Spectrophotometric Determination of Manganese (II) With 2-Hydroxy-1-Naphthaldehyde Isonicotinoylhydrazone

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A simple, rapid, sensitive and selective method is developed for the spectrophotometric determination of manganese (II). The reagent, 2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHNAINH) reacts with manganese (II) in aqueous DMF solutions in the pH range 5.0-10.0 and at room temperature to form a brown coloured 1:2 (metal:ligand) complex with absorption maximum at 495nm with a molar absorptivity 1.02×10^4 Lit mo1^{-1}cm^{-1} and Sandell's sensitivity 0.52×10^{-2}µg cm^{-2}. Beer's law is obeyed in the range of 0.27-4.12µg mL^{-1} of Mn (II). A method for the determination of manganese (II) by first order derivative spectrophotometry has also been proposed. Interference of various diverse ions has been studied. The present method is applied for the determination of manganese in tap water, cement samples, milk, steel alloys and plant samples.

Keywords: UV-visible spectrophotometer, Buffer solutions, 2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone, derivative spectrophotometry, Manganese (II)

INTRODUCTION

Manganese is a hard, brittle metal and is essential for the control of sulphur content in the manufacturing of steel. This application accounts for the major position of manganese consumption in all forms in the country. Manganese is considered as one of the five essential trace elements along with boron, zinc, copper and molybdenum for majority of higher plants. Manganese is found in all plants[1], animal tissues, foods[2] and drinking water[3]. It being an essential constituent of metallo-enzymes is an important nutrient for plant growth. It plays an important role in the fixation of carbon dioxide as the activator of the nitrite reductase and is active catalyst in the formation of primary photochemical oxidation product in photosynthesis. There are several methods available for Mn (II) determination including atomic absorption spectroscopy (AAS), flow injection analysis (FIA) spectrofluorimetry[5] and spectrophotometry.

In routine analysis, spectrophotometric methods are versatile and economical especially for developing countries. Several spectrophotometric reagents have been employed as chromogenic agents for the determination of manganese. It observed that the present method is more sensitive than the methods proposed by Czech et al.[6], Reddy, P.B.S et al.[7] and Salinas et al.[8, 9, 10], Some of the reported methods by Kesava Rao et al.[11], Jiang.Z.T et al.[12], and Praveen Kumar et al.[13] are more sensitive than the present method. However the present method is more selective than the methods reported by Reddy, P.B.S et al.,[7] and Jiang.Z.T et al.[12]

The reagent 2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHNAINH) is used for the spectrophotometric determination of Iron (II) and Iron (III)[14], Molybdenum (VI)[15,] Antimony (III)[16] and Thorium (IV),Uranium (VI)[17]

In the present note, a simple, rapid, selective and sensitive spectrophotometric method is reported for direct and first order derivative spectrophotometric determination of trace amounts of manganese (II) by complexing with 2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHNAINH).

MATERIALS AND METHODS

Instrument:

The absorbance and pH measurements were made on a Perkin-Elmer UV-visible (Lambda 25) double beam spectrophotometer fitted with 1cm quartz cells and Elico digital pH meter (model LI-120) respectively. The pH meter has a temperature compensate arrangement. The reproducibility of measurements is within ± 0.01 pH.

Reagents and chemicals:

The reagent, 2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHNAINH) was synthesized by condensing equimolar solutions of 2-Hydroxy-1-naphthaldehyde and isonicotinoylhydrazide in alkaline absolute ethanol as described earlier [18]

1×10^{-2} M solution of OHNAINH was prepared by dissolving 0.2910g of the crystallised compound in dimethylformamide. Lower concentrations were prepared by diluting the stock solution appropriately with the solvent.

Stock solution of manganese (1×10^{-1}M) was prepared by dissolving 1.6902g of $MnSO_4$ (AR, Merck) in distilled water. The solution was made up to the mark in 100 ml volumetric flask and standardized complexometrically.[19] Lower concentrations were prepared by diluting the stock solution appropriately with distilled water.

The buffer solutions were prepared by mixing appropriate volumes of 0.2M sodium acetate and 0.2M acetic acid (pH 3.0 to 7.0) and 2.0 M ammonium- hydroxide and 2.0 M ammonium chloride (pH 8.0 to 10.0). The pH of these buffer solutions was finally adjusted to the required value by using pH meter.

RESULTS AND DISCUSSION

Determination of Manganese (II):

In different sets of 10 ml volumetric flasks, each containing 4 ml of buffer solution (pH 8.0) and 0.25 ml of OHNAINH (1×10^{-2}M), varying volumes of 1×10^{-4} M or 1×10^{-3} M manganese(II) solution were added and made up to the mark with doubly distilled water. The absorbance was measured at

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495 nm against the reagent blank, and the calibration plot was prepared.

First order derivative spectra of above solutions containing variable amounts of Mn(II) and a fixed concentration of OHNAINH, buffer solution (pH 8.0) were recorded with a scan speed of fast (nearly 2400 nm min^{-1}), slit width of 1 nm with 49 degrees of freedom in the wavelength region 350-650nm. The derivative peak height was measured by the peak-zero method at 490nm and 425nm for first derivative curves. The peak height was plotted against the amount of manganese (II) to obtain the calibration plot.

The calibration graph follows the straightline equation, y= mc + b; where c is the concentration of the solution, y is measured absorbance or peak height and m and b are constants. By substituting the corresponding experimental data in the above equation, the calibration equations were calculated as $A_{495} = 0.1882c - 0.0249$ for zero order data and $A_{490} = 0.0054c - 0.0002$ and $A_{425} = 0.0027c - 0.0002$ for first derivative data, which give the best straight lines.

Manganese (II) forms brown coloured complex with 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHNAINH). The absorption spectra of OHNAINH and its Manganese (II) complex [Mn(II)-OHNAINH] were recorded in the wavelength range 350-600 nm at pH 8.0 against the buffer solution and reagent blank respectively. The spectra show that Manganese (II) complex possesses maximum absorbance at 495 nm where the reagent is showing relatively very low absorbance. Therefore, further analytical studies were carried out at 495 nm using the reagent blank.

The effect of pH on the colour formation was studied to arrive at the optimum pH. The plot obtained between absorbance data versus pH reveals that the reaction mixture shows constant colour intensity in the pH range 6.5 to 7.5. But the maximum absorbance was noticed at pH 8.0. Hence, the studies were carried out at pH 8.0.

The optimum concentration of the reagent required for the maximum colour formation was studied by measuring the absorbance at 495 nm. The results indicate that a10-fold excess of the reagent is necessary to develop maximum colouration with a given amount of manganese.

The brown colour formation between Mn(II) and OHNAINH at pH 8.0 was instantaneous and the colour was stable for more than 72 hours. The order of the addition of reactants had no any significant effect on the colour intensity.

The composition of the complex was determined using Job's method and confirmed by molar ratio and slope ratio methods. The results indicate a 1:2 stoichiometry between the metal ion and the reagent under the experimental conditions. The stability constant of the complex calculated from Job's method was found to be 1.38×10^8.

The composition of the complex and the geometry exhibited by manganese (II) indicate that the resultant Mn(II)-OHNAINH complex formed under the given conditions is as shown in Fig- 1.

Fig-1: [Mn(II)-OHNAINH] Complex:
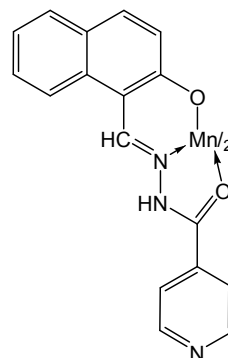
A linear plot was obtained when the absorbance was plotted against the amount of manganese indicating the validity of Beer's law in the range 0.27 - 4.12µg mL^{-1} of Mn(II). The molar absorptivity of the brown colored solution under the given experimental conditions was calculated as 1.02×10^4 Lit mol^{-1}cm^{-1} at 495 nm. The Sandell's sensitivity of the present method was found to be 0.53×10^{-2} µg cm^{-2}. The regression analysis of the linear curve gave the angular coefficient (m) and correlation coefficient (r) as 0.1882 and 0.9996 respectively.

Effect of foreign ions:
The effect of various anions and cations on the determination of Mn (II) under optimal conditions was studied and presented in Table-I. From the results in Table-I, we can notice that many anions and cations do not interfere in the present method even when presence in more than 100 folds excess. Mo (VI), Ti (IV), Pb(II), Ru(III), Co(II), Al(III), Mg(II) and Fe(III) are tolerable in 95, 90, 55, 45, 42, 35, 25 and 20 fold excess respectively. Ni (II), Cu (II), Sn (II) interferes seriously.

Table-I: Tolerance Limits Of Foreign Ions:

| Foreign ion	Tolerance limit (µg mL^{-1})	Foreign ion	Tolerance limit (µg mL^{-1})
Iodide	4500	W(VI)	185
Sulphate	1800	Zr(IV)	160
Chloride	1500	Cr(VI)	105
Acetate	1180	Mo(VI)	95
Thiocyanate	600	Ti(IV)	90
Nitrate	320	Pb(II)	55
Thiosulphate	225	Ru(III)	45
Carbonate	200	Co(II)	42
Tartrate	180	Al(III)	35
Fluoride	175	Mg(II)	25
EDTA	35	Fe(III)	20
Pd(II)	750	Zn(II)	10
Ba(II)	660	Hg(II)	10
Cd(II)	395	Sn(II)	3
Sr(II)	340	Cu(II)	2
Ca(II)	275	Ni(II)	1.5

[Amount of Mn(II) =1.37 µg mL^{-1}]

Derivative method:
A sensitive first order derivative spectrophotometric method was developed for the determination of manganese (II). First order derivative spectra of different solutions containing variable amounts of Mn(II) and a fixed concentration of OHNAINH, buffer solution (pH 8.0) were recorded in the wavelength region 350-650nm and presented in Fig-2. The derivative amplitudes were measured at 490nm and 425nm and plotted against the amount of Mn(II). Linear plots were obtained in the concentration range 0.27-2.47µg mL^{-1} at 490nm and 0.54-2.47µg mL^{-1}at 425nm. In the first order derivative method, the tolerance limits of Ni(II), Cu(II), Sn(II), Zn(II),

and Hg(II) were increased from 1.5,2.0,3.0,10, and 10 folds (direct method) to 30,50,80,110,and 120 folds respectively. The angular coefficients (m) of the linier plots were found to be 0.0054 and 0.0027 at 490 nm and 425 nm respectively. The correlation coefficients (r) were calculated as 0.9970 and 0.9886 at 490 nm and 425 nm respectively.

Fig-2: First order derivative spectra of [Mn(II)-OHNAINH] Vs Reagent blank:
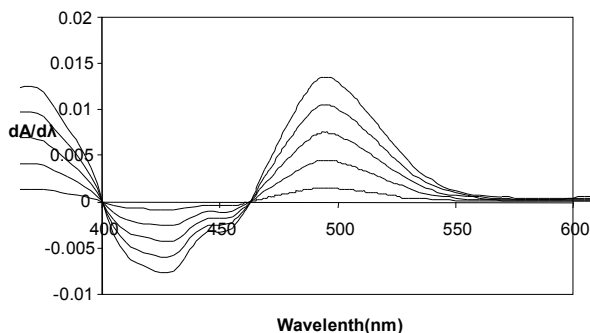
Amount of Mn (II) ($\mu g\ mL^{-1}$) = (a) 0.275; (b) 0.824; (c) 1.374; (d) 1.923; (e) 2.472. PH: 8.0

Application to real samples:

The proposed zero order method was employed for the determination of manganese (II) in tap water, cement sample and in milk.

The water samples were collected from different places of Anantapur district (Andhra Pradesh, India). The water samples (1litre) were collected in clean 2 litre beakers and slowly evaporated to about 25mL. To each sample, 5mL of H_2O_2 was added and evaporated to dryness[20]. It was then dissolved in 20mL of water and filtered to remove insoluble substance. The filtrate was collected in 100mL volumetric flask quantitatively and diluted up to the mark with distilled water.

Portland cement was collected from coramandal cement industries, yerraguntla, kadapa dist, Andhra Pradesh, India. 0.4g of the cement sample was dissolved in a mixture of 2mL HCl and 10mL of HNO_3. The resulting solution was evaporated to a small volume. To this 5mL of 1:1 H_2O: H_2SO_4 mixture was added and evaporated to dryness. The residue was dissolved in 15mL of distilled water and filtered through Whatman filter paper (No.41). The filtrate was collected in a 100mL volumetric flask and made up to the mark with distilled water. The solution was further diluted as required.

100mL 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; 1mL of conc. HNO_3 was added, evaporated to dryness and ignited again at 450-500°C for about one hour. The white ash was dissolved in minimum volume of dilute HNO_3 and made up to volume in a 10mL standard flask with distilled water.

Suitable aliquots of the samples solution were taken in 10mL standard flasks containing 4mL buffer solution of pH 8.0 and 1mL of 1×10^{-2} M OHNAINH solution. The contents were diluted to 10mL with distilled water and their absorbance was

measured at 495nm against the reagent blank. The absorbance values were referred to the predetermined calibration plot to compute the amount of manganese present. The results are presented in Table-II, III and IV respectively for water, cement and milk samples. The milk samples were also analyzed by atomic absorption spectrophotometric method and compared with those obtained by the present method.

Table-II: Determination of Mn (II) In Tap Water Samples

sample	Amount of Manganese ($\mu g\ mL^{-1}$)		Recovery (%)
	Added	Found*	
Water 1	–	2.2	–
	2.0	4.0	95
	4.0	6.0	97
	6.0	8.2	100
Water 2	–	1.9	–
	2.0	3.7	95
	4.0	5.9	100
	6.0	7.8	98
Water 3	–	1.5	–
	2.0	3.6	102
	4.0	5.3	96
	6.0	7.5	100

*Average of seven determinations

Table-III - Determination Of Mn(II) In Cement Samples

Sample	Certified compositions (%)	Mn certified (%)	Mn* found (%)	Relative error (%)
Portland cement BCS-372	SiO_2(21.3); TiO_2(0.33); CaO(65.8); Al_2O_3(5.35); MgO(1.30); Na_2O(0.21); Mn(0.046); K_2O(0.62); SO_3(2.35); P_2O_5(0.19)	0.046	0.047	+2.17
Lead concentrate BAS-426	Zn(3.40); S(14.2); Fe(1.35); Pb(75.6); Cu(0.14); As(0.32); Sb(0.15); Mn(0.21); Bi(0.020); Ag(0.074); Au(0.016)	0.210	0.208	-0.95
Lincolnshire iron ore BCS-301/1	Fe(23.8); SiO_2(7.40); Al_2O_3(4.26); TiO_2(0.16); CaO(22.6); MgO(1.73); Mn(0.970); Na_2O(0.07); K_2O(0.32); S(0.040); P(0.35)	0.970	0.980	+1.03

* Average of seven determinations

Table-IV: Determination Of Mn (II) In Milk Samples

Sample	Amount of Manganese ($\mu g\ mL^{-1}$)		Relative error (%)
	AAS method	*Present method	
Milk 1	0.278	0.280	+0.72
Milk 2	0.222	0.225	+1.35
Milk 3	0.166	0.163	-1.80
Milk 4	0.306	0.309	+0.98

* Average of seven determinations

First derivative method:

The first derivative method was employed for the determination of manganese present in some steel alloys and plant samples.

0.1g of steel sample was weighed accurately and placed in 50mL beaker. 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 after the addition of 5mL of Con. HNO_3 until all carbides were decomposed. Then, 2mL solution of H_2SO_4 (1:1) was added and the mixture was evaporated carefully until the dense white fumes of the oxides of nitrogen dried off 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 NH_4OH solution. The resulting solution was filtered through a Whatman (No-41) filter paper into a calibrated flask of known volume. The residue (silica) was washed with a small volume of hot 1% H_2SO_4 followed by water and the volume was made up to the mark with distilled water.

The contents of leaves of Oryza sativa L., Psidium guajava L., and Archras zapota L., (1g) were extracted in to ethyl alcohol after drying. The extract was diluted to 100ml with distilled water, from which suitable aliquots were taken for the determination of Mn (II).

4mL of buffer solution of pH 8.0 and 1mL of OHNAINH ($1X$ $10^{-2}M$) solution were taken in each of a series of 10mL 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 490nm were measured. The amount of manganese was then computed from a predetermined calibration plot. The results obtained were compared either with certified values or with those obtained by AAS method and presented in Table-V and VI.

Table-V: Analysis of Steel and Alloy Samples

Sample	Composition (%)	Amount of Mn (%)		Relative error (%)
		Certified	Found *	
BAS No.180/2	Cu(68.12); Fe(0.68); Co(0.04); Ni(30.35); Mn(0.75); S(0.006);	0.75	0.760	+1.33
BCS No.406	Mn(0.53); Ni(1.69); Mo(1.03); V(0.02); Cr(2.12); Cu(0.32)	0.530	0.525	-0.94
BAS No.179/2	Mn(0.86); Cu(58.50); Ni(0.56); Sn(0.70); Fe(1.20); Si(0.044); Zn(35.80); Pb(0.35); Al(2.22)	0.860	0.858	-0.23
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);	0.810	0.812	+0.24

*Average of seven determinations

Table-VI: Analysis of Plant Samples

Sample	Amount of Mn ($\mu g\ mL^{-1}$)		Relative error (%)
	AAS method	*Present method	
Oryza sativa L.	0.60	0.59	-1.66
	1.28	1.28	0
	1.86	1.88	+1.07
Pridium guajava L.	0.36	0.36	0
	0.90	0.92	+2.22
	1.08	1.07	-0.92
Archras zapota L.	0.36	0.35	-2.77
	0.87	0.87	0
	1.90	1.91	+0.52

* Average of seven determinations

The analytical characteristics of the zero order and First order derivative methods in the present investigations for manganese (II) show that the derivative method is more sensitive than the zero order method.

CONCLUSION

The present method is simple, less expensive and more sensitive than the methods proposed by Czech et al.[6], Reddy, P.B.S et al.[7], Salinas et al.[8, 9, 10] and more selective than some of the reported methods.[6, 7, 10, 12] The present method is applied successfully for the determination of manganese in alloy steels, cement, plant materials, milk and water.

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