
Chapter – 4

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE(II)

INTRODUCTION

Manganese is a hard, brittle metal and is essential for the control of sulphur content in the manufacture of steel. This application accounts for the major position of the manganese consumption in all forms in the country. 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.

In industry, manganese finds use in the manufacture of steel, ferroalloys and as an oxidising agent in chemical industry. Manganese has several oxidation states, the most stable being the divalent state, Mn(II). Manganese is found in all plants¹, animal tissues, foods² and drinking water³. It being an essential constituent of metallo enzymes is an important nutrient for plant growth. It plays an important role in the fixation of carbondioxide, as the activator of the nitrite reductase and is active catalyst in the formation of primary photochemical oxidation product in photosynthesis. In higher amounts, it is toxic to plants and also reduces the availability of iron to plants. It is an essential element for the maintenance of the normal health of animals and as well as human beings. Its deficiency causes skeletal abnormalities.

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 B₁₂.

Marczenko⁴ has commented that the major colorimetric methods for the determination of manganese are the permanganate, formaldoxime and pyridylazonaphthal methods. Chiswell and Rauchle⁵ reviewed the various spectrophotometric methods that used organic colour forming reagents for the determination of manganese. It reacts with several organic reagents forming complexes leading to its spectrophotometric determination⁶⁻⁸. The spectrophotometric method for the determination of manganese that is often employed was based on the oxidation of manganous ion to pink coloured permanganate ion. Though the method is highly selective, it is less sensitive. Higher sensitivities were reported with for maldoxime and P-(2-pyrdylazo)-2-naphthal (PHN).

Several spectrophotometric methods recently proposed for the determination of manganese are reviewed and the results obtained are listed in Table 4.1. The survey of literature showed that very few thiosemicarbazone derivatives were employed as the reagents for the spectrophotometric determination of manganese.

In view of the importance of manganese to plants, the author has investigated the colour reaction between manganese (II) and 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) in alkaline medium.

Present investigations

Manganese (II) forms a greenish coloured water soluble complex with 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) in alkaline medium. The colour formation was instantaneous and was stable for more than 48 hours. Hence, a detailed study of the system is under taken with a view to develop a new spectrophotometric method for the determination of Manganese (II).

Table 4.1

Analytical results of various spectrophotometric determinations for Manganese (II)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (Lmol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
1,5-Diphenylcarbazone	531	4.8	0.058	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
1-(4-Nitrophenyl)-5-phenylcarbazone	595	4.8	0.17	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
1-Phenyl-5-(4-nitro-phenyl) carbazone	572	4.8	0.15	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
Bipyridylglyoxal bis-(4-phenyl-3-thiosemicarbazone	-	-	-	0.2-1.2	-	10
2-(5'-Bromo-2'-pyridylozo)-5-diethylaminophenol	-	8.5	12.7	0-10	-	11
2,4-Dinitro-phenylazopyro-catechol	535	8.0	-	0.08-1.70	Ni(II), Co(II), Cd (II) and Zn (II)	12
3,5-Dichloro-2-hydroxyacetophenone-oxime	-	Ammonical	-	0.5	-	13
3,3'-Iminodipro-pionamidoxime	-	NH ₂ OH	-	-	-	14
Formaldoxime	450	9.6	-	-	-	15
a, b, g, d-Tetrakis-(4'-carboxyl phenyl)-porphine	469	-	10	25-560	Fe(III), Cu(II), Co(II) and V(V)	16
o-Hydroxyhydro-quinone phthalein	535	9.0	-	0-4.0	Fe(III), Cu(II) and Zn(II)	17
4-(2-Thiazolyl-azo) resorcinol	540	8.8	4.17	0.04-1.4	Co(II), Zn(II), Cd(II), Pb(II) and EDTA	18
Salicylaldoxime	410	9.2	0.2	-	Ti(IV), V(IV), Cr(III), Co, Ni,Cu(II) and Zn	19
5-Chloro-2,4-di-hydroxypropio-phenone-oxime	405	8.0-10.0	-	1.0-6.0	-	20

Table 4.1 (Continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (Lmol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
2,2'-Bipyridyl and (2,4-Dinitrophenyl-azo) pyrocatechol	-	10.0	-	-	-	21
Diphenyl succinimide monoxime	490	2N NH ₃	-	Up to 14	-	22
1, 10-Phenanthroline-tetraiodo fluorescein	544	9.5	10.5	-	-	23
Isophtalidi-hydroxamic acid	-	-	0.85	1.0-7.0	-	24
Dipicolinedihydroxamic acid	500	-	0.41	0.5-5.0	-	25
Potassium hydrogen phthalomon droxamate	465	-	-	1-17	Pd(II) and Pt(II)	26
o-Aminobenzohydroxamic acid	500	-	0.37	1.0-17.0	-	27
Thiothenoyltri-fluoracetone	375	7.3	0.35	-	-	28
1-Benzyl benzimidazolyl-5-phenyl formazan	-	8-10	-	-	-	29
Dibenzoylmethane	-	-	-	-	-	30
Salicylhydroxamic acid	-	-	0.36	0.3-7.0	-	31
a,b,g, d-tetra kis (4-sulfophenyl prophine)	-	7.8-10.0	32.0	0-0.125	-	32
1,10-Phenanthroline chrome azurol S and Cetyltrimethyl ammonium bromide	635	-	8.0	-	-	33
Bromophrogallol red	-	-	-	-	-	34
Isophtalidihy-droxamic acid	-	-	-	3-9	-	35
Thiocyanate	-	-	36	0.2-2.0	-	36
1-(2'-Pyridylazo)-2-naphthal	-	-	-	-	-	37
Formaloxime	-	-	-	Up to 5.0	-	38
Formaloxime	-	-	-	-	-	39

Table 4.1. (Continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (Lmol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
Formaloxime	-	-	-	-	-	40
Eriochrome Azural-2,2'-dipyridyl cetyl-trimethylammonium bromide	625	9.5-10.5	8.3	0.15	-	41
2-Oximinocyclo-hexanone thiosemi-carbazone	-	-	-	-	-	42
Khimduchlorophos-phonazo-1	574	7.5-8.5	2.5	0-60	-	43
5,5'-Dithiodi (salicylo-0.196 hydroxamic acid)	495	9.0	0.196	0.3-2.3	-	44
Xylenol orange	-	-	-	0.0-1.6 1.6-4.2	-	45
8-Hydroxyquinoline	420	Basic	2.2	0.1-3.5	-	46
Tributyl phosphate and (Nitrophenyl) azo pyro-catechols	520 560	12.4 12.4	2.09 2.63	-	-	47
1,10-phenanthroline isodeosin	542	-	-	-	-	48
Benzohydroxamic acid	500	9.0	0.569	-	-	49
Eriochrome Black T	611	-	-	Up to 10	-	50
o-Nitrophenyl fluorine and Cetylpyridinium	600	9.4-10.0	13.0	1-6	-	51
1-2(-Pyridylazo)-2-naphthol	-	-	-	-	The method developed for the determination of dissolved manganese in seawater.	52
Benzyl tributyl ammonium chloride	548	6.0	-	-	The system has been applied to the determination of manganese in a variety of steels.	53

Table 4.1 (Continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (Lmol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
Resacetophenone oxime	380	10.5	2.5	0.09-1.7	Applied to the determination of manganese in some steel and alloy samples	54
Dithiozone and potassium thiocyanate	506	6.0		0.1-2.0	Cd, Cu, Ni, Co, Cu are interfere	55
Neotetrazolium chloride	-	-	91.0		The method is applicable to analysis of soils and steels.	56
Diantipyryl-(P-chloro)phenyl methane	480	Alkaline medium	13.8	0.0-400	The method can be applied to the determination of Mn in ore and alloys	57
2-(5-bromo-2-pyridylazo)-5-diethyl amino phenol	558		-	-	The method is useful for the determination of manganese in black rice and tea	58
1,2,4-trihydroxy anthraquinone	-	8.5	-	-	The analysis of cement materials of variable manganese content is feasible over the concentration range 1.67-8.13 $\mu\text{g ml}^{-1}$ Mn(II)	59
Picolinaldehyde nicotinoylhydrazone	385	8.7-10.5	4.606	0.02-1.5	Extraction method	60
Schiff's bis base	460	6.0	9.8		Fe (II), Fe(III) and Ni (II) are interfere	61
1-(2-pyridylazo)-2-naphthol	514	-	-	-	Molybdenum, lead, cobalt, chromium, iron, nickel, zinc, tin, cadmium, and copper are interfere	62
N, N'-bis (2-hydroxy-5-bromo-benzyl) 1,2 diamino propane	-	7.0-10.0	-	0.12 to 13.2	The method is applied for the determination of manganese in water samples.	63

Table 4.1 (Continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (Lmol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBTSC)	435	9.0-10.0	1.96	0.1373-2.746	The method is applied for the tap water, cement samples, milk, steel alloys and plant samples	64
2-hydroxy-1-napthaldehyde isonicotinoyl hydrazone	495	5.0-10.0	1.02	0.27-4.12	The method is applied for the tap water, cement samples, milk, steel alloys and plant samples	65
2-Hydroxy-4-methoxy acetophenone oxime	410	8.0-11.0	2.40×10^2	1-12	Antimicrobial activity	66
Pyridine 2, 6 dicarboxylic acid.	500	1.5-2.5	9.89×10^2	50-225	-	67
7- Bromo, 8 –Hydroxy Quinoline	390	8.0	4.12×10^3	0.8-6.4	Environmental samples	68
2-Amio Acetophenone Isonicotinoyl Hydrazone	435	9.5	1.49	0.13-2.74	-	Present method

* Unless otherwise indicated.

Section i : Zero order spectrophotometric determination of manganese (II)

a. Absorption spectra of 2-AAINH and manganese (II) complex in solution

The absorption spectra of greenish colored [Mn(II)-2-AAINH] complex were recorded in the wavelength range 400 – 580 nm at pH 9.5 against the buffer blank and reagent blank respectively by adopting the procedure described in 3a. Typical spectra are presented in Fig. 4.i.1. The spectra show that manganese (II) complex has an absorption maximum at 435 nm, where as the reagent has considerably negligible absorbance. Therefore, Mn (II) was determined by measuring the absorbance of experimental solutions at 435 nm using reagent blank as reference solution.

b. Effect of pH on the absorbance of the complex solution

To arrive at the optimum pH required for full colour development, the effect of pH on the colour intensity was studied by the procedure outlined in 3b. A plot was made between pH and absorbance and presented in Fig. 4.i.2. The figure indicates that absorbance is maximum and constant in the pH range 9.0 -10.0. Hence, the pH 9.5 was chosen for further studies.

c. Effect of reagent concentration on absorbance of the complex solution

The absorbance of the complex solution was measured at various concentrations of the reagent solution keeping Mn (II) concentration constant at 435 nm and at pH 9.5 by following the procedure 3c. The results are presented in Table 4.i.1.

The results were indicated that a 20 fold molar excess of the reagent is necessary for maximum colour development which was maintained throughout the studies.

Table 4.i.1: Effect of 2-AAINH Concentration

$$\text{Mn (II)} = 5 \times 10^{-5} \text{ M}$$

$$\text{pH} = 9.5$$

$$\text{Wavelength} = 435 \text{ nm}$$

[Mn (II) : [2-AAINH]	Absorbance
1:5	0.558
1:10	0.624
1:15	0.699
1:20	0.735
1:25	0.732
1:30	0.728

d. Time stability of the colour of the reaction mixture

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex as described in 3d. It was noticed that the greenish colour development was instantaneous and remained constant for more than 48 hours.

e. Adherence of the system to Beer's law

To explore the possibility of employing the colour reaction for the determination of manganese (II) at micro levels, the absorbance of the solutions containing different amounts of the metal ion was measured by adopting the procedure 3e. The calibration plot drawn between absorbance and the amount of manganese (II) (Fig. 4.i.3). The straight line obeys the equation $A_{435} = 0.3211C - 0.0026$. Further, Beer's law was obeyed in the range of $0.1373\text{-}2.746 \mu\text{g mL}^{-1}$ of Mn(II). The molar absorptivity and Sandell's sensitivity were $1.49 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $3.5 \times 10^{-3} \mu\text{g cm}^{-2}$ respectively.

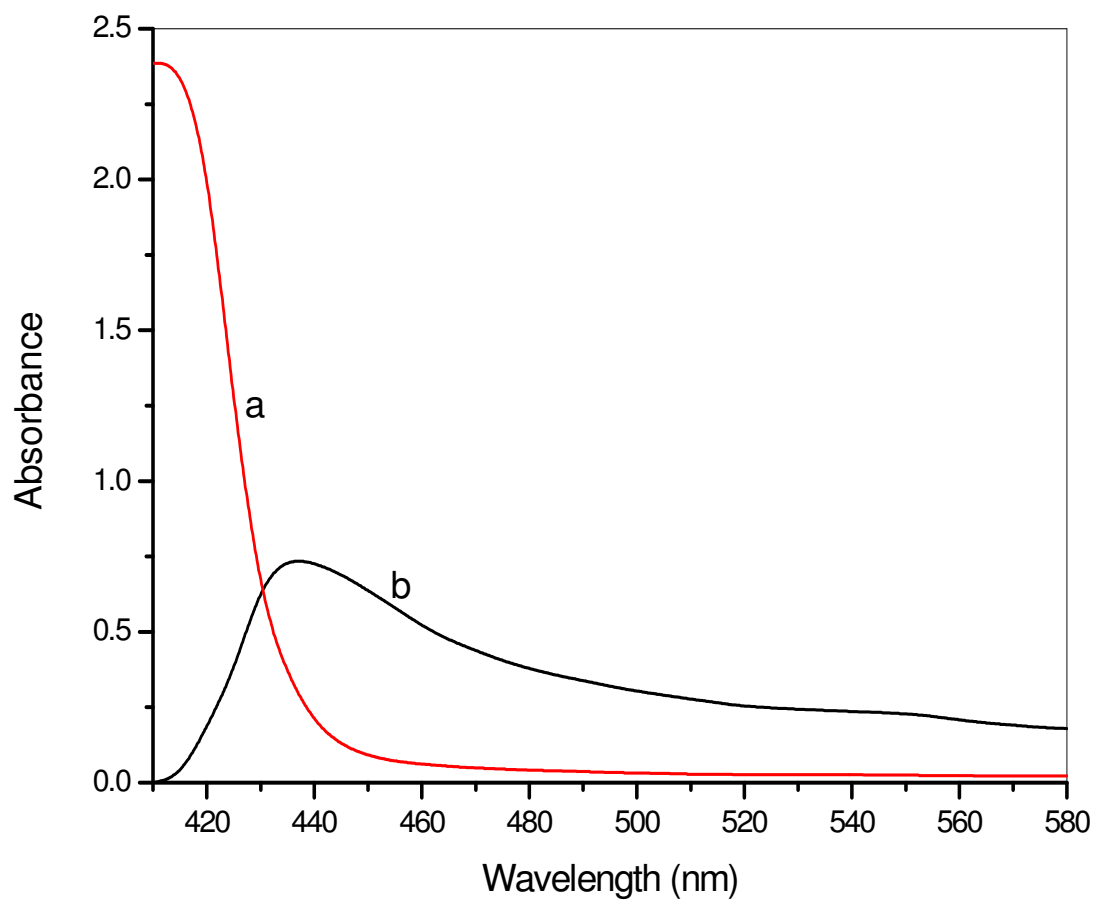


Fig. 4.i.1 **Absorption spectra of**
 (a) [Mn(II) – 2-AAINH] Vs reagent blank
 (b) 2-AAINH Vs Buffer blank
 [Mn(II)] = 5×10^{-5} M; [AAINH] = 5×10^{-4} M ; pH = 9.5

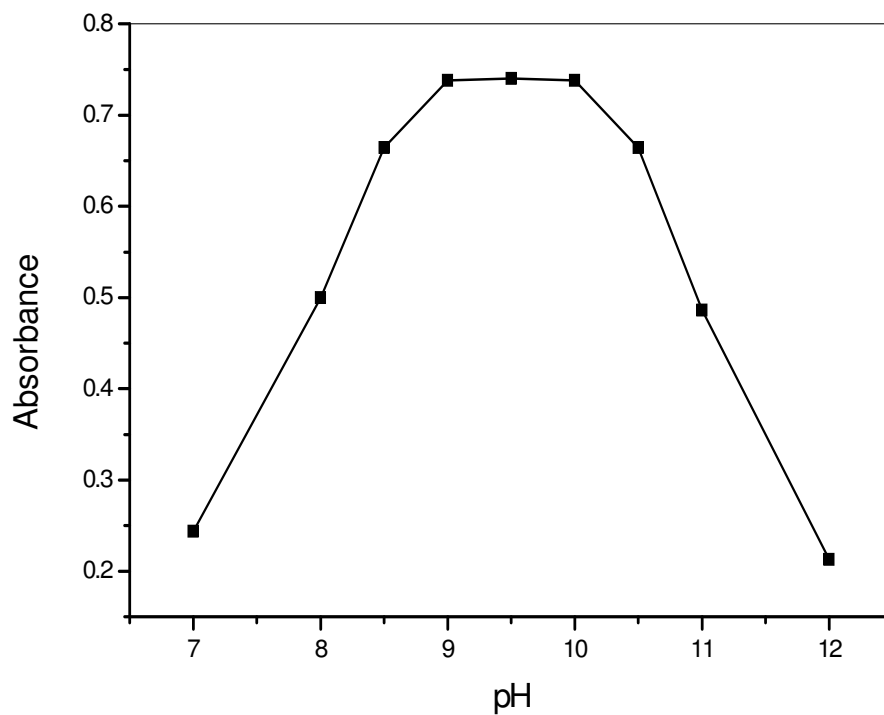


Fig. 4.i.2. Effect of pH on absorbance of Mn(II) – AAINH
 [Mn(II)] = 5×10^{-5} M ; [2-AAINH] = 5×10^{-4} M
 Wavelength = 435nm

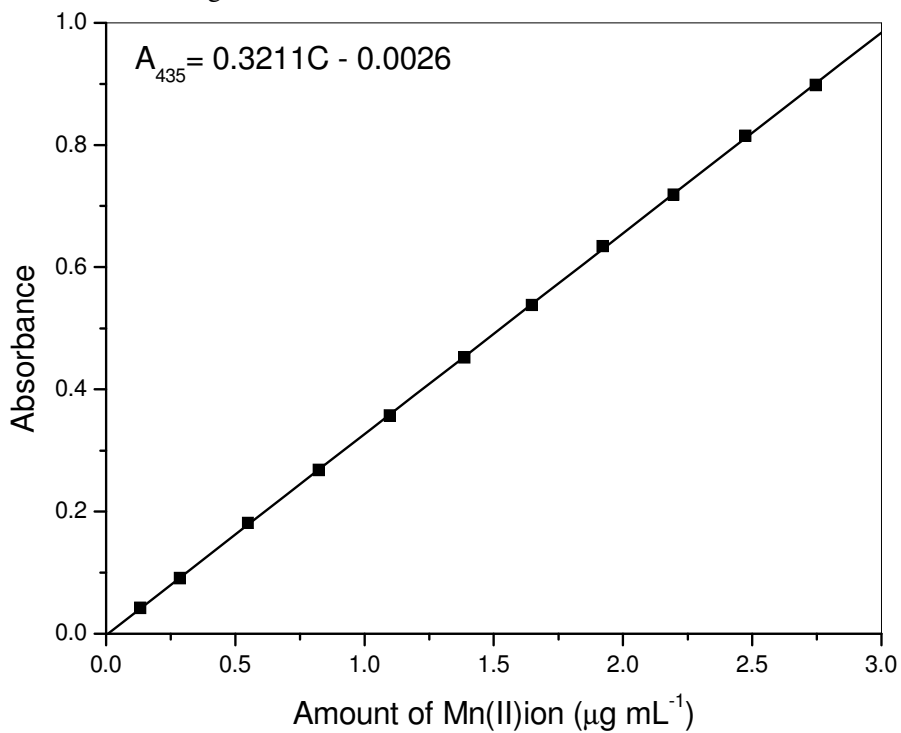


Fig. 4.i.3. Calibration plot
 [2-AAINH] = 1×10^{-3} M
 Wavelength = 435nm; pH = 9.5

Statistical analysis of results

In the spectrophotometric determination of Mn (II), the results obtained were subjected to statistical analysis and the results obtained are given in Table 4.i.2.

Table 4.i.2: Statistical analysis for the determination of Mn (II)

Parameter	Mn (II) – 2-AAINH
Angular coefficient (m)	0.3211
Y- Intercept (b)	0.0026
Correlation coefficient (r)	0.9996
Standard deviation (s)	± 0.0102

The statistical results indicate that the method obeys Beer's law perfectly and the results obtained are accurate and reproducible.

f. Effect of diverse ions

Effect of diverse ions normally associated with manganese (II) ion on its determination under optimum conditions developed was studied by the procedure presented in 3f. The results are presented in Table 4.i.3. Almost all the studied anions do not interfere even when present in more than 100 fold excess. The tolerance limits of the cations are also reasonably high. Further, Pd (II), Au (III), Ni (II), Mo (VI), Co(II), Fe (II) and V (V) interferes when present in 60–95-fold excess. It was noticed that all the ions did not interfere in the determination of manganese (II) by zero order method.

Table 4.i.3: Tolerance limits of diverse ionsAmount of Mn (II) = 2.745 $\mu\text{g mL}^{-1}$

Diverse ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Diverse ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Ascorbic acid	1420	Na(I)	720
Bromate	1300	Li(I)	640
Tartrate	1250	K(I)	600
Citrate	1020	Te(IV)	560
Sulphate	920	W(VI)	520
Thiosulphate	900	Mg(II)	490
Phosphite	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
Fluoride	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

Composition and stability of the complex

The stoichiometry of the complex was determined by Job's and molar ratio methods.

g. Job's method

For Job's method, the procedure described in 3g was adopted. The Job's curve shown in Fig. 4.i.4 gives a composition of 1:1 (metal: reagent) for the complex. The stability constant of the complex was calculated as 2.7×10^{11} .

h. Molar ratio method

Molar ratio method was followed using the general procedure 3h. The molar ratio plot shown in Fig. 4.i.5 confirms the 1:1 complex formation between Mn (II) and 2-AAINH.

Applications

The proposed method was employed for the determination of manganese in tap water and diverse samples. The preparation of the sample solution was outlined in 3r and 3(1). Portland cement was collected from Coramandal cement industries, Yerraguntla, Kadapa district (A.P).

Procedure

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 5 ml of buffer solution of pH 9.5 and 1ml of (1×10^{-2} M) 2-AAINH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at 435 nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of manganese present. The results are presented in Tables 4.i.4 and 4.i.5.

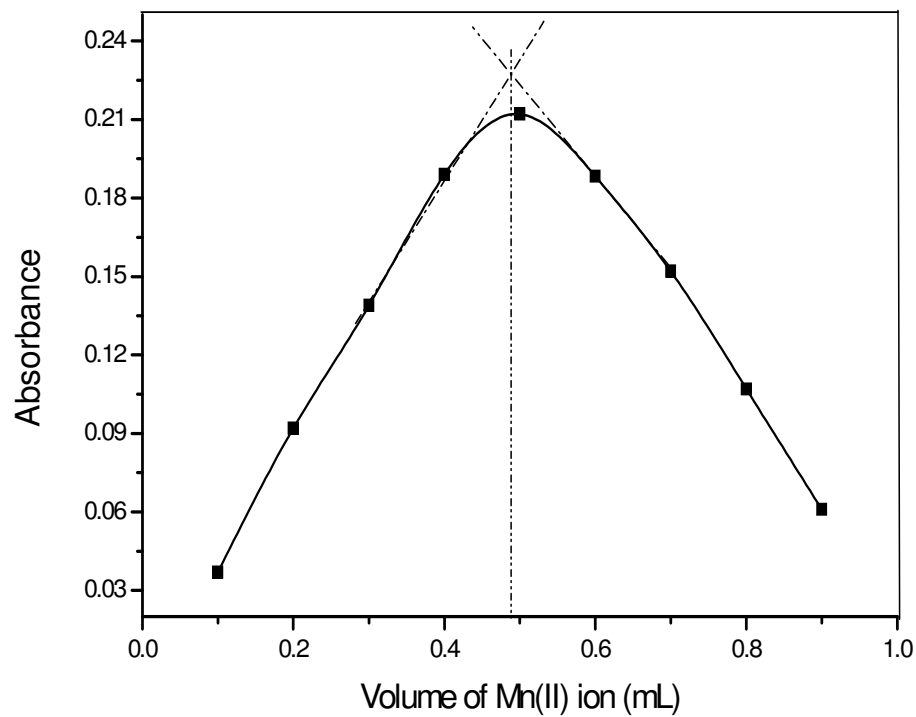


Fig. 4.i.4. Job's curve
 [Mn(II)] = [2-AAINH] = 1×10^{-3} M
 Wavelength = 435nm ; pH = 9.5

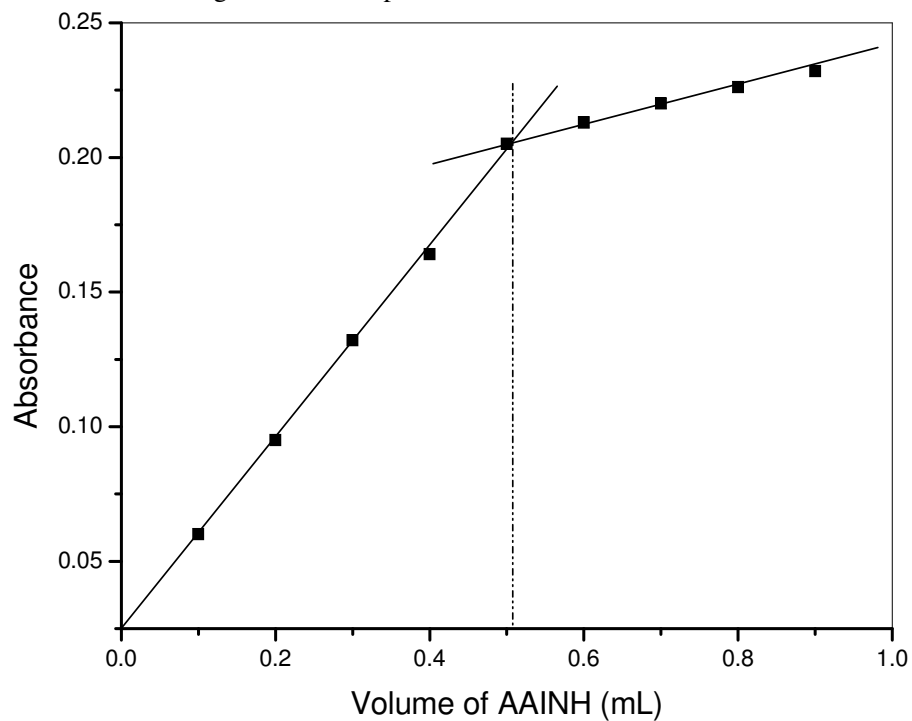


Fig. 4.i.5. Molar ratio plot
 [Mn(II)] = [2-AAINH] = 1×10^{-3} M
 Wavelength = 435nm; pH = 9.5

Table 4.i.4: Determination of Mn (II) in tap water

Sample	Manganese ($\mu\text{g mL}^{-1}$)		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

* Average of five determinations.

Table 4.i.5: Determination of Mn (II) in diverse samples

Sample	Certified composition (%)	Mn certified (%)	Mn* found (%)	Relative error (%)
Portland cement BCS-372	SiO ₂ (21.3); TiO ₂ (0.33); CaO(65.8); Al ₂ O ₃ (5.35); MgO(1.30); Na ₂ O(0.21); K ₂ O(0.62); SO ₃ (2.35) P ₂ O 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); 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 ₂ O ₃ (4.26); TiO ₂ (0.16); CaO(22.6); MgO(1.73); Na ₂ O(0.07); K ₂ O(0.32); S(0.040); P(0.35)	0.970	0.960	-1.03

* Average of five determinations.

Section ii : Derivative spectrophotometric determination of Manganese (II)

A highly selective first and second order derivative spectroscopic method were also developed for the determination of micrograms quantities of manganese (II). The results of these derivative studies are given in the following paras.

Derivative spectra

The first and second derivative spectra of greenish coloured manganese (II)-2-AAINH complex were recorded in the wave length region 350-550 nm at pH 9.5 for various amounts of Mn (II) by the procedure described in 3i & j and are shown in Figs. 4.ii.1 and 4.ii.3 respectively.

The first derivative spectra show a maximum peak at 453 nm. The second derivative spectra show a peak at 465 nm and a zero cross at 450 nm. Therefore, 453nm and 465 nm were selected for the first and second order derivative spectrophotometric determination of Mn (II) respectively.

First derivative method

The first derivative spectra of [Mn (II)-2-AAINH] colored complex for different concentrations of Mn (II) were recorded in the wave length region 350-600 nm and presented in Fig4.ii.1. The derivative amplitudes (zero to peak) at 453 nm was found to be proportional to the concentration of manganese (II) solution. The derivative amplitudes were measured at 453 nm for different concentrations of Mn(II) and plotted against the amount of Mn (II) (Fig4.ii.2). The plot was linear in the range 0.068-8.238 $\mu\text{g mL}^{-1}$ of Mn (II). The standard deviation of the method for ten determinations of 0.274 $\mu\text{g ml}^{-1}$ of Mn (II) was ± 0.0068 .

Second derivative method

The second derivative spectra of [Mn (II)-2-AAINH] colored complex for different concentrations of Mn (II) were recorded in the wave length region 350-550 nm and presented in Fig. 4.ii.3. The derivative amplitudes (zero to peak) at 465 nm was found to be proportional to the concentration of manganese (II) solution. The derivative amplitudes were measured at 465 nm for different concentrations of Mn(II) and plotted against the amount of Mn (II) (Fig4.ii.4). The plot was linear in the range 0.068-7.963 $\mu\text{g mL}^{-1}$ of Mn (II). The standard deviation of the method for ten determinations of 0.274 $\mu\text{g mL}^{-1}$ of Mn(II) was ± 0.0008 .

Effect of foreign ions

The effect of various cations and anions were examined by applying the method to a fixed amount of manganese in the presence of increasing amounts of the ion being studied by following the general procedure 3k. The tolerance limit was taken as the amount that caused an error of $\pm 2\%$ in the absorbance. When compared to the zero order method, the tolerance limits to larger number of ions which were very low in the zero order method, were found to be much higher in the derivative method. This shows the greater selectivity of the derivative methods, when compared to zero order method. The results obtained in the studies are presented in Table 4.ii.1.

Table 4.ii.1: Effect of diverse ions

S. No	Diverse Ion	Zero Order	First Derivative	Second Derivative
1.	Co(II)	85	>100	>100
2.	Mo(VI)	80	90	>100
3.	Ni(II)	80	85	>100
4.	Au(III)	75	Interferes	85
5.	Pd(II)	60	Interferes	75

Applications

The second derivative method was employed for the determination of manganese present in some steel alloys and plant samples. Preparation of the alloy steel sample solution was outlined in 3I. 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).

Procedure

5ml of buffer solution of pH 9.5 and 1ml of 2-AAINH ($1 \times 10^{-2} \text{M}$) 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 second derivative spectra were recorded and the amplitudes at 465 nm were measured. The amount of Mn (II) was calculated from a predetermined calibration plot. The results obtained were compared either with certified values or with those obtained by AAS method and presented in Tables 4.ii.2 and 4.ii.3.

Table 4.ii.2: Analysis of 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

* Average of five determinations.

Table 4.ii.3: Analysis of plant samples

Sample	Amount of manganese($\mu\text{g mL}^{-1}$)		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

* Average of five determinations.

Comparison of the results

The results obtained in zero order and derivative spectrophotometric methods for Mn(II)-2-AAINH complex were compared and presented in Table 4.ii.4, it was clear that the derivative methods are more sensitive than the zero order method.

Table 4.ii.4: Comparison of the results for Mn (II)

Parameter	Zero order	First derivative	Second derivative
Analytical wave length (nm)	435	453	465
Beer's law range ($\mu\text{g mL}^{-1}$)	0.1373-2.746	0.068 - 8.238	0.068 - 7.963
Molar absorptivity($\text{Lmol}^{-1}\text{cm}^{-1}$)	1.49×10^4	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	3.5×10^{-3}	-	-
Stability constant	2.7×10^{11}	-	-
Angular coefficient (m)	0.3211	0.2052	0.9984
Y-intercept (b)	0.0026	0.0134	0.0274
Correlation coefficient (r)	0.9996	0.9998	0.9999
Standard deviation	± 0.0102	± 0.0068	± 0.0008
Detection limit($\mu\text{g mL}^{-1}$)	0.0267	0.092	0.0905
Determination limit ($\mu\text{g mL}^{-1}$)	0.0801	0.2698	0.2715

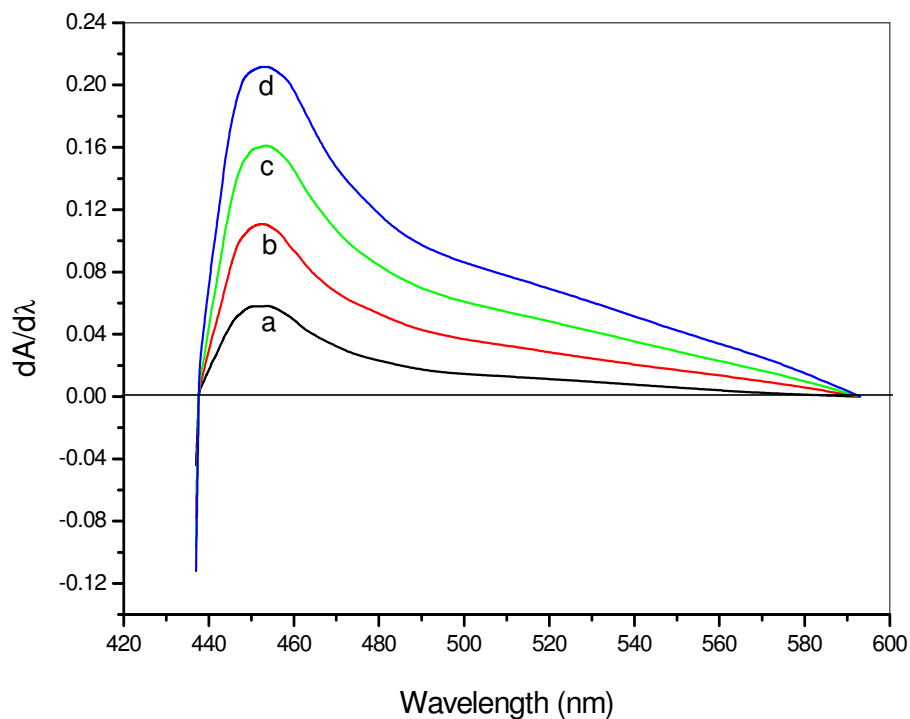


Fig. 4.ii.1. First derivative spectra of
 Mn(II) – 2-AAINH Vs reagent blank
 Mn(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2746; (b) 0.5492; (c) 0.8238; (d) 1.0984

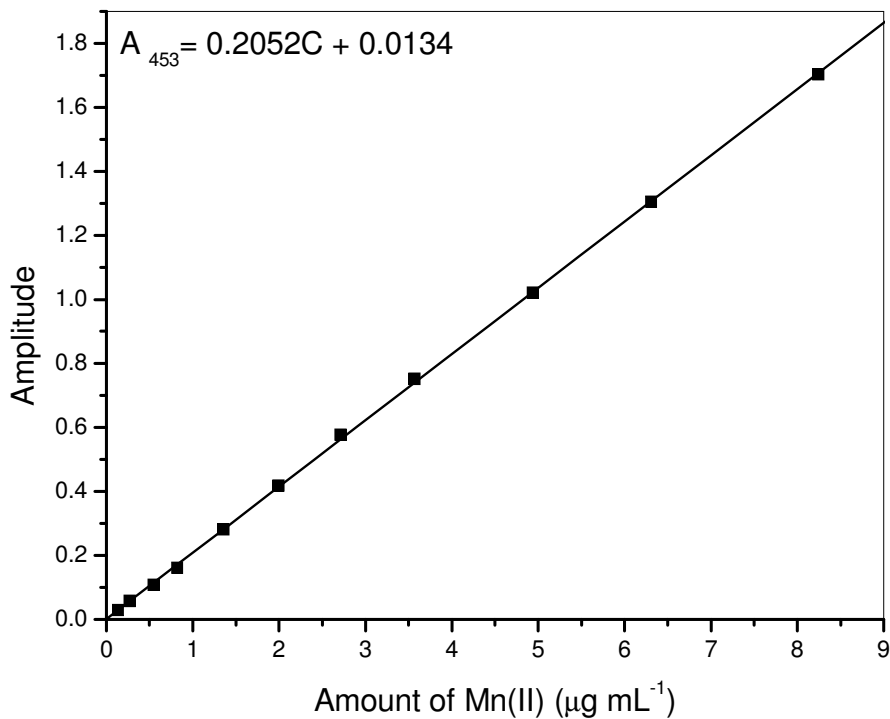


Fig. 4.ii.2. First derivative amplitude Vs amount of Mn(II)
 $\lambda = 453$; pH = 9.5

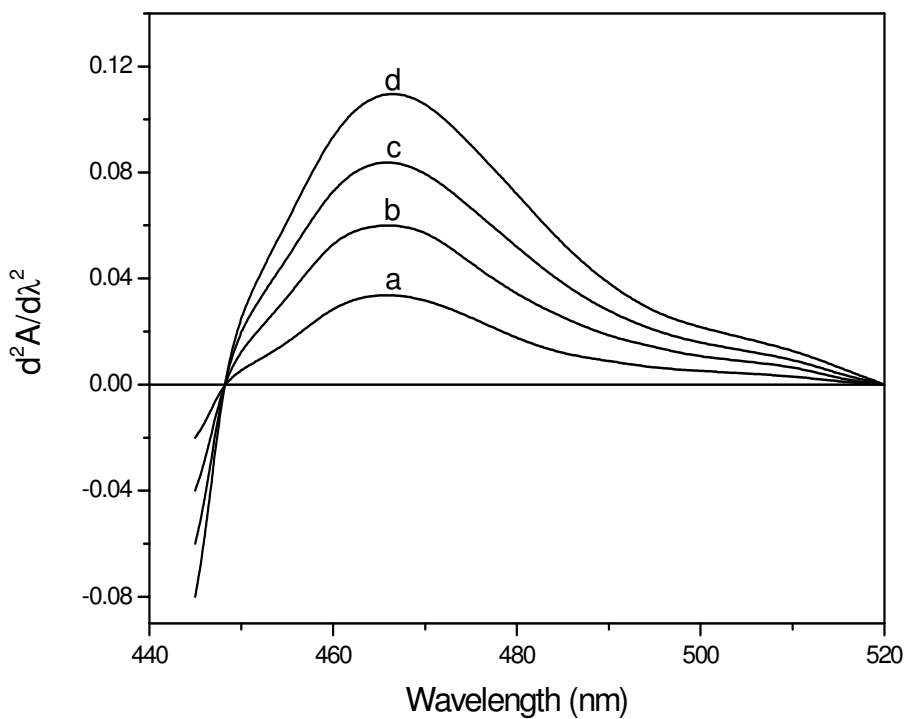


Fig. 4.ii.3. Second derivative spectra of Mn(II) – 2-AAINH Vs reagent blank
Mn(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2746; (b) 0.5492; (c) 0.8238; (d) 1.0984

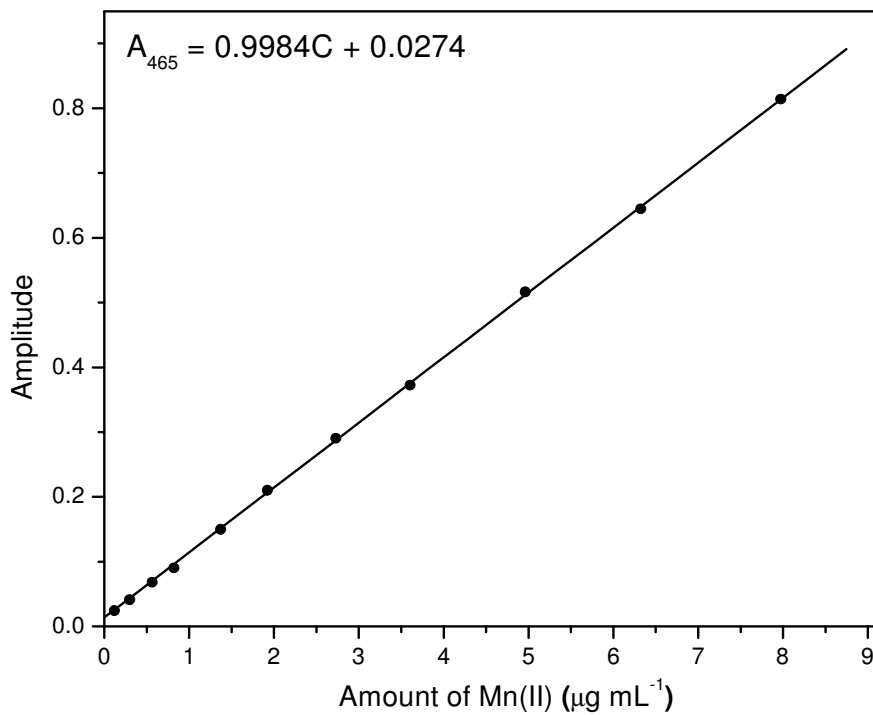


Fig. 4.ii.4. Second derivative amplitude Vs amount of Mn(II)
 $\lambda = 465$; pH = 9.5

Discussion

The present direct spectrophotometric method is simple, fast, and sensitive for the determination of Mn (II). The metal ion reacts with 2-amino acetophenone isonicotinoyl hydrazone forming greenish coloured water soluble complex in basic pH condition. The greenish colour was stable for more than 48 hours. The absorption spectrum of [Mn (II) - 2-AAINH] complex showed maximum absorbance at 435 nm, the reagent absorbance was negligible at this wavelength. A 20 fold molar excess of reagent was necessary to obtain maximum colour intensity with a given amount of metal ion.

The complex system was found to obey Beer's law in the range 0.13-2.74 $\mu\text{g mL}^{-1}$ with Molar absorptivity $1.49 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, Sandell's Sensitivity $3.5 \times 10^{-3} \mu\text{g cm}^{-2}$. The present method was applied for the determination of manganese in tap water and diverse samples.

The stoichiometric studies on the greenish coloured water soluble complex showed a 1:1 composition. The stability constant of the complex was calculated as 2.7×10^{11} . The analytical results obtained by the proposed method are in good agreement with the amounts of Mn (II) added. In order to improve the sensitivity and selectivity of the analytical method proposed, an attempt has been made to develop derivative spectrophotometric methods for the determination of manganese (II), in which Beer's law range is improved and tolerance limits of interference ions such as Ni (II), Au (III) and Pd (II) which were low in the direct method were improved in derivative method. The derivative method was applied for the determination of manganese in manganese steels. The results of the present method were compared with those of some of the reported spectrophotometric methods and are presented in Table 4.ii.5.

The results reveal that the present method is non-extractive, comparable in its sensitivity and selectivity with some of the reported methods establishing its place among the spectrophotometric methods for the determination of manganese.

Table 4.ii.5
Analytical results of various spectrophotometric determinations for Manganese

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
1,5-Diphenylcarbazone	531	4.8	0.058	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
1-(4-Nitrophenyl)-5-phenylcarbazone	595	4.8	0.17	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
1-Phenyl-5-(4-nitro-phenyl) carbazone	572	4.8	0.15	-	Cu(II), Zn(II), Cd(II), Hg(II) Co(II), Ni(II)	9
o-Aminobenzohydroxamic acid	500	-	0.37	1.0-17.0	-	27
Thiothenoyltri-fluoracetone	375	7.3	0.35	-	-	28
5,5'-Dithiodi (salicylo-0.196 hydroxamic acid)	495	9.0	0.196	0.3-2.3	-	44
Benzohydroxamic acid	500	9.0	0.569	-	-	49
Resacetophenone oxime	380	10.5	2.5	0.09-1.7	Applied to the determination of manganese in some steel and alloy samples	54
Picolinaldehyde nicotinoylhydrazone	385	8.7-10.5	4.606	0.02-1.5	Extraction method	60
Picolinaldehyde nicotinoylhydrazone	385	8.7-10.5	4.606	0.02-1.5	Extraction method	60
2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBTSC)	435	9.0-10.0	1.96	0.1373- 2.746	The method is applied for the tap water, cement samples, milk, steel alloys and plant samples	64

Table 4.ii.5 contd....

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ (l mol ⁻¹ cm ⁻¹)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone	495	5.0-10.0	1.02	0.27-4.12	The method is applied for the tap water, cement samples, milk, steel alloys and plant samples	65
7- Bromo, 8 –Hydroxy Quinoline	390	8.0	4.12×10^3	0.8-6.4	Environmental samples	68
2-Amio Acetophenone Isonicotinoyl Hydrazone	435	9.5	1.49	0.13-2.74	-	Present method

REFERENCES

1. Vincent Sanchlli, "Trace elements in Agriculture", Vannosto and Reinhold; New York (1969).
2. Conor Reilly, "Metal contamination of Food", Applied Science Publishers Ltd; London (1980).
3. Platte, J.A., **Trace Inorganic in water Adv. Chem. Ser., 73**, 247(1968).
4. Marczenko, Z., **Seperation and Spectrophotometric Determination of Elements**, Horwood, Chichester (1986).
5. Chiswell, B. and Rauchle, G., *Talanta*, **37**, 237 (1990).
6. Marczenko, Z., *Crit. Rev. Anal. Chem.*, **11**, 195 (1981)
7. Onishi, H., **Photometric Determination of Traces of Metals**, Part IIA, Individual metals, Aluminium to Lithium. Willy, New York (1986).
8. Lobinski, R. and Marczenko, Z., *Crit. Rev. Anal. Chem.* **23(1)**, 55 (1992).
9. Czech, N., Friese, B. and Umaland, F., *Anal. Chim. Acta*, **121**, 275 (1980).
10. Asuero, A.G. and Gonzalez-Balairan, M., *Microchem. J.*, **25**, 14 (1980).
11. Wei, F., Qu, P. and Zhu, Y., *Fen His Hua Hsueh*, **9**, 345 (1981); **Chem. Abstr.**, **5**, 231307h (1981).
12. Guseinov, I.K. and Zeinalova, S.A., *Azerb Khim. Zh.*, **2**, 130 (1980).
13. Lal, K., Malhotra, S.R. and Katyal, R.P., *J. Inst. Chem. (India)*, **53**, 13 (1981).
14. Mantecon, A., Cadiz, V. and Cerda, V., *Afinidad*, **38**, 137 (1981); **Chem. Abstr.**, **95**, 125431j (1981).
15. Yan, B.Z., Qin, Y.F. and Zeng, X.G., *Ssu-Chuan I Hsueh Yuan Hsueh Pao*, **12**, 68 (1981); **Chem. Abst.**, **95**, 111183t (1981).
16. Ishii, H., Koh, H. and Saton, K., *Anal. Chim. Acta*, **136**, 347 (1982).
17. Mori, I., Fujita, Y., Sakaguchi, K. and Kitano, S., *Bunseki Kagaku*, **31**, E 239 (1982); **Chem. Abstr.**, **97**, 119729n (1982).
18. Gaokar, U.G. and Eshwar, M.C., *Mikrochim. Acta*, **II**, 247 (1982).
19. Reddy, P.B.S. and Rao, S.B., *Acta Cienc. Indica*, **7**, 100 (1981); **Chem. Abstr.**, **97**, 48885x (1982).
20. Singh, J., Sharma, K.N., Jetley, U.K., Rastogi, S.N. and Bhuee, G.S., *Chem. Era*, **18**, 218 (1982); **Chem. Abstr.**, **99**, 98456v (1983).

21. Zeibnalova, S.A., Guseinov, I.K. and Rustamov, N. Kh., *Zh. Analit. Khim.*, **38**, 241 (1983); *Chem. Abstr.*, **98**, 172181z (1983).
22. Mongay, C., Rodriguez, E., Borrull, F. and Cerda, V., *Anal. Quim. Ser. B.*, **78**, 247 (1982); *Chem. Abstr.*, **98**, 46045v (1983).
23. Hoshi, S. and Inoue, S., *Bunseki kagaku*, **32**, 287 (1983); *Chem. Abstr.*, **99**, 15674r (1983).
24. Salinas, F., Jimenez-Arrabal, M. and Mahedero, M.C., *Anal. Lett.*, **16**, 1449 (1983).
25. Salinas, F., Forteza, R. and March, J.G., *Quim. Anal. (Barcelona)*, **2**, 283 (1983); *Chem. Abstr.*, **102**, 142416p (1985).
26. Salinas, F., Estela, J.M. and Forteza, R., *Afinidad*, **40**, 359 (1983).
27. Salinas, F., Linas, M. and Estela, J.M., *Quim. Anal. (Barcelona)*, **2**, 38(1983).
28. Deguchi, M. and Hayakawa, S., *Bunseki kagaku*, **31**, 612 (1982).
29. Oglobina, R.I., Kholevinskaya, L.V. and Emelyanova, L.N., *O.S.S.R. Patent*, S.U. 1033939 (1983); *Chem. Abstr.*, **99**, 168730f (1983).
30. Khalikov, S.S. and Alekseevskii, V.A., *Fiz-Khim. Issled. Sint. Prir. Soedin*, **42**, (1983); *Chem. Abstr.*, **99**, 1511235a (1983).
31. Salinas, F. and March, J.G., *Quim. Anal. (Barcelona)*, **3**, 11 (1984); *Chem. Abstr.*, **102**, 159644j (1985).
32. Li, H. and Tu, M., *Fenxi Huaxue*, **12**, 695 (1984); *Chem. Abstr.*, **102**, 55255s (1985).
33. Li, Z., *Fenxi Huaxue*, **13**, 96 (1985).
34. Xu, Q., Zhou, Z. and Yin, Z., *Fenxi Huaxue*, **13**, 170 (1985).
35. Salinas, F. and Jimenez-Arrabal, M., *Microchem. J.*, **31**, 113 (1985).
36. Khan, H. and Amin, M., *Pak. J. Sci. Ind. Res.*, **27**, 263 (1984); *Chem. Abstr.*, **102**, 71980e (1985).
37. Ohshita, K., Wada, H. and Nakagawa, H., *Anal. Chim. Acta*, **140**, 291 (1982).
38. Kastelan-Macan, M., Cerjan-Stefanovi, S., Pavlinic, M. and Kapoor, F., *Kem. Ind.*, **36**, 113 (1987).
39. Hydes, D.J., *Anal. Chim. Acta*, **199**, 221 (1987).
40. Kuroda, R., Matsuzawa, Y. and Oguma, K., *Z. Anal. Chem.*, **326**, 156 (1987).
41. Cheng, D. and Li, Z., *Fenxi Huaxue*, **107**, 189871b (1987).
42. Salinas, F., Jimenez Sanchez, J.C. and Galeano Diaz, T., *Microchem. J.*, **36**, 285 (1987).

43. Zhang, Y. and Xiang Lihua Jianyan, L., *Huaxue Fence*, 24, 54 (1988); *Anal. Abstr.*, 50, 10B207 (1988).
44. Martinez Vidal, J.L., Gonzalez Parra, J. and Salinas, F., *Microchem. J.*, 37, 241 (1988).
45. Zheng, Z. and Zheng, Q., *Huaxue Shiji*, 10, 75 (1988); *Anal. Abstr.*, 51, 1B152 (1989).
46. Menon, S.K., Agarwal, Y.K. and Desai, M.N., *Talanta*, 36, 675 (1989).
47. Rustannov, N., Kh., *Azerb. Khim. Zh.*, 2, 125 (1988).
48. Zhang, W. and Jianyan, L., *Huaxue Fence*, 24, 210(Ch) (1988).
49. Mustafa, A.I. and Chakraborty, A.K., *J. Bangladesh Chem. Soc.*, 2, 167 (1989).
50. Li, C. and Li, Z., *Fenxi Huaxue*, 14, 682 (1986); *Anal. Abstr.*, 49, 6B164 (1987).
51. Ishchenki, N.N., Gauago, L.I. and Starobinets, L.G., *Vestsi Akad. Navuk. Ser. Khim. Navuk*, 2, 3 (Russ) (1990).
52. Chin, C.S., Johnson, K.S. and Coale, K.H., *Marine Chemistry*, 37, 65 - 82 (1992).
53. Thorburn Burns, D., Harriott, M. and Barakat, S.A., *Anal. Chim. Acta*, 258, 325 - 328 (1992).
54. Kesava Rao, C., Babaiah, O., Krishna Reddy, V. and Sreenivasulu Reddy, T., *Talanta*, 39, 1383 - 1385 (1992).
55. Chakraborti, N. and Roy, S.K., *Talanta*, 40, 1499 - 1503 (1993).
56. Kamburova, M., *Talanta*, 46, 1073 - 1078 (1998).
57. Yin, J., yang, G., Yang, Y. and Xu, Q., *Metallurgical Analysis (China)*, 18, No.3, 12 - 13 (1998).
58. Zi-Tao Jian, Rong Li, Jian-Bo Xi and Bu-Qing Yi, *Anal. Chim. Acta*, 50, 913 - 919 (1999).
59. Idriss, K.A., Sedaira, H., Abdel-Aziz, M.S. and Ahmad, H.M., *Talanta*, 50, 913 - 919 (1999).
60. Powar, R.B., Padgaonkar, S.B. and Sawant, A.D., *Indian journal of chemical technology*, 8, 200-203 (2001).
61. Tantanu, G., Dorneanu, V. and Stan, M., *Journal of Pharmaceutical and Biomedical Analysis*, 27, 827 - 832 (2002).

62. Jiang, Z.T., Li, R. and Yu, J.C, *Supramolecular Chemistry*, **14**, 373 - 378 (2002).
63. Mahir Alkan and Derya Kara, *Journal of Trace and Microprobe Techniques*, **21**, 479 - 491 (2003).
64. Pravenkumar,A., Raveendra Reddy,P and Krishna Reddy,V., *Eurasian journal of analytical chemistry*, **4**, 66-75 (2009).
65. Saifulla khan, P., Raveendra Reddy, P and Krishna Reddy, V., *International journal of chemical and analytical sciences*, **2**, (2011).
66. Rehman, F and Samya, M., *Oriental Journal of Chemistry*, **28**, 881-885 (2012).
67. Chauhan, J.S and Pandya, A.V. *International journal of engineering science invention*, **2**, 2(2013).
68. Rahul, R.W., *International journal of Pharmaceutical research and development*, **6**,153-156 (2014).