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RESEARCH ARTICLE

SPECTROPHOTOMETRIC MICRO DETERMINATION OF THE SCHIFF'S BASE DERIVED FROM SALICYLALDEHYDE AND SULPHANILAMIDE (SASN) & Mn(II) USING THE REACTION BETWEEN HYDROGEN PEROXIDE AND THE SCHIFF'S BASE IN THE PRESENCE OF DMF SOLVENT CATALYSED BY Mn(II)

[1,*] Ramachar, T., [2] Nuzhath Fathima, [3] Umamahesh, M. and [3] Naga Mouli, D.

[1] Department of Humanities & Basic Sciences, G. Pulla Reddy Engineering College (Autonomous), Kurnool,-518007 (A.P), India
[2] Department of Humanities & Sciences, Al-Habeeb College of Engineering & Technology , Hyderabad, (A.P), India
[3] Department of Chemistry, R.G.M. Engineering College (Autonomous), Nandyal, (A.P), India

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ABSTRACT

A simple sensitive precise and accurate method for the spectrophotometric micro determination of both Schiff's base which is derived from Salicylaldehyde and Sulphanilamide (SASN) and also the catalyst Mn(II) is proposed using the redox reaction between H_2O_2 and the Schiff's base in the presence of 10% (v/v) DMF solvent and alkaline buffer solution of pH 10 and at a concentration of 1 x 10^{-3} H_2O_2 catalyzed by Mn(II) at a wavelength of 445nm. The method proposed is suitable for the spectrophotometric determination of the Schiff's base (SASN) in the concentration range 2 x 10^{-4} M to 10 x 10^{-4} M(55µg/ml to 276 µg/ml) and the estimation of Mn(II) in the range 11 ng/ml to 88 ng/ml. The results agree well with initial kinetic rate method. The thermodynamic parameters are evaluated and the effect of various foreign ions on the redox reaction is also presented. The molar absorptivity and the Sandell sensitivity in respect of SASN estimation are 2 X 10^3 lit. $mole^{-1}$. cm^{-1} and 0.1380 µg/cm^2 and that in the case of Mn(II) determination are 2 X 10^5 lit. $mole^{-1}$. cm^{-1} and 0.0002747 µg/cm^2 respectively.

INTRODUCTION

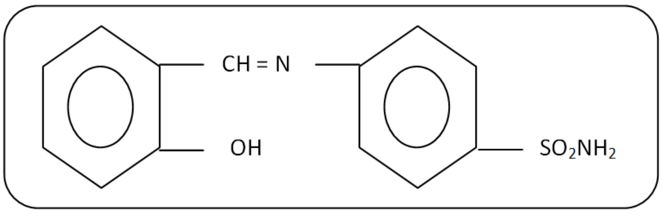
It is reported in Chemical Literature that the color developing redox reactions of organic substrates such as schiff's bases including thiosemicarbazones and phenyl hydrazones have been oxidized by hydrogen peroxide in presence of Mn(II) and methods were developed for the determination of trace amount of Mn(II) (Moreno, *et al.,* 1983), (Perez-Bendito *et al.,* 1977), (Raja Saro, 1983), Perez-Bendito *et al.,* 1984), (VazqueRuiz *et al.,* 1984), (Salinas,F. 1987). (Khan *et al.,* 1987), (Kumble Divya *et al.,* 2016) and (Siddiqi *et al.,* 1988) have reported that the schiff's bases derived from sulpha drugs are pharmaceutically important and analytically ideal for the metal complexation processes. (Perez – Bendito *et al.,* 1984) described a kinetic method for the determination of nano gram amounts of Mn(II) based on its catalytic effect on H_2O_2 oxidation of a Schiff's base. These observations prompted the authors to evolve investigations using Schiff's bases derived from sulphanilamide and sulphamethaxazole. The present study is restricted to the Schiff's base obtained from salicylaldehyde and sulphanilamide. It is noticed the Schiff's base is susceptible for oxidation by H_2O_2 in a buffer solution of pH 9 and above. Since the oxidation reactions of Organic substrates by H_2O_2 giving colored products are slow. Therefore they are generally catalyzed by the presence of transition metal ions such as Mn(II). Reports from chemical literature have shown that these catalyzed oxidation reactions were successfully employed for the determination of trace amounts of the transition metal ion, Mn(II). The results obtained in the present investigations are incorporated in this communication. The present study is in continuation of the extensive work (Ramachar,T *et al.,* 2016) the authors have carried out on the sulpha drugs (Ramachar, T *et al.,* 2012 and 2013) and their derivative Schiff's bases (Ramachar,T *et al.,* 2014 and 2016).

Corresponding author: Ramachar, T.,
Department of Humanities & Basic Sciences, G. Pulla Reddy Engineering College (Autonomous), Kurnool,-518007 (A.P), India.

Experimental

Preparation of Reagents and Solutions

Preparation of Schiff's base**:** The Schiff's base derived from Salicylaldehyde and Sulphanilamide (SASN) is prepared according to the procedure reported by (Khan et al 1987). Equimolar quantities of Salicylaldehyde, Sulphanilamide each dissolved in alcohol are mixed, refluxed for an hour and the contents are cooled, filtered and finally recrystalized from ethyl alcohol.



It is a light yellow crystalline solid not soluble in water but readily soluble in DMF. The solution in DMF is yellow in color and is stable for more than three months.

Preparation of Stock solutions

- **SASN Solution :** 0.276 gm of SASN is dissolved and diluted to the volume with DMF in a 100ml standard flask to obtain 0.01M stock solution.
- **Mn(II) solution :** About 3.0768 gm of Manganese sulphate mono hydrate is dissolved in distilled water and diluted to 250 ml standard flask. The solution is standardized with EDTA(Vogel,A.I 1951).
- **H_2O_2 Solution :** About 5.0 ml of 30% w/v ,100 volume H_2O_2 is diluted with distilled water in 250 ml standard flask. The solution is standardized with potassium permanganate[5] solution.
- **Buffer Solutions:** Buffer solutions are prepared by adopting the standard procedures (Vogel, A.I 1951) by mixing suitable quantities of the components of the buffer mixture and the pH of the solutions are checked with pH meter.

All the other necessary chemicals used in the present investigations are of analytical grade quality.

Description of instruments employed

- A Systronics Spectrophotometer Model-106 with wavelength range 300-900 nm is used for absorbance measurements. A toluene Hg thermostat is used for maintaining the temperature of the reaction mixture constant.
- pH measurements are made using an Elico LI-10 digital pH meter.

RESULTS AND DISCUSSION

Absorption Spectra

With a view to establish the optimum experimental conditions for the favorable oxidation reaction between SASN and H_2O_2 catalyzed by Mn(II) ions, the absorption spectrum of the test solution containing 4 ml of buffer solution of pH 10 + 3ml of water + 1ml H_2O_2 (0.17 M) + 1ml Mn(II) (1×10^{-5} M) + 1ml SASN (1×10^{-2} M) is recorded against the blank containing 4ml of buffer solution pH 10 + 5ml water + 1ml SASN (1×10^{-2} M). The spectrum is presented in Fig-1 which suggests that the absorbance maximum is observed at 445 nm. Hence, the optimum wavelength of 445 nm is fixed for further studies.

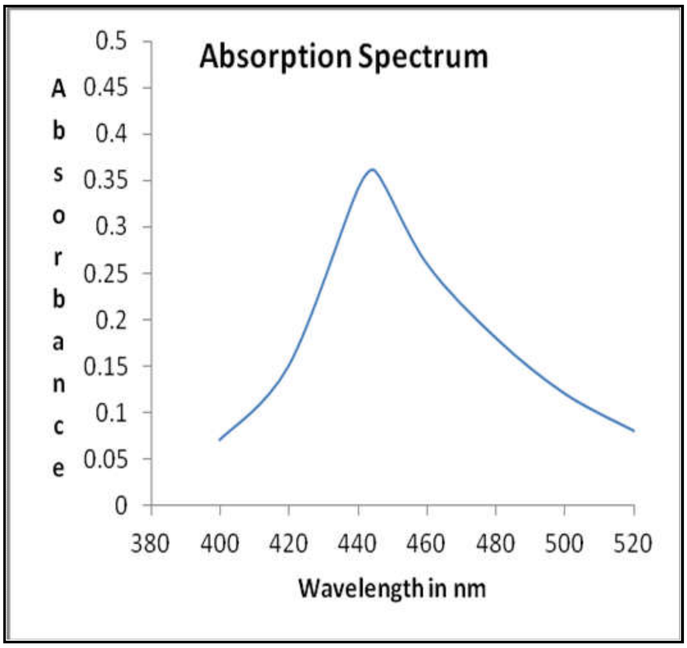


Fig 1. Absorption Spectrum

Effect of pH

In order to elucidate the effect of pH on the rate of oxidation and to establish the optimum pH at which the oxidation study of SASN can be conveniently carried out, the absorbance of the test solution in buffer solutions of pH 9-11 are recorded and the results obtained are presented in Table-1.

Table 1. Effect of pH

pH	Absorbance at	
	10 min	30 min
9.0	0.02	0.05
9.5	0.03	0.06
9.8	0.05	0.09
10.0	0.08	0.18
10.5	0.06	0.13
11.0	0.05	0.09

4 ml Buffer solution(9.0 to 11.0) + 3 ml of water + 1 ml H_2O_2 (0.17 M) + 1 ml Mn(II) (1×10^{-5} M) + 1 ml SASN (1×10^{-2} M) Total volume = 10 ml.
λ_{max} = 445 nm

The data in Table-1 suggests that highest absorbance is observed with a buffer solution of pH 10. Therefore, buffer solution of pH 10 is chosen as the optimum pH for further studies.

Effect of volume percentage of DMF

The substrate is not freely soluble in water but soluble in DMF. Hence DMF is used as the solvent in these studies. The effect of volume percentage of DMF in the range 10% to 40% on the absorbance of the test solution is studied at 445 nm and the results are present in Table-2.

Table 2. Effect of volume percentage of DMF

%DMF (v/v)	Absorbance at	
	10 Min	30 Min
10	0.08	0.18
20	0.05	0.10
30	0.04	0.08
40	0.03	0.04

3 ml of Buffer Solution (pH 10) + (4-x)l of water +xml(1 to 4)DMF + 1 ml H_2O_2 (0.17 M) + 1 ml Mn(II) (1 x 10^{-5} M) + 1 ml SASN (1 x 10^{-2} M) Total volume = 10 ml. λ_{max} = 445 nm

The data present in Table-3 indicates that the absorbance of the test solution is maximum with 10% of DMF solvent. Hence, for further studies 10%(v/v) DMF is fixed.

Effect of SASN concentration: Determination of SASN

The effect of SASN concentration on the absorbance of the test solution is studied in the concentration range 0.2 x 10^{-3} M to 1.4 x 10^{-3} M in order to establish its influence on the oxidation reaction. The absorbance values observed in each concentration of SASN are recorded at 445 nm and data is presented in Table-3.

Table 3. Effect of SASN concentration

S.No	[SASN] x 10^3M	Absorbance at	
		10 Min	30 Min
1	0.2	0.02	0.04
2	0.4	0.04	0.08
3	0.6	0.06	0.12
4	0.8	0.08	0.16
5	1.0	0.10	0.20
6	1.2	0.11	0.22
7	1.4	0.11	0.22

4 ml of Buffer Solution (pH 10)+2ml of water + (2-x) ml of DMF + 1 ml H_2O_2 (0.17 M) + 1 ml Mn(II) (1 x 10^{-5} M) + x ml SASN (1 x 10^{-2} M), Total volume = 10 ml. λ_{max} = 445 nm

It is seen from the above Table-3 that the absorbance value are almost remaining the same beyond 1.2 x 10^{-2} M. Therefore SASN concentration is fixed at 1.2 x 10^{-2} M for further studies. However a careful observation of the results in the table-3 indicate the proportionate increase in the absorbance values with increase in the concentration of SASN upto 1.0 x 10^{-3} M indicating the obedience of Beer-Lambart's law and the suitability of the method for the quantitative determination of SASN in the range 0.2 x 10^{-3} M to 1.0 x 10^{-3} M (55µg/ml to 276 µg/ml)

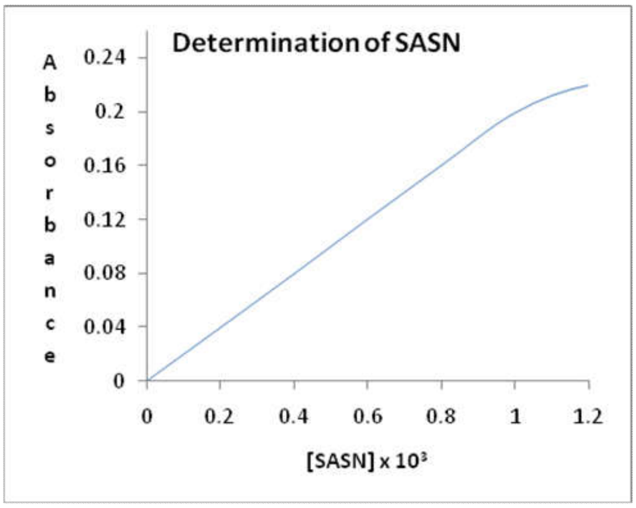


Fig. 2. Determination of SASN

Effect of H2O2 Concentration

The effect of concentration of H_2O_2 on the absorbance of the test solution is studied by carrying out the reaction in the presence of different concentrations of H_2O_2 in the range 0.17 x 10^{-2} M to 2.55 x 10^{-2} M. The data obtained are recorded in Table-4.

Table 4. Effect of H_2O_2 solution concentration

S.No	[H_2O_2] x 10^2 M	Absorbance at	
		10 Min	30 Min
1	0.17	0.04	0.15
2	0.43	0.05	0.18
3	0.85	0.06	0.18
4	1.28	0.07	0.18
5	1.70	0.08	0.18
6	2.12	0.07	0.18
7	2.55	0.07	0.18

4 ml of Buffer Solution (pH 10), (3-x) ml of water + x ml H_2O_2 (0.17 M) + 1 ml Mn(II) (1 x 10^{-5} M) + 1 ml SASN (1 x 10^{-2} M) Total volume = 10ml. λ_{max} = 445 nm

The results in the above table clearly show the absorbance is almost constant in the concentration range of H_2O_2 0.17 x 10^{-2} M to 2.55 x 10^{-2} M. Hence, an optimum concentration in the range 0.04 to 1.144 x 10^3 is fixed for further studies.

Effect of Mn(II) concentration: Determination of Mn(II)

To examine the effect of Mn(II) ions concentration on the rate of the reaction, the absorbance of the test solution is recorded at different concentrations of Mn(II) ion in the range 2 x 10^{-7} M to 20 x 10^{-7} M. The results obtained are presented in Table-5.

Table 5. Effect of Mn(II) solution concentration

S.No	Mn(II) x 10^7 M	Absorbance at	
		10 Min	30 Min
1	2.0	0.02	0.04
2	4.0	0.03	0.08
3	6.0	0.05	0.12
4	8.0	0.06	0.16
5	10.0	0.08	0.2
6	12.0	0.09	0.24
7	14.0	0.10	0.28
8	16.0	0.11	0.32
9	18.0	0.12	0.34
10	20.0	0.16	0.35

3ml of Buffer Solution (pH 10) + (4-x) ml of water + 1 ml of DMF + 1 ml H_2O_2 (0.17 M) + x ml Mn(II) (5 x 10^{-6} M) + 1 ml SASN (1.2 x 10^{-2} M), Total volume = 10ml. λ_{max} = 445 nm

The results shown in the above table-5 indicate that the absorbance increases with the amount of Mn(II) proportionately. A graph is drawn between the concentration (amount) of Mn(II) and the absorbance. A linear curve is obtained as shown in Fig-3 suggesting the suitability of the method for the quantitative determination of Mn(II) in trace amounts in the range 11 ng/ml to 88 ng/ml.

Kinetic Initial Rate Method

It is known that better results are obtained in the initial rate method than in the fixed time method. Therefore the absorbance of the test solution containing known aliquots of Mn(II) ions is recorded at 445 nm at different time intervals and the initial rates are calculated. The results are presented in Table-6.

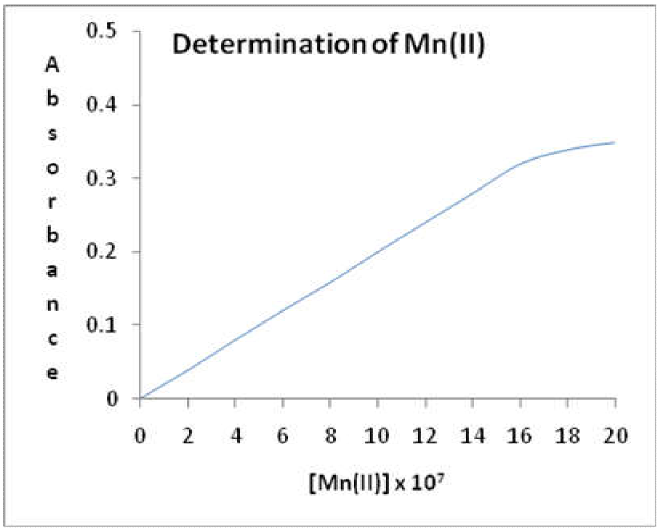


Fig 3. Determination of Mn(II)

Table 6. Effect of Mn(II) concentration on the initial rate at 445 nm

Amount of Mn(II) (ng/ml)	Initial rate x 10^4 (sec^{-1})
11.0	1.3
22.0	2.6
33.0	3.9
44.0	5.2
55.0	6.5
66.0	7.8
88.0	10.4
110.0	11.9
132.0	13.3

A graph drawn between the amount of Mn(II) and the initial rate is linear in the range 11 ng/ml to 88 ng/ml of Mn(II) as shown in Fig 4 . This shows that the initial rate method can be employed for the successful determination of Mn(II) in the range 11 ng/ml to 88 ng/ml.

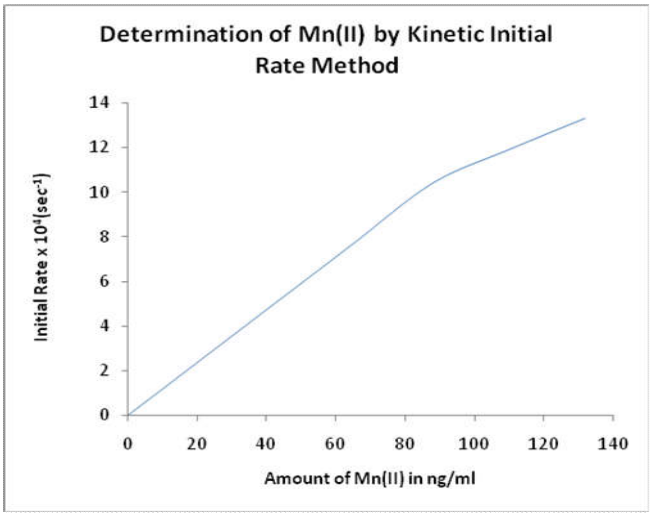


Fig 4. Determination of Mn(II) by Kinetic Initial Rate Method

Effect of Foreign ions

The absorbance of the test solution containing known aliquote (0.05 µg/ml or 50 µg/ml) of Mn(II) ion is reacted in the presence of different amounts of added ions to find out the tolerance limit. The amount of the added ion causing ±2 % deviation in the absorbance is taken as the tolerance limit. The results are shown in Table-7.

Table 7. Effect of Foreign Ions

Foreign ions	Tolerance limit (µg/ml)
Cd^{+2}	47.0
Co^{+3}	39.0
Al^{+3}	35.0
Mg^{+2}	31.0
Ni^{+2}	19.0
Pb^{+2}	11.0
Ti^{+2}	3.1
Cu^{+2}	2.4
Vn^{+2}	0.18
PO_4^{-3}	115.0
EDTA	1.5

Thermodynamic Parameters

The initial rate of the reaction is calculated from the absorbance – time data for the reaction at the optimum conditions by the plane mirror method (Latshaw, 1925). The specific reaction rate K for the reaction is obtained by dividing the initial rate by the concentrate of the reactant taken in excess. The Thermodynamic Parameters E*, Δ H* ΔS* and ΔG* for the reaction are then evaluated using the following equations from the specific rate K measured at three different temperatures.

$$\text{Log } K = - E^*/2.303RT + \text{Constant}$$

$$\Delta H^* = E^* - RT$$

$$\Delta S^* = 19.146 (\log K - 10.753 - \log T) + E^*/T$$

$$\Delta G^* = 19.147T (\log T + 10.319 - \log K)$$

Table 8. Thermodynamic parameters

Temperature ^{0}K	Initial rate x 10^4 Sec^{-1}	ΔE^* (Kcal/ mole)	ΔH^* (Kcal/ mole)	ΔS^* (Kcal/ mole)	ΔG^* (Kcal/ mole)
296	5.3	10.66	10.06	-31.10	19.41
300	7.0				
305	9.0				

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