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Spectrophotometric determination of Manganese by Biologically active 3,5-Dibromo-2,4-Dihydroxy Acetophenone oxime

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Abstract: 3,5-Dibromo-2,4-Dihydroxy acetophenone oxime (DDAO) has been successfully employed as a reagent for spectrophotometric determination for Mn(II) at pH range 10.3 to 10.8 in chloroform medium. The composition of the complex 1:2 (metal:ligand) has been confirm by job's method for continuous variation, Yoe & jones mole ratio method &slope ratio method. The stability constant of the complex is found to be $5.437x10^7$. The water soluble brown coloured complex obeys Beer's law over the concentration range1 to 10.0 µg for Mn(II) ion. The complex has molar absorptivity 5.2 x 10^3 $mol^{-1}cm^{-1}$. While their sensitivity is 0.0105 µg Mn/cm^2.Limits of interference due to the presence of foreign ions in the spectrophotometric determination has also been determined. The standard free energy of the complex is 10.57 Kcal/mole at 27°C.
The complex is stable for one week DDAO has also been found to give quite satisfactory results for Mn(II) present in synthetic mixtures. The antimicrobial activity of DDAO and Mn-DDAO complex have also been calculated.
Key words: Mn-complex,antimicrobial activity, Richards liquid medium.

Introduction

A number of reagents are known for spectrophotometric and complexometric determination of Mn(II) and other transition metal ions[1-5]. The present communication deals with the spectrophotometric determination of Mn(II) with DDAO & compare their biological behaviour with standard drug.

Experimental

Standard stock solution (0.1M) of Mn(II) has been prepared by dissolving appropriate amount of $MnCl_2$ (AR) in double distilled water. The amount of Mn(II) in stock solution was determined by standard method.[6]

Preparation of 3,5-Dibromo-2,4-Dihydroxy acetophenone oxime (DDAO)

3,5-Dibromo-2,4-dihydroxy acetophenone oxime (DDAO) was prepared by refluxing an alcoholic solution of DDA (50.0g) with hydroxylamine hydrochloride (80.9) for two hours in the presence of anhydrous sodium acetate (50.01). The reaction mixture was cooled and poured over crushed ice. The precipitated product (DDAO) was filtered, washed with water, dried and crystallized from ethanol, yield 80% m.p. 198-100°C. It was characterized by elemental analysis & infrared spectroscopy.

Preparation of Mn(II) –DDAO complex and selection of solvent

When metal ion solution was treated with an ethanolic solution of DDAO and the mixture was stirred for about an hour at room temperature, water soluble brown precipitates of complex were obtained in the pH range 10.3-10.8 The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non polar solvents like chloroform, benzene, CCl_4 etc. This complex was more soluble in chloroform so it was elected as a solvent for extractive spectrophotometric determination of Mn(II).

Apparatus

Systronic. pH meter (type 322) was used for pH measurement & calibrated at pH 9.18 with borax buffer.

Results and Discussion:

Selection of optimum wavelength & pH

The formation of Mn(II) complex with DDAO & their stability are depend on the pH of solution. While absorbance is depend upon the wavelength.

The method of Vosburg & cooper showed the formation of only one complex having λmax at 395 nm.The absorbance of complex formation was measured at room temperature (300 K) at regular intervals of time up to two week & also different temperature varies from 300K to 325K. The results show that complex is stable for one week & upto 318K without change of absorbance.

The Mn(II) complex exhibit maximum & almost constant absorbance in the pH range 10.3 to 10.8(Table-2). The subsequent studies were, therefore, carried out at pH 10.5. It was also found that a 36 fold excess of the reagent was necessary to attain the maximum colour intensity.

Table-1: Vosburg And Cooper's Method For Mn(II) AND DDAO

Concentration of Mn(II) = DDAO Solution = 1.0×10^{-3} M

Total Volume = 25.0 ml

Wave length	Ratio of Metal to ligand			
(nm)	1:1 OD	1:2 OD	1:3 OD	1:4 OD
380	0.265	0.445	0.345	0.180
390	0.325	0.495	0.410	0.215
395	0.335	0.505	0.420	0.220
400	0.325	0.495	0.410	0.215
410	0.280	0.430	0.355	0.190
420	0.225	0.350	0.285	0.150
430	0.175	0.265	0.215	0.120
440	0.135	0.200	0.170	0.095
450	0.110	0.165	0.140	0.080
460	0.085	0.135	0.110	0.065
470	0.075	0.115	0.095	0.055
480	0.060	0.100	0.080	0.050
490	0.055	0.085	0.065	0.045
500	0.045	0.075	0.060	0.040

Table-2: Effect Of pH On The Absorbance Of Mn(II)-DDAO AT 395 nm

Volume of 1.0×10^{-3} M Mn(II) Solution = 2.0 ml

Volume of 1.0×10^{-2} M DDAO Solution = 5.0 ml

Total Volume = 25.0 ml

pH	O.D	pH	O.D
7.5	0.020	10.3	0.350
8.0	0.065	10.6	0.355
8.5	0.100	10.8	0.350
9.0	0.170	11.0	0.300
9.5	0.245	11.5	0.245
10.0	0.305	-	-

Reproducibility

Absorbance measurements of a set of six solution prepared in a similar way & have the same concentration of all the reagents show that the reproducibility of measurements are quite good with standard deviation ± 0.432 i.e. 0.26 %.

Stoichiometry and stability constant of the complex

Results of yoe and jones mole ratio method[9], slope ratio method[10] and job's method of continuous variation[11] establish the formation of 1:2 (metal: ligand) complex.(Fig 2,3)

The stability constant of the complex was calculated from the following relationship using mole ratio method. (Table-3)

$$\alpha = \frac{Em - Es}{Em}, \qquad K = \frac{1-\alpha}{(m\alpha c)^m \times (n\,\alpha\, c)^n}$$

Came to be 5.437×10^7. The volume of the standard free energy of the formation of complex from the expression $\Delta G = -2.303\ RT \log K$, came to be 10.57 Kcal/ mol at 27°C.

Table-3: Composition Of The Mn(II) DDAO-Complex By Mole Ratio Method At395 nm

Concentration of Mn(II) Solution = 1.0×10^{-3} M

Constant Volume of Mn(II) = 1.0 ml

Concentration of DDAO = 2.0×10^{-3} M

Total Volume = 25.0 ml

Ionic strength = 0.1 M $NaClO_4$

Volume of DDAO Solution (ml)	OD	Volume of DDAO Solution (ml)	OD
1.0	0.140	12.0	0.680
2.0	0.210	14.0	0.720
3.0	0.300	16.0	0.750
4.0	0.365	18.0	0.750
6.0	0.470	20.0	0.750
8.0	0.580	22.0	0.750
10.0	0.640		

Validity of Beer's law and optimum concentration range

It was observed that the Beer's law is obeyed in the concentration range 1-10 µg of Mn(II). The optimum concentration range for determination of Mn(II) in solution as deduced from Ringbom plot[12] . From the slope ratio curves the molar extinction coefficient of the complex is 5.2×10^3 while the value of photometric sensitivity as per sendell's scale is found to be 0.0105 $\mu g_{-Mn/Cm^2}$

Effect of foreign ions

It was observed that at 4.0 ppm of Mn(II), 150 ppm of Cl^-, SO_4^{2-} and CH_3COO^-; 100 ppm of NH_4(I), K(I),Na(I),NO_3, Br^- and I^-; 50 ppm of Ca(II),Ba(II),Sr(II),SO_3^{2-}, NO_2^-, tartrate and citrate; 20 ppm of Cd(II) and Be(II) could be tolerated . However Cu(II),Ni(II),Co(II),Pd(II),Fe(III) and UO_2^{2+} interfered seriously.

A limit of 2.0% change in absorbance was observed as a limiting concentration.

Determination of Manganese from different samples

The usefulness of the reagent in estimation of manganese was determined from various samples of Mn(II) concentration having different concentration. The sample mixture containing manganese metal were taken for spectrophotometric analysis at different wavelength. The result are given in table 4.

Table 4: Analysis of Manganese in various sample

Sample	Mn taken µg	Mn found µg	Absorbance	Relative error
Synthetic Mixture No.1	160	0.425 0.412 0.428 Avg.	165.5 162.3 158.3 162.7	0.25
Synthetic Mixture No.2	120	0.320 0.336 0.344 Avg.	122.6 118.1 126.4 122.0	0.91
Synthetic Mixture No. 3	216	0.569 0.557 0.562 Avg.	211.3 219.6 221.6 217.8	0.83

Analysis

The extracted complex was concentrate & crystallized in desiccator. The elemental analysis of the complex shows metal:ligand (M:L) ratio to be 1:2

Found	C 27.42	H 1.81	N 3.82	Br 45.68	Mn 7.76
Calculated	C 27.31	H 1.70	N 3.98	Br 45.52	Mn 7.81

The IR spectra of DDAO and complex revealed that the –OH (Stretch) band at 3400 Cm^{-1} for the DDAO disappears during complexation .i.e. complex formation takes place through the N of oximino group and oxygen of the hydroxyl group.

The general composition of the complex is [$C_{16}H_{12}N_2O_6$]Mn

Antimicrobial activity

DDAO & Mn-DDAO were screened for their antibacterial activity against E.Coli & antifungal activity against Aspergillus niger using agar diffusion[13] method & dry weight increased method[14]. The results indicate that DDAO & its Mn(II) complex exhibit more antimicrobial activity with respect to standard drug. (Table-5, 6 & Fig.1,2).

Mode of action

Antimicrobes exert their action in the different ways

1. Inhibitors of cell wall synthesis.
2. Inhibition of cell membrane
3. Inhibition of Biosynthesis (i.e. production of purines,pyrimidine,Amino acid, Vitamins, Protein, RNA, DNA)
4. Inhibitors of energy production (inhibit the respiration or by uncoupling of oxidative phosphorylation (Disruption the metabolic activities.)

The studies demonstrated that chelation can increase antimicrobial activities than ligand. It has been suggested that metal chelation reduced polarity of metal ion[15] mainly because of the partial shairing of its positive charge with the donor group and possibility the d-electron delocalization occurring with in the whole chelate ring system formed during coordination. This process of chelation thus increase the lipophilic nature of the central metal atom which in turn favours its permeation through the lipoid layer of the membrane.[16]

Table-5: Fungicidal Screening Data Of Dda,It's Derivatives And Metal Chelates Of DDAO Against Aspergilus Niger At Varying Concentrations

Test Solution	0.05%conc.		0.10%conc		0.15 % conc.		0.20% conc	
	Weight	% inhi bition	Weight	% inhi bition	Weight	% inhi bition	Weight	% inhi bition
Control	1.046	-	1.041	-	1.036	-	1.030	-
Flucona Zole	1.0446	.132	1.0173	2.75	0.995	4.85	0.992	5.18
DDAO	1.0266	1.85	1.01	3.45	0.990	5.40	0.972	7.10
DDAO-Mn(II)	0.9848	5.80	0.943	9.85	0.897	14.30	0.864	18.10

Table-6: Antibacterial Activity Data Of DDA, It's Derivativves And Metal Chelates Of Ddao Against E Coli At Varying Concentration

Test Solution	**Inhibition Zone (mm)**			
	0.15Conc.	0.20 Conc.	0.30 Conc.	0.40 Conc.
Control	-	-	-	-
Ciproflaxacin				
HMAO			5.6	7.4
HMAO-Mn(II)		6.3	7.2	9.8

% of inhibition

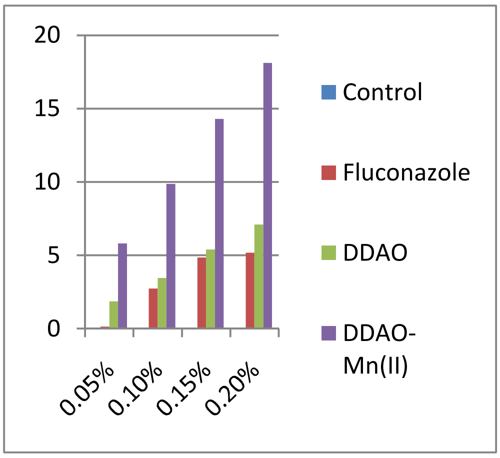

Fig 1: Effects of conc. of DDAO & Mn(II) DDAO complex on its antifungal potential.

% of inhibition

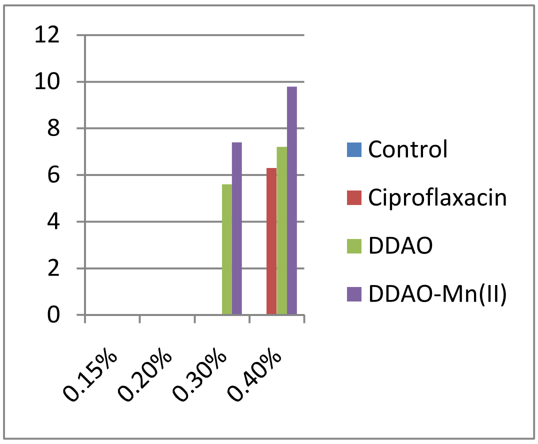

Fig 2: Effect of conc. Of DDAO & Mn(II) DDAO complex on its antibacterial potential.

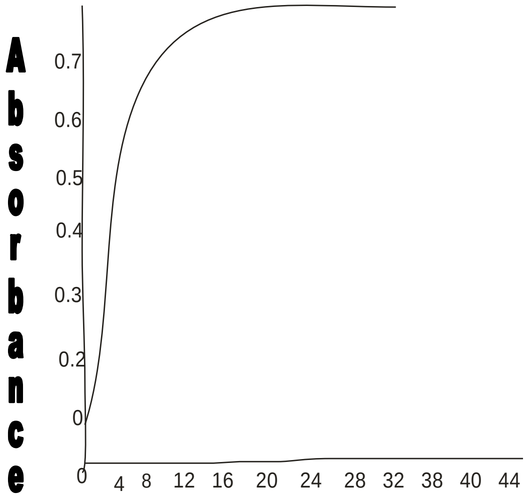

Fig.3: Wave length (nm) Mole of Reagent/Mole of Mn(II) composition of the Mn(II)-DDAO complex by Mole Ratio Method

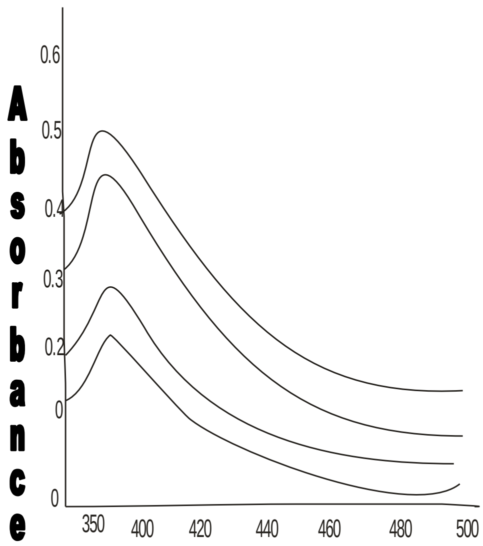

Fig.4: Wave length (nm) Vosburg and cooper's Method for Mn(II) –DDAO Complex

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