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Direct and Second Derivative Spectrophotometric Determination of Manganese (II) in Tap Water, Alloy Steels and Plant samples.

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ABSTRACT

A simple, rapid, sensitive and selective method was developed for the spectrophotometric determination of manganese(II).The reagent 2-aminoacetophenone isonicotinoylhydrazone (2-AAINH) gives greenish colored water soluble complex in aqueous DMF medium with manganese(II).The greenish colored Mn(II) - 2AAINH complex shows maximum absorbance at 435nm in the pH range 9.0-10.0, where the reagent blank shows negligible absorbance. Hence, the analytical studies were carried out at 435nm.The molar absorptivity and sandell's sensitivity were 1.49×10^4 L mol^{-1} cm^{-1} and 3.5×10^{-3}µg cm^{-2} respectively. Beer's law is obeyed in the range 0.1373-2.746 µg mL^{-1}.The composition of the complex has 1:1 and stability constant of the complex was calculated as 2.7×10^{11}. The effect of various diverse ions also incorporated. A second derivative spectrophotometry has also been proposed for the determination of Mn (II). The present method was applied for determination of manganese in tapwater, alloy steels and plant samples.

Keywords: Direct and second derivative spectrophotometry, Determination of Mn(II), 2-AAINH

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INTRODUCTION

Manganese is found in all plants [1], animal tissues [2], foods [3] and drinking water [4] Manganese is a microelement actively absorbed by plants and has an effect on the fertility of soils [5]. It is a component of enzymes, such as superoxide dismutase, glutamine synthetase and arginase [6]. Manganese dioxide, manganese oxide, potassium permanganate and few organic compounds such as manganese naphthanate, oleate, linoleate etc. are used chiefly as dryers in paint and varnish industries. Most commonly, manganese is used as deoxidiser of molten steels.

Manganese is considered as one of the five essential trace elements along with boron, zinc, copper and molybdenum for majority of higher plants. A number of enzymes concerned with the oxidation of carbohydrates in respiration are activated by manganese especially for an enzyme called oxalo succinic carboxylase. In plants the shortage of manganese first becomes evident, in the form of an intervenal chlorosis (lack of chlorophyll). In many parts of India, the soil is deficient in manganese and so it is frequently added to fertilizers usually in the form of manganese sulphate. Manganese is widely distributed throughout the animal kingdom and may possibly be essential for the utilization of vitamin B_{12}.

There are several methods available for manganese (II) determination including atomic absorption spectroscopy(AAS), Flow injection analysis (FIA), Spectrofluorimetry [7] and simple spectrophotometry [8-17].The oxidants ,such as potassium periodate and ammonium persulfate are commonly used for determination of manganese(II) by spectrophotometry[18]. At present catalytic methods [19] for the determination of manganese(II) in water systems have been frequently reported.

The present work describes rapid, simple, sensitive, and selective direct and second derivative spectrophotmetric methods for the determination of trace amounts of Mn (II) by complexing with 2-aminoacetophenone isonicotinoylhydrazone (2-AAINH). The developed methods were applied for the spectrophotometric determination of micro amounts of Mn (II) in tapwater, alloy steels and plant samples.

EXPERIMENTAL

Apparatus

The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pHmeter of (Model LI 613), respectively.

Reagents and Chemicals

2-aminoacetophenone and isonicotinoyl hydrazone were taken from SD Fine Chemicals, India and $MnCl_2.4H_2O$ 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 by diluting the stock solution to an appropriate volume.

Solution of 2-aminoacetophenone isonicotinoylhydrazone (2-AAINH) (1x 10^{-2}M) was prepared by dissolving 0.255g of 2-AAINH in dimethyl formamide (DMF) and diluting to 100mL with DMF. Lower concentrations were prepared by diluting the appropriate volume of 0.01reagent solution with DMF.

Stock solution of Mn(II) (1 x 10^{-2}M) was prepared by dissolving 0.20g of $MnCl_2.4H_2O$(Mol.wt.197.91) in doubly distilled water and the solution was standardized complexometrically [20].

Buffer solutions

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

PROCEDURE

General method

Aliquots of solutions containing manganese (II) were transferred into a series of 10ml volumetric flasks. To these 2-AAINH (5 X 10^{-4}) was added and the contents were diluted to the mark with distilled water and mixed well. The absorbance was measured at 435nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of Mn(II) ions.

Derivative method

For the solutions as prepared above, the second derivative spectra were recorded with reference to the reagent blank in the wavelength range 440-520nm. The derivative amplitudes were measured at 465nm for second order curves. Calibration graphs were constructed by plotting the derivative amplitudes against the concentration of Mn(II).

Determination of manganese in water samples

The water samples were collected from different places of Anantapuramu district, Andhra Pradesh, India. The water samples (1 L) were collected in a clean 2 L beaker and slowly evaporated to about 25ml.Then, 5ml of H_2O_2 was added and evaporated up to dryness [21]. 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.

Determination of manganese in alloy steels

A 0.1g 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 14M HNO_3 until all carbides were decomposed. Then, 2 mL solution of H_2SO_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 NH_4OH 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% H_2SO_4 followed by water and the volume was made up to the mark with water.

Determination of manganese in plant samples

The contents of leaves of oryza sativa L., pridium guajava L. and Archras zapota L. (1g) 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 2-AAINH ($1x10^{-2}M$) solution were taken in each of a series of 10 mL volumetric flasks. Different know aliquots of each sample solution were added to these flasks and made up to the mark with distilled water. The second derivative spectra were recorded and the amplitudes at 465nm were measured. The amount of Mn(II) was then computed from a predetermined calibration plot.

RESULTS AND DISCUSSION

Absorption spectra

The reaction of 2-AAINH with Mn (II) at room temperature gives a green colored water soluble complex. The Mn (II) - 2AAINH complex shows maximum absorbance at 435nm where the reagent blank does not absorb appreciably was shown in **Fig 1**.

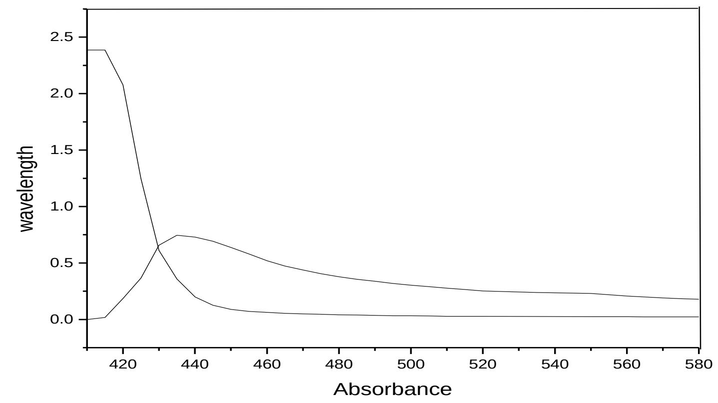

Figure 1: Absorption spectra of; a) 2-AAINH Vs Buffer Blank; b) [Mn(II)-2-AAINH] Vs reagent blank; c) [Mn(II)]=5 x 10-5; [5-BrSAINH]= 5 x 10-4; pH=9.5

Effect of pH on the absorbance of the experimental solution

The plot between absorbance and of pH reveals that the metal complex shows maximum and constant absorbance in the pH range 9.0-10.0. Therefore, pH 9.5 was selected for further studies.

Effect of reagent concentration on absorbance of the complex solution

The minimum amount of reagent to acquire maximum color intensity with a given amount of Mn(II) was evaluated from the absorbance measurements of experimental solution with different amounts of reagents. The results prove that a 20-fold molar excess of the reagent was required for the development of maximum color intensity with a given amount of manganese(II).

Composition and stability of the complex

The composition of the complex was determined using Job's continuous variation method. The results indicate a 1:1 stoichiometry between the metal ion and the reagent. The stability constant of the complex was determined as 2.7×10^{11}.

Validity of Beer's law

The calibration plot between absorbance and concentration of Mn (II) shows that Beer's law is obeyed by the system in the concentration range 0.1373-2.746 µg mL^{-1} of Mn (II). The straight line obeys the equation $A_{435}= 0.3211C - 0.0026$. The molar absorptivity and sandell's sensitivity of the method were found as 1.49×10^{4} L.mol^{-1} cm^{-1} and 3.5×10^{-3} µgcm^{-2}, respectively.

Effect of foreign ions

The effect of various anions and cations normally associated with Mn (II) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by +2% were calculated and presented in **Table 1.** Almost all the tested anions possess high tolerance levels (>100 fold). The metal ions Pd(II), Au(III), Ni(II), Mo(VI), Co(II), Fe(II), V(V) interferes in 30-45 fold excess. It was noticed that all the ions which did not interfere in the zero order determination of manganese (II) also did not interfere in the second order derivative method.

Derivative Method

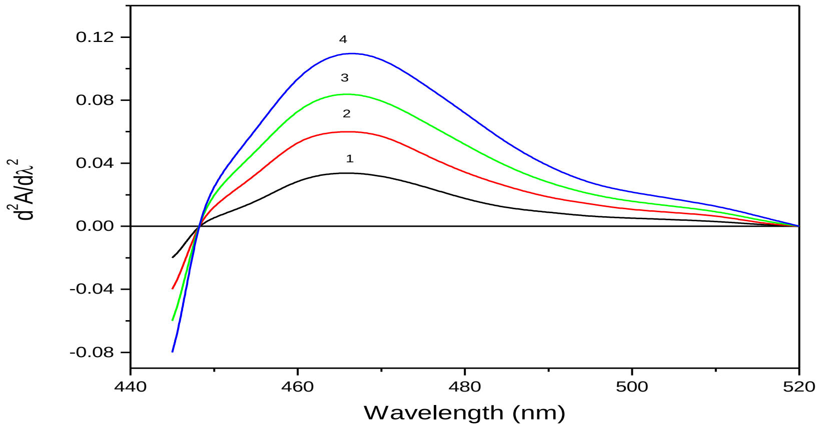

Figure 2: Second derivative spectra of Mn(II) – 2AAINH Vs reagent blank Mn(II) (µg mL^{-1}) = (1) 0.2746; (2) 0.5492; (3) 0.8238; (4) 1.0984.

In order to improve the sensitivity and selectivity of the direct spectrophotometric method developed; the absorbance data was derivatised once and twice and plotted against the wavelength (440-520nm) which gave the corresponding second order derivative curves **(Fig 2).** The second derivative curve shows a peak at 465nm. At this wavelength, the derivative amplitudes were proportional to the amount of Mn (II) in the range 0.068 - 7.963 μg mL^{-1}.

Table 1: Tolerance limits of foreign ions Amount of Mn(II) = 2.745 μg ml^{-1}

Foreign ion	Tolerance limit (μg ml^{-1})	Foreign ion	Tolerance limit (μg ml^{-1})
Ascorbic acid	1420	Na(I)	720
Bromate	1300	Li(I)	640
Tartrate	1250	K(I)	600
Citrate	1020	Te(IV)	560
Sulphate	920	W(IV)	520
Thiosulphate	900	Mg(II)	490
Phosphate	850	Zr(IV)	410
Oxalate	810	Ce(IV)	380
Thiourea	780	Al(III)	320
Bromide	710	Th(IV)	290
Urea	700	Cd(II)	230
Nitrate	610	Pb(II)	195
Flouride	600	Zn(II)	150
Acetate	560	Co(II)	120
Formate	420	Ru(III)	110
Chloride	315	Cu(II)	100
Iodide	200	V(V)	95
		Fe(II)	90
		Co(II)	85
		Mo(VI)	80
		Ni(II)	80
		Au(III)	75
		Pd(II)	60

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

Sample	Manganese (μg mL^{-1})		Recovery (%)
	Added	Found*	
Water 1	-	2.0	-
	2.0	3.6	92
	4.0	6.4	98
	6.0	8.5	100
Water 2	-	1.4	-
	2.0	3.7	98
	4.0	5.9	100
	6.0	7.6	106
Water 3	-	1.3	-
	2.0	3.2	104
	4.0	6.3	98
	6.0	6.9	96

Applications

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

Table 3: Analysis of Mn(II) in steel and Alloy samples.

Sample	Composition (%)	Amount of Mn (%)		Relative error (%)
		Taken	Found*	
BAS No.180/2	Cu(68.12); Fe(0.68); Co(0.04); Ni(30.35); Mn(0.75); S(0.006)	0.750	0.741	+1.20
BCS No.406	Mn(0.53); Ni(1.69); Mo(1.03); V(0.02); Cr(2.12); Cu(0.32)	0.530	0.524	+1.13
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)	0.860	0.864	-0.46
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	0.819	-1.11

Table 4: Determination of Mn(II) in plant samples.

Sample	Amount of manganese(μg ml^{-1})		Relative error (%)
	AAS method	Present method*	
Oryza sativa L.	0.60	0.59	1.66
	1.28	1.23	2.34
	1.86	1.82	2.15
Pridium guajave L.	0.36	0.37	-2.77
	0.90	0.87	3.33
	1.08	1.06	1.85
Achras zapota L.	0.36	0.38	2.77
	0.87	0.83	-5.55
	1.90	1.93	-1.57

CONCLUSIONS

Table 5: Analytical Characteristics of Mn(II)-2-AAINH.

Parameter	Zero order	Second derivative
Analytical wave length (nm)	435	465
Beer's law range (μg mL^{-1})	0.1373-2.746	0.068 - 7.963
Angular coefficient (m)	0.3211	0.9984
Y-intercept (b)	0.0026	0.0274
Correlation coefficient	0.9996	0.9999
Standard deviation	±0.0102	±0.0008
Detection Limit (μg mL^{-1})	0.0267	0.0905
Determination Limit (μg mL^{-1})	0.0801	0.2715

The proposed methods for the spectrophotometric determination of manganese(II) in tapwater, 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 second order derivative spectrophotometric methods for Mn(II)-2-AAINH complex were compared and presented in **Table 5**. From the results in Table 5, it was clear that the second order derivative method was more sensitive than zero order method.

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