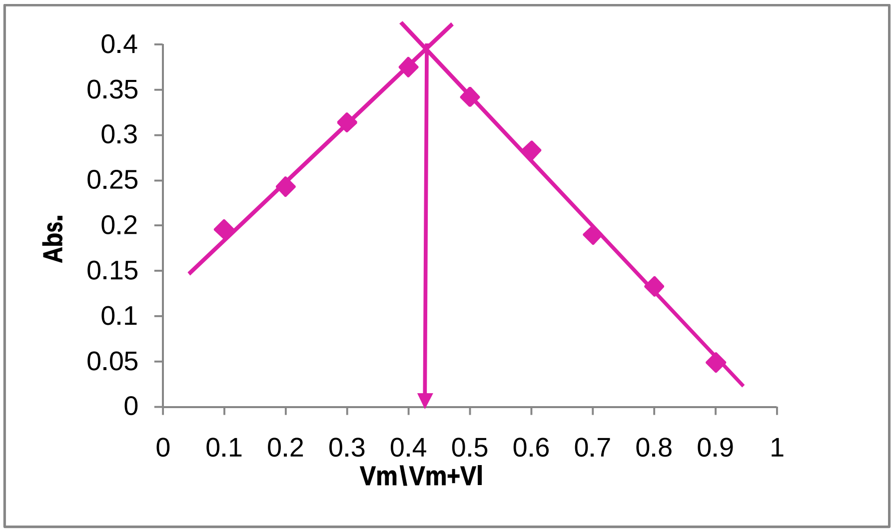


Fig. 7. Continuous variation method for Mn complex at optimum conditions.

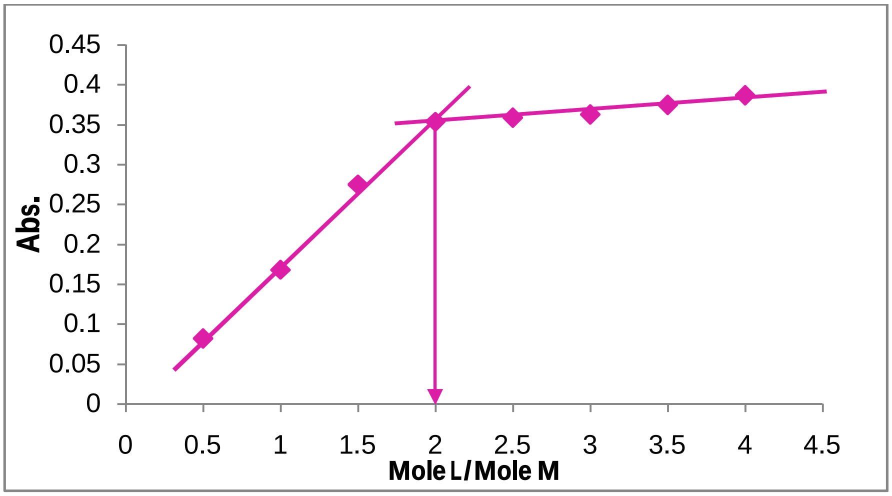


Fig 8. Molar ratio method for Mn complex at optimum conditions.

Analytical characteristics: The calibration curvemade as described in the experimental procedure and good correlation coefficient found in fig. (9), the some analytical parameters for this Spectrophotometric determination of Mn (II) using this reagent summarized in table (2) [24]:

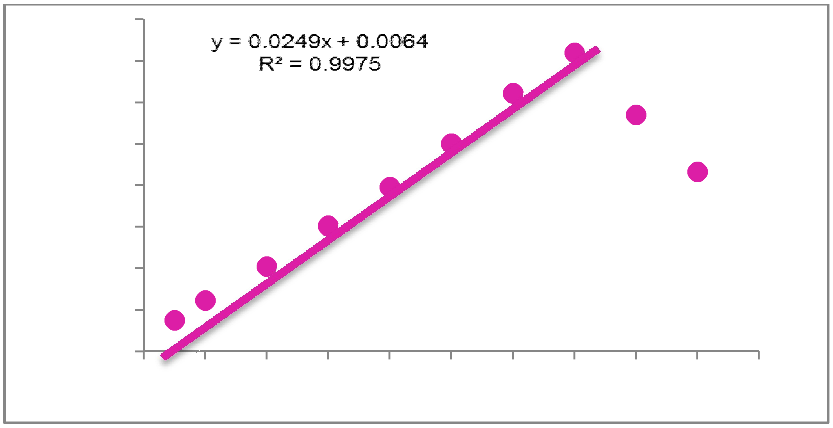


Fig. 9: Calibration curve of Mn Complex.

Table 2: Analytical characteristics of the proposed procedure (N=No. of determination).

Analytical parameter	**Value**
Molar absorptivity ε,L.mol^{-}.cm^{1}	1.3695*10^{3}
Sandell's sensitivity gm.Cm^{-2}	0.0402
Correlation coefficient(R)	0.9975
Detection Limit(D.L), ppm	0.177
Linear dynamic range, ppm	(1-14)
Standard deviation(S.D) , for (12 ppm)	0.00147
Relative Standard Deviation (R.S.D %), (N=7)	0.492 %
Percent Relative error (E rel.%) for (12 ppm)	-2.5%
Percent Recovery (Re %)	97.5%

These results indicate that this method is highly accurate and suitable for the determination of Mn (II) spectrophotometrically.

Interferences: The ions (Hg^{2+} Cd^{2+}, Fe^{2+}, Co $^{2+}$ Ni^{2+},Cu^{2+} were formed the complexes with the reagent 7-(6-BrBTA8HQ) during its reaction with manganese, the effect of these ions are studied, as in table 3.

Table 3: Effect of foreign ions on the determination of Mn (II) and suitable Masking agents.

Mn ppm	**erferences ion 50ppm**	**Error %** Before addition masking agent	***Masking agent ( )ml,[0.1]M***	**Error %** after addition masking agent
10	Cu	-140.7	*(1) Oxalic acid*	0.5
10	Cd	-37.8	*(0.5) Oxalic acid*	0.4
10	Fe	-25.4	*(0.75) Tartaric acid*	-0.5
10	Hg	2.9	*(0.5) Tartaric acid*	0.5
10	Co	-56	*(0.5)Ascorbic acid*	0.1
10	Ni	-130.3	*(1.5)Ascorbic acid*	0.3

Determination of stability constant and thermodynamic parameter

Effect of temperature on stability constant: The stability constant of Mn complex was calculated by measuring the absorbance of complex at different temperatures (10-50) ^{o}C, and by using the equation (1 and 2). Figure 10 and table 3 shows the effect of temperature on Mn complex absorbance and stability constant:

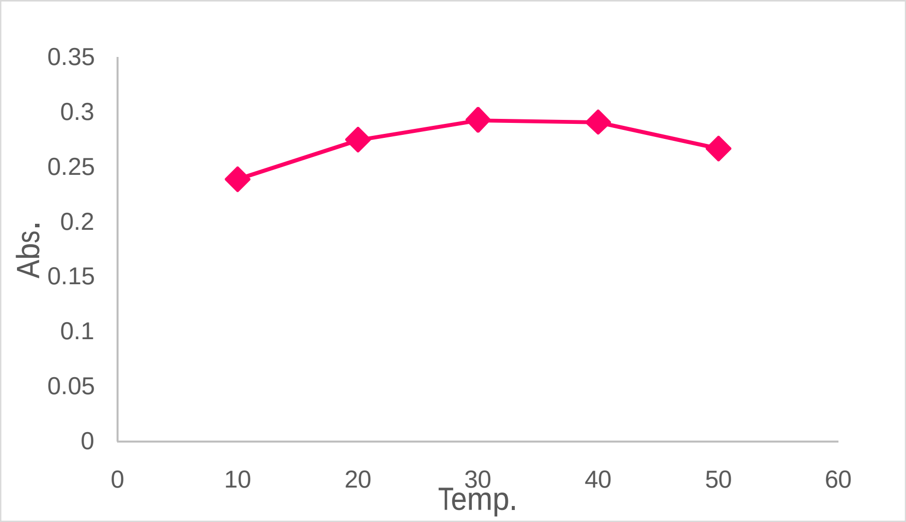


Fig. 10: Effect of temperature on Mn complex.

Table 4: Effect of temperature on stability constant.

Temp. C^o	Temp. K	1/T x10^3	α	K x 10^{10}	Log K
10	283	3.53	0.0831	3.99	10.60
20	293	3.41	0.0841	3.19	10.50
30	303	3.30	0.1082	1.75	10.24
40	313	3.19	0.1510	0.62	9.79
50	323	3.09	0.2148	0.19	9.29

Calculation of the Thermodynamic parameters [25-28]: The thermodynamic parameters such as Gibb's free energy, enthalpy change and entropy change for formation of complexes were determined. The change in free energy of the complex calculated by using following equation:

$$\Delta G = -RT \ln K_{st}$$

Where: R= Universal gas constant, T= temperature in K, log K = Stability constant.

The changes in enthalpy (ΔH) are calculated by plotting 1/ T vs log K. The equation utilized for the calculation of changes in enthalpy is as under:

$$\text{Slope} = \frac{-\Delta H}{2.303\ R}$$

The evaluation of changes in entropy (ΔS) done by the following equation

$$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T$$

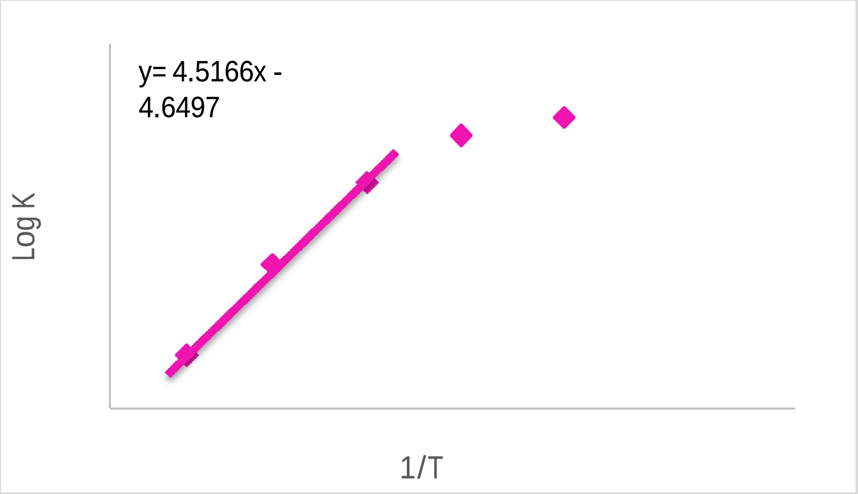


Fig. 11: Isotherm Van't hoff for Mn complex.

Table 5: Effect of temperature on thermodynamic parameters for Mn complex

Temp.C^0	*Temp. K*	*1/T x10^3*	K x 10^{10}	Ln K	-ΔH (J/mol)	-ΔG (J/mol)	-ΔS (J/mol.K)
10	*283*	*3.53*	3.99	24.41	86.48	57.43	0.103
20	*293*	*3.41*	3.19	24.19		58.93	0.094
30	*303*	*3.30*	1.75	23.59		59.43	0.089
40	*313*	*3.19*	0.62	22.55		58.68	0.088
50	*323*	*3.09*	0.19	21.37		57.39	0.090

These results indicates that the reaction between reagent and manganese is exothermic and the ability for complex formation increase when the temperature decrease, while the negative value for Gibbs free energy and entropy refer to the reaction is occur spontaneously when temperature is decrease.

APPLICATIONS

The determination can be used analytically to determine the unknown concentration of Manganese metal in drank water and another source.

CONCLUSIONS

In this work, 7-(6-BrBTA8HQ) was prepared and the color reaction of 7-(6-BrBTA8HQ) with manganese was firstly studied. 7-(6-BrBTA8HQ) isone of the sensitive and selective spectrophotometric reagents for manganese. The molar absorptivity reaches to $1.3695*10^3$L mol^{-1} cm^{-1}. Most foreign ions do not interfere with manganese when masked with oxalic acid, tartaric acid, and ascorbic acid. Because the7-(6-BrBTA8HQ) can rapidly react with manganese (II) at room temperature, this method can determine manganese spectrophotometrically without heating or extraction. It is a sensitive, selective, rapid, and convenience method for manganese.

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