

## Direct and First Derivative Spectrophotometric Determination of Manganese (II) in Tap Water, Milk, Alloy Steels and Plant Samples

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### Abstract

A simple, rapid, sensitive and selective method is developed for the spectrophotometric determination of manganese (II). The reagent, 2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) gives greenish brown colored water soluble complex in aqueous DMF medium with manganese (II). The greenish brown colored Mn (II) – HMBATSC complex shows maximum absorbance at 435 nm in the pH range 9.0 – 10.0. However, at this wavelength, the reagent shows considerable absorbance. At 445 nm, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence, the analytical studies are carried out at 445 nm at pH 9.5. The molar absorptivity and Sandell's sensitivity are  $1.96 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.028 \mu\text{g cm}^{-2}$  respectively. Beer's law is obeyed by Mn (II) in the range  $0.1373\text{--}2.746 \mu\text{g mL}^{-1}$ . The composition (M:L) of the complex has 1:1 and stability constant of the complex is calculated as  $1.22 \times 10^7$ . The effect of various diverse ions also incorporated. A first order derivative spectrophotometry has also been proposed for the determination of Mn (II). The present method is applied for the determination of manganese in tap water, milk, alloy steels and plant samples.

### Keywords:

Direct and first derivative Spectrophotometry; Determination of manganese (II); HMBATSC

### 1. Introduction

Manganese is a microelement actively absorbed by plants and has an effect on the fertility of soils [1]. It is a component of enzymes, such as super oxide dismutase, glutamine synthetase and arginase [2]. This element is widely utilized in metallurgic and chemical industry, which emitted it into the atmosphere, hydrosphere and biosphere. Prolonged exposure to low levels of manganese may enhance the onset of Parkinsonian disturbances [3]. Manganese exists naturally in rivers, lakes, and groundwater. The pH–pE diagram of Mn–CO<sub>2</sub>–H<sub>2</sub>O system [4] shows that in acidic-neutral waters at normal pE (i.e.  $-20 \leq \text{pE} \leq +10$ ), Mn (II) is the predominant manganese species, its coastal and surface seawater concentrations may show considerable variations and may reach several ppb levels due to its presence in the enzyme co-factors involved in photosynthesis, and also in nitrate reduction [5].

There are several methods available for manganese (II) determination including atomic absorption spectroscopy (AAS), flow-injection analysis (FIA), spectrofluorimetry [6] and spectrophotometry. In routine analysis, spectrophotometric methods are versatile and economical especially for developing countries. The oxidants, such as potassium periodate and ammonium persulfate are commonly used for determination of manganese (II) by spectrophotometry [7–11]. However, the methods mentioned above are time consuming or less sensitive. Catalytic kinetic methods have received considerable attention because of the

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significant advantages in the determination of many analytes at trace levels. At present, catalytic methods [12–16] for the determination of manganese (II) in water systems have been frequently reported. Catalytic–Spectrophotometric methods for Mn (II) using periodate, dissolved oxygen or hydrogen peroxide as the oxidizing agent [17] are not directly applicable to manganese determination in seawater because of possible interferences caused by organic substances and variations in salinity [18].

Derivative spectrophotometry has recently been shown to be more versatile than classical spectrophotometry for solving analytical problems. It leads, not only to an increase in selectivity, but also in many cases, to an increase in sensitivity. The scale of this increase depends on the shape of the normal absorption spectra of the analyte and the interfering substances, as well as on instrumental parameters and the measurement technique (e.g. peak-to-trough or zero-crossing), chosen by the analyst in a given analytical procedure [19, 20].

In the present paper, a simple, rapid, selective and sensitive method is reporting for direct and first order derivative spectrophotometric determination of trace amounts of manganese (II) by complexing with 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC).

## **2. Experimental**

### **2.1. Apparatus**

The absorbance and pH measurements were made on a Shimadzu UV–visible spectrophotometer (Model UV–160A) fitted with 1 cm Quartz cells and Philips digital pH meter (model L1 613) respectively. The pH meter has temperature compensate arrangement and has reproducibility of measurement within  $\pm 0.01$  pH.

### **2.2. Reagents and Chemicals**

2-hydroxy-3-methoxy benzaldehyde and thiosemicarbazide were taken from SD Fine Chemicals, India and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was taken from E-Merck, India. All chemicals and solvents used were of analytical reagent grade, and doubly distilled water was used for preparation of all solutions and experiments. The working solutions were prepared daily by diluting the stock solution to an appropriate volume.

Solution of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) ( $1 \times 10^{-2}$  M) was prepared by dissolving 0.23 g of HMBATSC in dimethyl formamide (DMF) and diluting to 100 mL with DMF. Lower concentrations were prepared by diluting the appropriate volume of 0.01 M reagent solution with DMF.

Stock solution of Mn (II) ( $1 \times 10^{-2}$  M) was prepared by dissolving 0.20 g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (Mol.wt. 197.91) in doubly distilled water and the solution was standardized complexometrically [21].

### **2.3. Buffer solutions**

The buffer solutions were prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5 – 7.0) and 2.0 M ammonia + 2.0 M ammonium chloride (pH 8.0 – 12.0). The pH of these solutions was checked with the above mentioned pH meter.

## 2.4. Determination of manganese (II)

### 2.4.1. Direct spectrophotometry

In each of a set of different 10 mL standard flasks, 5 mL buffer solution (pH 2.5), varying volumes of  $5 \times 10^{-3}$  M Mn (II) solution and 1 mL of HMBATSC ( $1 \times 10^{-2}$  M) were taken and the volume was made up to the mark with doubly distilled water. The absorbance was measured at 445 nm against the reagent blank. The calibration curve was constructed by plotting the absorbance against the amount of manganese (II). The calibration graph follows the straight line equation  $Y = a c + b$ ; where  $c$  was the concentration of the solution,  $Y$  was measured absorbance or peak height and  $a$  and  $b$  were constants.

### 2.4.2. First order derivative method

For the above solutions, first order derivative spectra were recorded with a scan speed of fast (nearly  $2400 \text{ nm min}^{-1}$ ); slit width of 1 nm with one degree of freedom, in the wavelength range 420 – 585 nm. The derivative peak height was measured by the peak–zero method at 450 nm. The peak height was plotted against the amount of manganese (II) to obtain the calibration.

### 2.4.3. Determination of manganese in water samples

The water samples were collected from different places of Anantapur district, Andhra Pradesh, India. The water samples (1 L) were collected in a clean 2 L beaker and slowly evaporated to about 25 mL. Then, 5 mL of  $\text{H}_2\text{O}_2$  was added and evaporated up to dryness [22]. It was then dissolved in 2 mL of water and filtered to remove insoluble substance. The filtrate was collected in 100 mL volumetric flask quantitatively and diluted to the mark with distilled water.

### 2.4.4. Determination of manganese in milk samples

100 mL of milk samples were added drop wise to a heated crucible to evaporate it without frothing. After the moisture has been removed, the contents were heated strongly to 450–500 °C. The contents were cooled; 1 mL of 14 M nitric acid was added, evaporated to dryness and ignited again at 450–500 °C for about one hour. The white ash was dissolved in a minimum volume of 8 M nitric acid and made up to volume in a 10 mL standard flask.

### 2.4.5. Determination of manganese in alloy steels

A 0.1 g of a steel sample containing 0.25% of manganese was weighed accurately and placed in a 50 mL beaker. To it, 10 mL of 20% (v/v) sulfuric acid was added and carefully covered with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5 mL of 14 M  $\text{HNO}_3$  until all carbides were decomposed. Then, 2 mL solution of  $\text{H}_2\text{SO}_4$  (1:1) was added and the mixture was evaporated carefully until the dense white fumes dried off the oxides of nitrogen and then cooled at room temperature. After appropriate dilution with water, the contents of the beaker were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with  $\text{NH}_4\text{OH}$  solution, the resulting solution was filtered through a Whatman 41 filter paper into a calibrated flask of known volume. The residue (silica) was washed with a small volume of hot 1%  $\text{H}_2\text{SO}_4$  followed by water and the volume was made up to the mark with water.

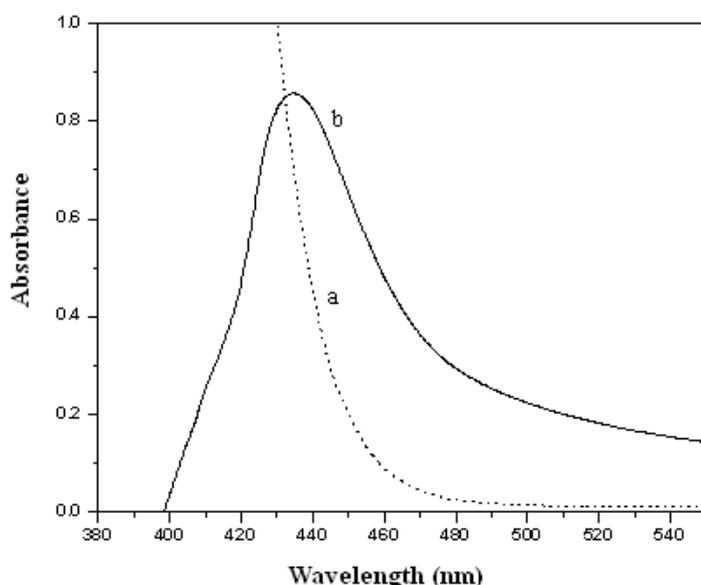
### 2.4.6. Determination of manganese in plant samples

The contents of leaves of *Oryza sativa* L., *Pteridium guajava* L. and *Archras zapota* L. (1 g) were extracted into ethyl alcohol after drying. The extract was diluted to 100 mL with distilled water, from which suitable aliquots were taken for the determination of Mn (II). For the determination of manganese in alloy steels and plant leaves, a sample following procedure was employed. 5 mL of buffer solution of pH 9.5 and 1 mL of HMBATSC ( $1 \times 10^{-2}$  M) solution were taken in each of a series of 10 mL volumetric flasks. Different known aliquots of each sample solution were added to these flasks and made up to the mark with distilled water. The first derivative spectra were recorded and the amplitudes at 450 nm were measured. The amount of Mn (II) was then computed from a predetermined calibration plot.

## 3. Results and Discussion

### 3.1. Absorption spectra of HMBATSC and manganese (II) complex in solution

The absorption spectra of the HMBATSC and the complex were recorded in the wavelength range 380–550 nm at pH 9.5 against the buffer blank and reagent blank respectively. Typical spectra were presented in Fig. 1. The spectra show that manganese (II) complex has an absorption maximum at 435 nm. However, at this wavelength, the reagent shows considerable absorbance. At 445 nm, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at 445 nm.



**Fig. 1.** Absorption spectra of: a. HMBATSC Vs Buffer blank; b. [Mn (II) - HMBATSC] Vs reagent blank; c. [Mn (II)] =  $5 \times 10^{-5}$  M; [HMBATSC] =  $1 \times 10^{-3}$  M; pH = 9.5

To arrive at the optimum pH required for full color development, the effect of pH on the color intensity was studied. The plot between pH and absorbance shows that maximum and constant color was obtained in the pH range 9.0–10.0. Hence the pH 9.5 was chosen for further studies. The absorbance of the complex solution was measured at various concentrations of the reagent solution keeping Mn (II) concentration constant at 445 nm and at pH 9.5. The absorbance values indicate that a 20 fold molar excess of the reagent was necessary for maximum color development which was maintained throughout the studies. The absorbance of the solution was measured at different time intervals to ascertain the time stability of the color of the complex. It was noticed that the greenish brown color development was instantaneous and remained constant for more than 48 hours. The

stoichiometry of the complex was determined by Job's and molar ratio methods. The Job's curve shown in Fig. 2 gives a composition of Mn (II) + HMBATSC (1:1). The stability constant of the complex was calculated as  $1.22 \times 10^7$ .

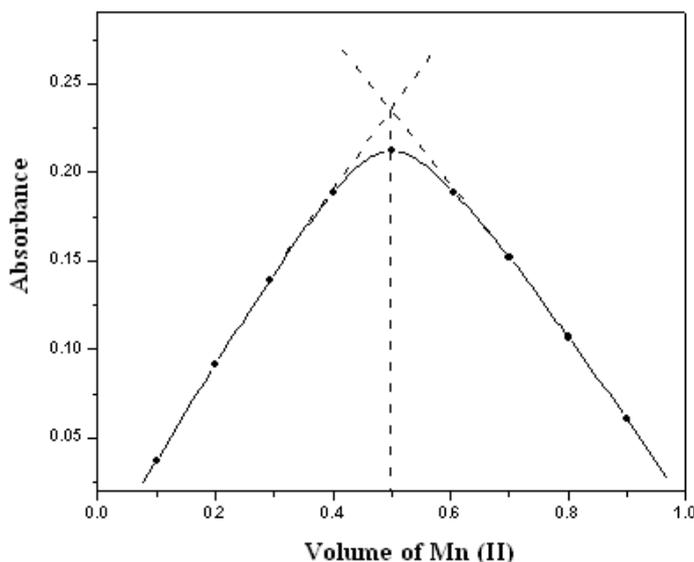


Fig. 2. Job's curve [Mn (II)] = [HMBATSC] =  $1 \times 10^{-3}$  M, Wavelength = 445 nm; pH = 9.5

### 3.2. Adherence of the system to Beer's law

#### 3.2.1. Zero order method

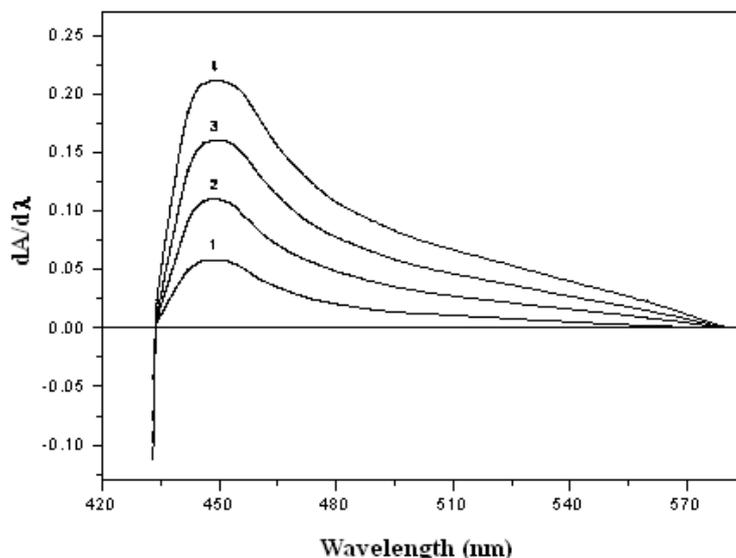
To explore the possibility of employing the color reaction for the determination of manganese (II) at micro levels, the absorbance of the solutions containing different amounts of the metal ion was measured. A linear plot was obtained between absorbance and the amount of molybdenum, and it obeys the equation  $A = 0.3321C - 0.0028$ . Beer's law was obeyed by Mn (II) in the range  $0.1373 - 2.746 \mu\text{g mL}^{-1}$ . The molar absorptivity and Sandell's sensitivity were  $1.96 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.028 \mu\text{g cm}^{-2}$  respectively.

#### 3.2.2. First order derivative method

The first derivative spectra (Fig. 3) show a peak at 450 nm. The derivative amplitudes at 450 nm were proportional to different amounts of Mn (II) and were measured. A plot was made between the amount of Mn (II) and the derivative amplitude. The plot was linear and obeys the equation  $A = 0.2076C + 0.0165$ . Beer's law was obeyed in the range of  $0.137 - 8.238 \mu\text{g mL}^{-1}$ . The standard deviation of the method for ten determinations of  $0.274 \mu\text{g mL}^{-1}$  of Mn (II) was  $\pm 0.0012$ .

#### 3.2.3. Effect of diverse ions

In zero order method, the effect of diverse ions normally associated with manganese (II) ion on its determination under optimum conditions developed was studied and the results were presented in Table 1. It can be seen from Table 1 that all the anions studied do not interfere even when present in more than 100 fold excess. The tolerance limits of the cations were also reasonably high. Further, Co (II) and Ni (II) interfere when present in 4-fold excess; Fe (II) and V (V) interfere when present in 8-fold excess. However, Co (II) and Fe (II) were tolerable up to 40-fold excess in presence of 1760  $\mu\text{g}$  of ascorbic acid. In presence of 1400  $\mu\text{g}$  of thiourea, Ni (II) and V (V) do not interfere even when present up to 40-fold excess.



**Fig. 3.** First derivative spectra of Mn (II) – HMBATSC Vs reagent blank, Mn (II) ( $\mu\text{g ml}^{-1}$ ) = (1) 0.2746; (2) 0.5492; (3) 0.8238; (4) 1.0984

**Table 1.** Tolerance limits of diverse ions for Mn (II) ( $2.75 \mu\text{g mL}^{-1}$ )

Diverse ion	Tolerance limit ( $\mu\text{g ml}^{-1}$ )	Diverse ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
Ascorbic acid	1760	Cd (II)	560
Thiourea	1400	Th (IV)	460
Thiosulphate	1000	Pb (II)	420
Sulphate	960	Ti (IV)	400
Oxalate	880	K (I)	390
Iodide	635	W (VI)	370
Fluoride	625	Na (I)	340
Tartrate	560	Ce (IV)	280
Citrate	490	U (VI)	240
EDTA	420	Co (II)	22,168 <sup>a</sup>
Bromide	400	Li (I)	150
Nitrate	380	Zr (IV)	140
Acetate	360	Ni (II)	20,126 <sup>b</sup>
Chloride	350	Pb (II)	120
Formate	300	Fe (II)	12,120 <sup>a</sup>
Phosphate	200	V (V)	12,110 <sup>b</sup>
Phosphate	200	Zn (II)	84
		Cu (II)	64
		Pd (II)	60
		Pt(IV)	55
		Au (III)	54
		Ru (III)	50
		Mo (VI)	46

Masked in the presence of a) 1760  $\mu\text{g}$  of Ascorbic acid; b) 1400  $\mu\text{g}$  of Thiourea

In the first order derivative method, the effect of various cations and anions on the derivative amplitude was studied and it was noticed that all the ions that did not interfere in the zero order determinations of Mn (II) (cf. Table.1) also did not interfere in the first derivative spectrophotometric determinations. Co (II) and Ni (II) in 4-fold excess and Fe (II) and V (V) in 8-fold excess interfered in zero order method. But they did not interfere even when present in more than 30-fold excess in first order derivative method.

#### 4. Applications

The proposed zero order method was applied for the determination of manganese (II) in tap water and milk samples, and the results were presented in Tables 2 and 3, respectively. First derivative method was employed for the determination of manganese present in some steel alloys and plant samples, and the results were shown in Tables 4 and 5, respectively. The results presented in Table 2 represent that good recoveries were obtained in all samples. The results presented in Tables 3 and 5 were shown to be in good agreement with those obtained by AAS method.

**Table 2.** Determination of Mn (II) in tap water

Sample	Concentration, $\mu\text{g mL}^{-1}$		Recovery (%)	Standard deviation <sup>b</sup>
	Added	Found <sup>a</sup>		
Water 1	-	2.2	-	3.2
	2.0	3.8	90	2.5
	4.0	6.0	97	2.8
	6.0	8.2	100	2.6
Water 2	-	1.9	-	3.0
	2.0	3.8	97	2.8
	4.0	5.9	100	2.4
	6.0	7.5	104	1.9
Water 3	-	1.5	-	3.4
	2.0	3.6	102	2.6
	4.0	6.4	98	2.9
	6.0	7.2	96	2.2

<sup>a</sup> Average of five determinations.

<sup>b</sup> Standard deviation obtained is based on five determinations on separate occasions within 95% confidence level.

**Table 3.** Determination of Mn (II) in Milk

Sample	Concentration, $\mu\text{g mL}^{-1}$		Standard deviation <sup>b</sup>
	AAS method	Present method <sup>a</sup>	
Milk 1	0.278	0.282	1.8
Milk 2	0.222	0.220	2.6
Milk 3	0.166	0.170	2.3
Milk 4	0.306	0.304	1.5

<sup>a</sup> Average of five determinations.

<sup>b</sup> Standard deviation obtained is based on five determinations on separate occasions within 95% confidence level.

**Table 4.** Analysis of steel and alloy samples

Sample	Composition (%)	Concentration of Mn (II), %		Relative error (%)
		Taken	Found <sup>a</sup>	
BAS No.180/2	Cu(68.12); Fe(0.68); Co(0.04); Ni(30.35); Mn(0.75); S(0.006)	0.75	0.74	-1.33
BCS No.406	Mn(0.53); Ni(1.69); Mo(1.03); V(0.02); Cr(2.12); Cu(0.32)	0.53	0.52	-1.89
BAS No.179/2	Mn(0.86); Cu(58.50); Ni(0.56); Sn(0.70); Fe(1.02); Si(0.044); Zn(35.80); Pb(0.35); Al(2.22)	0.86	0.85	-1.16
BCS No.219/4	Mn(0.81); Cr(0.66); Mo(0.58); Ni(2.55); Cu(0.088); Sn(0.011); Fe(95.0)	0.81	0.82	+1.23

<sup>a</sup> Average of five determinations.

**Table 5.** Analysis of plant samples

Sample	Concentration of Mn (II), $\mu\text{g mL}^{-1}$		Relative error (%)	Standard deviation <sup>b</sup>
	AAS method	Present method <sup>a</sup>		
Oryza sativa L.	0.60	0.62	3.33	3.6
	1.28	1.29	0.78	1.5
	1.86	1.84	-1.07	2.4
Pridium guajave L.	0.36	0.34	-5.55	3.8
	0.90	0.92	2.22	2.9
	1.08	1.09	0.92	1.8
Achras zapota L.	0.36	0.37	2.77	2.6
	0.87	0.86	-1.14	2.1
	1.90	1.92	1.05	1.8

<sup>a</sup> Average of five determinations.

<sup>b</sup> Standard deviation obtained is based on five determinations on separate occasions within 95% confidence level.

## 5. Conclusions

The proposed methods for the spectrophotometric determination of manganese (II) in tap water, milk samples, steel alloys and plant samples were rapid, simple, selective and sensitive. In this method, avoid organic solvents for the extraction of color derivatives; it indicates the present methods were non-toxic and safer than those methods using other organic solvents. Statistical analysis of the results indicates that the methods yield good values. The results obtained in zero order and first order derivative spectroscopic methods for Mn (II) – HMBATSC complex were compared and presented in Table 6. From the results in Table 6, it was clear that the first order derivative method was more sensitive than zero order method.

**Table 6.** Comparison of the results for Mn(II)

Parameter	Zero order	First derivative
Analytical wave length (nm)	445	449
Beer's law range ( $\mu\text{g ml}^{-1}$ )	0.1373-2.746	0.1373-8.238
Angular coefficient (m)	0.3321	0.2076
Y-intercept (b)	0.0028	0.0165
Correlation coefficient (r)	0.9992	0.9996
Standard deviation (s)	$\pm 0.0112$	$\pm 0.0012$
Detection limit ( $\mu\text{gml}^{-1}$ )	0.1112	0.0191
Determination limit ( $\mu\text{gml}^{-1}$ )	0.3372	0.0578

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