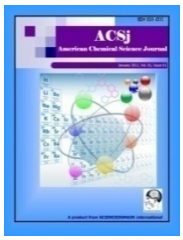

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High Sensitive and Selective Spectrophotometric Method for the Determination of Trace Level of Manganese in Some Real, Environmental, Biological, Soil, Food, Fertilizer and Pharmaceutical Samples Using Bis(2-hydroxy-1-naphthaldehyde) Orthophenylenediamine

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Authors' contributions

This work was carried out in collaboration between all authors. Author MJA designed the study, wrote the protocol, wrote the first draft of the manuscript and supervised the overall works. Authors MTI and SPL were carried out all the laboratory works, performed the statistical analysis, managed the literature searches and prepared the final manuscript. All three of us read and approved the final manuscript.

Original Research Article

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ABSTRACT

A very simple, ultra-sensitive and highly selective non-extractive spectrophotometric method is present for the determination of manganese at trace level using bis(2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA) has been proposed as new analytical reagent for the direct non-extractive spectrophotometric determination of manganese(II). HNA-OPD-HNA reacts in a slightly acidic (0.000002-0.00001M H_2SO_4) with manganese (II) in 50% N, N-dimethylformamide (DMF) to produce highly absorbent an orange chelate which has an absorption maximum at 508 nm. The reaction is instantaneous and the absorbance remains stable for over 24 h. The average molar absorption co-efficient and

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Sandell's sensitivity were found to be 4.89×10^6 L $mol^{-1}cm^{-1}$ and 10 ng cm^{-2} of manganese (II), respectively. Linear calibration graphs were obtained for 0.02-25 mg L^{-1} of manganese(II) having detection limit of 1 µg L^{-1} and quantification limit of the reaction system were found to be 10 µg L^{-1} and RSD 0-2%. The stoichiometric composition of the chelate is 1:1 (Mn: HNA-OPD-HNA). A large excess of over 60 cations, anions and complexing agents (like, chloride, phosphate, azide, tartrate, oxalate, SCN^- etc.) do not interfere in the determination. The developed method was successfully used in the determination of manganese in several Standard Reference Materials (alloys and steels) as well as in some environmental waters (portable and polluted), biological samples (human blood, urine and hair), soil samples, food samples (vegetables, fruits, tea, rice, wheat), fertilizer samples and pharmaceutical samples (multivitamin-mineral tablet and syrup), solution containing both manganese (II) and manganese (VII) and complex synthetic mixtures. The results of the proposed method for biological and food samples were comparable with AAS and were found to be in excellent agreement. The method has high precision and accuracy (s=±0.01 for 0.5 mg L^{-1}).

Keywords: Spectrophotometry; manganese determination; bis (2-hydroxy-1-napthaldehyde) orthophenylenediamine; alloys; steels; environmental; biological; soil; food samples; pharmaceutical sample.

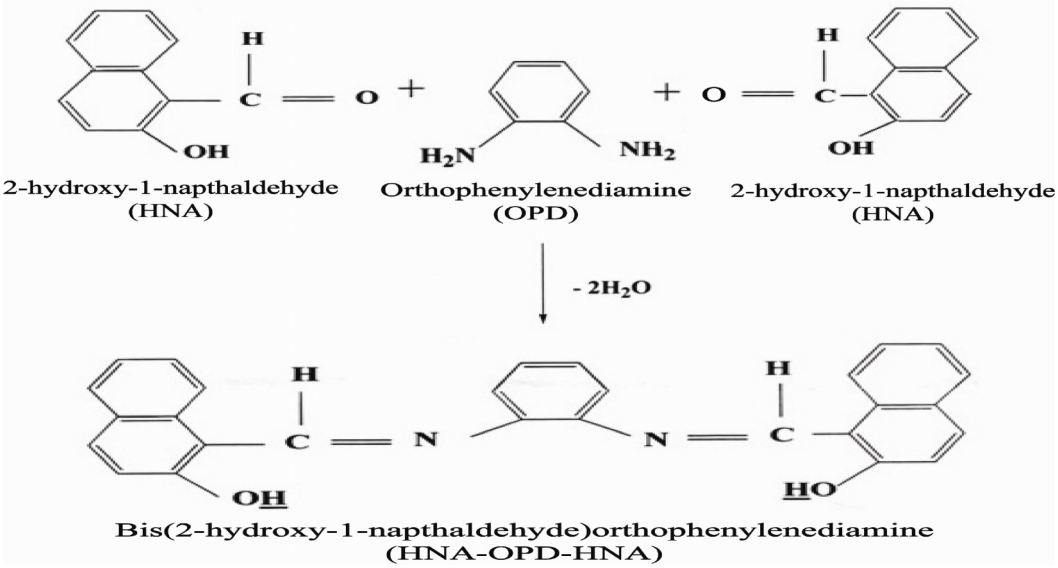
1. INTRODUCTION

Manganese is an essential element for humans, animals, plants and is required for growth, development, and maintenance of health [1]. It plays an important role in the fixation of carbon dioxide as the activator of the nitrite reductase and it is active catalyst in the formation of primary photochemical oxidation product in photosynthesis [2,3]. Manganese is a microelement actively absorbed by plants and contributes towards the fertility of soils [4]. Manganese is also a well known essential trace element for human beings. It is an active component of several enzymes, including superoxide dismutase, glutamine synthetase and arginase [5]. Manganese is necessary for the proper function of several enzymes and is an essential micronutrient for the function of the brain, nervous system and normal bone growth [6,7]. It optimizes enzyme and membrane transport function [8,9]. Similar to other essential metals, both excess and deficiency of manganese in the body can cause serious impairment of vital physiological and biochemical processes [10]. On the other hand, the toxic role of the metal is also well recognized. Its toxicity varies with its two stable oxidation states, manganese (VII) being significantly more toxic than manganese (II) and also a carcinogen even at trace levels. Therefore, oxidation-state specific determination of manganese is of particular interest. Increasing accumulation of manganese in the environment through numerous pharmaceutical, food, drinks and industrial sources, poses danger to public health. All these findings cause great concern regarding public health, demanding accurate determination of this metal ion at trace and ultra-trace levels.

In expanding analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop the simple, sensitive and selective analytical techniques that do not use expensive or complicate test equipment. Many sophisticated technique, such as pulse polarography, NAA, HPLC, Spectrophotometry, Spectrofluorimetry, AAS, FAAS, ICP-OES and ICP-MS have been widely applied to the determination of manganese. However, the spectrophotometric method still has the advantages of being simple and without requiring expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric methods for determination of

manganese has been developed. Several authors have reported on the extractive spectrophotometric determination of manganese (II) using complexes formed variety of reagents [11-22]. In most of the methods [11-22] cited above, manganese forms soluble or insoluble complexes with reagents with varies organic solvents for spectrophotometric determination. Most of these methods [11-22] are solvent extractive, expensive and non-recoverable. A comparison of few selected methods [11-22], their spectral characteristics and draw backs are summarized in Table 1.

The aim of this study was to develop a simpler direct spectrophotometric method for the trace determination of manganese. In the search for a more sensitive reagent, in this work a new Schiff's base reagent bis (2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA) was synthesized Scheme 1 according to the method of Sacconi [23] and a color reaction of HNA-OPD-HNA with Mn(II). HNA-OPD-HNA has not previously been used for the spectrophotometric determination of any metal. This paper reports first time on its use in a very sensitive, highly specific spectrophotometric method for the trace determination of manganese. The method possesses distinct advantages over existing methods [11-22] Table 1 with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent HNA-OPD-HNA in a slightly acidic solution (0.000002-0.00001M H_2SO_4) with Mn (II) in 50% DMF medium to produce a highly absorbent orange colored chelate product, followed by a direct measurement of the absorbance in an aqueous solution. With suitable masking, the reaction can be made to be highly selective and the reagent blank solution does not show any absorbance.



Scheme 1. Bis (2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA)

Table 1. Summary of review on the existing spectrophotometric methods for the determination of manganese

Reagent	$\lambda_{max/nm}$	€(L mol $^{-1}$ cm $^{-1}$)	Beer's Law mg L $^{-1}$	Interference	Remarks	Ref.
1-(2-quinolylazo)-2,4,5-trihydroxybenzene	560	4.60× 10 ^{4}	0.5- 20	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH- dependent. iv) Solvent extractive hence, lengthy and time consuming. v) Application in foodstuffs only.	11
Protocatechuic acid	480	4.8 × 10 ^{3}	1.4-11.2	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH - dependent. iv) Solvent extractive hence, lengthy and time consuming.	12
Potassium periodate, sulphanilic acid	540	4.6 × 10 ^{3}	0.2- 6.0	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH - dependent. iv) Solvent extractive hence, lengthy and time consuming.	13
Palmitoyl quinolin-8-ol (P.Ox)-functionalized Amberlite XAD-2 copolymer resin (XAD-P.Ox)	485	4.2 × 10 ^{4}	0.08-15	Many	i) pH - dependent . ii) Less sensitive. iii) Less selective due to much interference. iv) Solvent extractive hence, lengthy and time consuming.	14
α, β, γ, δ-tetrakis(4-carboxyphenyl)porphine [T(4-CP)P]	469	3.8 × 10 ^{3}	25-560	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH- dependent. iv) Solvent extractive hence, lengthy and time consuming. v) Limited application.	15

Table 1 Continued…

5,8-dihydroxy-1,4-naphthoquinone (naphthazarin, NAZA)	695	1.88×10^4	0.28-5.6	Many	i) Less sensitive. ii) Less selective due to much interference. iii) Solvent extractive hence, lengthy and time consuming. iv) Limited application.	16
Penoxazine (PNZ),3-methyl-2-benzothiozolinone hydrazone hydrochloride hydrate (MBTH), amiloride (ALR) and acyclovir (AYR)	520	2.69×10^4	0.21-1.82	Many	i) Less sensitive. ii) Less selective due to much interference. iii) Solvent extractive hence, lengthy and tim consuming. iv) Limited application.	17
Iminodiacetate (IDA) resin (Toyopearl AF-chelate 650M), Nitrilotriacetic acid	460	4.5×10^4	0.08-50	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH- dependent. iv) Limited application.	18
3-methyl-6-(2-chloroethoxy)-2-[2-methoxy-4-(N,N-diethylamino) phenylazo] benzothiazolium methyl sulfate, Ptassium periodate	550	4.8×10^4	0.03-3.0	Many	i) pH - dependent. ii) Less sensitive. iii) Less selective due to much interference. iv) Solvent extractive hence, lengthy and tim consuming. v) Limited application.	19
Diphenylcarbazone (DFC)	560	4.6×10^3	0.10-4.00	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH - dependent. iv) Solvent extractive hence, lengthy and time consuming. v) Limited application.	20

					i) pH - dependent ii) Less sensitive. iii) Less selective due to much interference. iv) Solvent extractive hence, lengthy and time consuming. v) Limited application.	21
Gluconic acid	440	3.5×10^{3}	9.44-47.2	Many		
7,7,8,8-tetracyanoquinodimethane	530	3.8×10^{4}	0.06-15	Many	i) Less sensitive. ii) Less selective due to much interference. iii) pH- dependent. iv) Solvent extractive hence, lengthy and time consuming. v) Application in natural waters only.	22
Bis(2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA)	508	4.89×10^{6}	0.02-25	Using suitable masking agents, the reaction can be made highly selective	i) Highly selective. ii) Ultra sensitive. iii) Aqueous reaction medium. iv) Simple and rapid. v) Color stable more than 24 h at 25 ± 5^{0}C. vi) Non -extractive. vii) Application in various real, environmental, biological, soil, food, fertilizer and pharmaceutical samples.	Present method

2. EXPERIMENTAL SECTION

2.1 Apparatus

A Shimadzu (Kyoto, Japan) (Model-1800) double-beam UV/VIS spectrophotometer and a Jenway (England, UK) (Model-3010) pH meter with combined of electrodes were used for measurements of the absorbance and pH, respectively. A Thermo Fisher Scientific (Model-iCE 3000, origin USA) atomic absorption spectrophotometer equipped with a microcomputer-controlled nitrous oxide-acetylene flame was used to compare the results. Infrared spectrum was recorded with FTIR Spectrophotometer, Shimadzu (Model-IR Prestige 21, Detector-DTGS KBr) in the range 7500-350 cm^{-1}.

2.2 Synthesis and Characterization of the Reagent

2.2.1 Synthesis of the reagent

The reagent was synthesized in the laboratory according to the method recommended by Sacconi [23] and Salam et al [24]. The reagent bis(2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA) was synthesized by following steps. Solutions of 2-hydroxy-1-napthaldehyde (20 mmol) in 30 mL of ethanol and orthophenylenediamine (10 mmol) in 20 mL of ethanol were prepared separately by gentle warming. The two solutions have been mixed together in drop-wise with continuous stirring. Then it was refluxed for about 1 hour. Some yellowish brown product was seen after cooling. It was kept in ice for proper precipitation. The product was filtered off, washed with ethanol and dried in a desiccator over calcium chloride. Yield of the product was 70%. The structure of the reagent is shown in Scheme 1.

2.2.2 Characterization of the reagent

The reagent was characterized by taking melting point, elemental analysis, FTIR spectrum and thermogravimetric analysis. The melting point of the reagent was 110-112°C (Lit. 113°C) [23]. The results of elemental analysis (C = 70.65, N= 11.94, H=5.48) % of the reagent was in good coincidence with the calculated values (C=70.85, N=11.02, H=5.55) % [23]. The presence of FTIR peak at 1651.4 cm^{-1} was due to the characteristic C=N double bond peak ($v^{C=N}$,1590 - 1660 cm^{-1}) [23] of the Schiff's base reagent indicating the formation of HNA-OPD-HNA. The steadiness of the thermogravimetric curve indicated that the reagent did not contain any moisture.

The elemental analysis were performed by the National Center of Excellence in Analytical Chemistry, University of Sindh, Pakistan and FTIR spectra was recorded with FTIR spectrophotometer, Shimadzu (Model-IR Prestige 21, Detector-DTGS KBR) in the range 7500-350 cm^{-1} from our laboratory.

2.3 Reagents and Solutions

All the chemicals used were of analytical reagent grade of the highest purity available. High-purity DMF (N, N-dimethylformamide) and high-purity de-ionized water, which are non-absorbent under UV radiation, were used in all experiments. High-purity water was obtained by passing tap water through cellulose absorbent and to mixed-bed ion exchange columns, followed by distillation in a corning AG-11 unit. The Al level in the high-purity water was

found to be below the spectrophotometric detection limit (3s of the blank) of 1 μg L^{-1}. Glass vessel were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with concentrated HNO_3 and rinsed several times with high purity de-ionized water. Stock solutions and environmental water sample (1000 mL each) was kept in polypropylene bottles containing 1mL conc. HNO_3. More rigorous contamination control was used when the manganese levels in the specimens were low.

2.3.1 Bis (2-hydroxy-1-napthaldehyde) orthophenylenediamine solution (2.40×10^{-3}M)

The reagent solution was prepared by dissolving the requisite amount of HNA-OPD-HNA, in a known volume of N, N-dimethylformamide (DMF). More dilute solutions of the reagent were prepared as required.

2.3.2 Mn (II) standard solution (1.83×10^{-2}M)

A 100 mL amount of stock solution (1 mg mL^{-1}) of divalent manganese was prepared by dissolving 307.7 mg of purified-grade (E Merck proanalysis grade) monohydrated manganese sulphate ($MnSO_4.H_2O$) (super special grade J. T. Baker) in doubly distilled de-ionized water and subsequently standardized titrimetrically with disodium ethylenediamine tetraacetate (Na_2EDTA) using Eriochrome Black T [25]. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water if and when required.

2.3.3 Manganese (VII) standard solution

A 100-mL amount of stock solution (1 mg mL^{-1}) of heptavalent manganese was prepared by dissolving 287.66 mg of potassium permanganate ($KMnO_4$) (Aldrich A.C.S. grade) in doubly distilled de-ionized water. Aliquots of this solution were standardized with oxalic acid. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water if and when required.

2.3.4 Potassium dichromate solution

A 100 mL amount of stock solution (0.1 N) was prepared by dissolving 500 mg of finely powdered $K_2Cr_2O_7$ (Merck) in 100 mL deionized water.

2.3.5 Sodium azide solution

Sodium azide solution (2.5 % w/v) (Fluka purity > 99%) was freshly prepared by dissolving 2.5 gm in 100 mL of deionized water.

2.3.6 Tartrate solution

A 100 mL stock solution of tartrate (0.01 % w/v) was prepared by dissolving 10 mg of A.C.S.-grade (99%) potassium sodium tartrate tetrahydrate in (100 mL) de-ionized water.

2.3.7 Aqueous ammonia solution

A 100 mL solution of an aqueous ammonia solution was prepared by diluting 10 mL concentrated NH_4OH (28-30%, A.C.S.-grade) to 100 mL with de-ionized water. The solution was stored in a polypropylene bottle.

2.3.8 EDTA solution

A 100 mL stock solution of EDTA (0.01 % w/v) was prepared by dissolving 10 mg A.C.S.-grade (≥ 99%) ethylenediaminetetraacetic acid as disodium salt dihydrate in (100 mL) deionized water.

2.3.9 Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their AnalaR grade or equivalent grade water-soluble salts (or the oxides and carbonates in hydrochloric acid); those of niobium, tantalum, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure, Johnson Matthey) according to the recommended procedures of Mukharjee [26]. In the case of insoluble substances, special dissolution methods were adopted [27].

2.4 Procedure

A volume of 0.1-1.0 mL of a neutral aqueous solution containing 0.2-250 µg of manganese (II) in a 10 mL calibrated flask was mixed with a 1:100-1:500 fold molar excess of the bis(2-hydroxy-1-napthaldehyde) orthophenylenediamine (HNA-OPD-HNA) reagent solution (preferably 1 mL of 2.40×10^{-3} M) followed by the addition of 0.02 -0.10 mL (preferably 0.05 mL) of 0.001 M of sulfuric acid. After 1 min, 5ml of N, N-dimethylformamide (DMF) was added and the mixture was diluted to the mark with de-ionized water. The absorbance was measured at 508 nm against a corresponding reagent blank. The manganese content in an unknown sample was determined using a concurrently prepared calibration graph.

2.5 Sample Collection and Preservation

2.5.1 Environmental samples

Water and soil samples were collected in polythene bottles from different places of Bangladesh. After collection, HNO_3 (1 mL^{-1}) was added as preservative.

2.5.2 Blood and urine

Blood and urine samples were collected in polythene bottles from effected persons of Chittagong Medical College Hospital, Bangladesh. Immediately after collection they were stored in a salt-ice mixture and latter, at the laboratory, they were at-20°C.

2.5.3 Soil samples

Soil samples were collected from different locations of Bangladesh. Samples were dried in air and homogenized with a mortar.

2.5.4 Food samples

Food samples (rice, wheat, tea, fruits and vegetables) were collected from local market of Chittagong. After collection the samples (fruits and vegetables) were stored in refrigerator for preservation. Samples (rice, wheat, tea) were used under dry condition and homogenized with a mortar.

2.5.5 Pharmaceutical samples

Pharmaceutical samples (tablet and syrup) of different companies were collected from local pharmacy of Chittagong. Samples (tablet) were homogenized with a mortar.

3. RESULTS AND DISCUSSIONS

3.1 Factors Affecting the Absorbance

3.1.1 Absorption spectra

The absorption spectra of the Mn(II)-HNA-OPD-HNA in 0.001M sulfuric acid medium was recorded using a spectrophotometer. The absorption spectra of the Mn(II)-HNA-OPD-HNA is asymmetric curve with maximum absorbance at 508nm; an average molar absorption coefficient of 4.89×10^6 L mol^{-1} cm^{-1} is shown in Fig. 1. HNA-OPD-HNA did not show any absorbance. In all instances, measurements were made at 508 nm against a reagent blank. The reaction mechanism of the present method is as reported earlier [24].

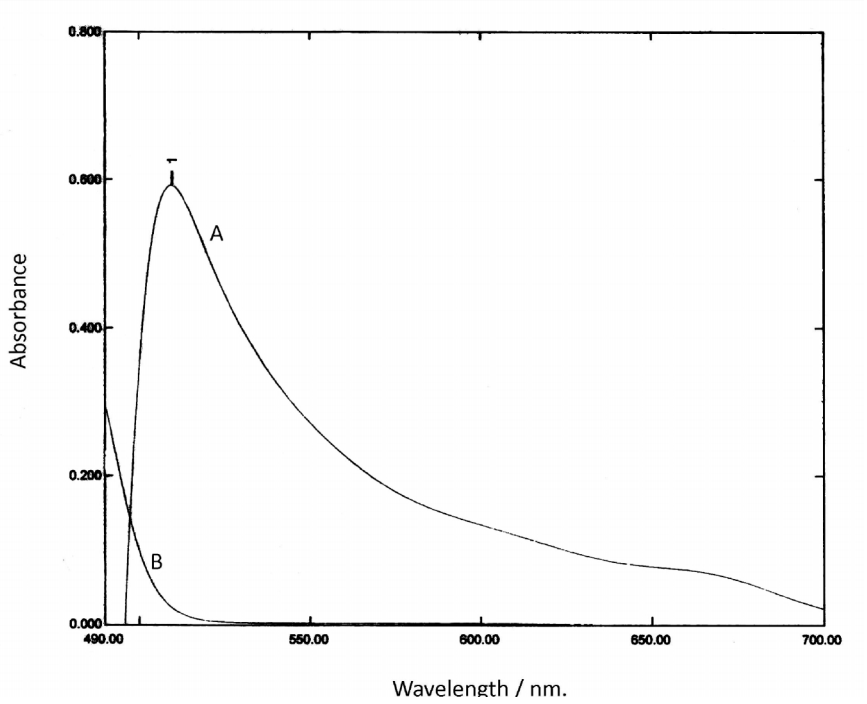


Fig. 1. A and B absorption spectra of Mn(II) -HNA-OPD-HNA system and the reagent blank (λ_{max} = 508 nm) in aqueous solutions.

3.1.2 Effect of solvent

Because HNA-OPD-HNA is insoluble in water, an organic solvent was used for the system. Of the various solvents [chloroform, benzene, carbon tetrachloride, n-butanol, isobutanol, ethanol, 1, 4-dioxane and N, N-dimethylformamide (DMF)] were tested for the system, DMF was found to be the best solvent for the system. No absorbance was observed in the organic

phase with the exception of n-butanol. In 50±2% v/v DMF medium, however maximum absorbance was observed; hence a 50% (5-mL) DMF solution was used in the determination procedure. It was observed that at 1 mg L^{-1} of Mn(II) - HNA-OPD-HNA,50-80%(5-8 mL) of DMF solution produced a constant absorbance of the Mn(II)-Chelate Fig.2.

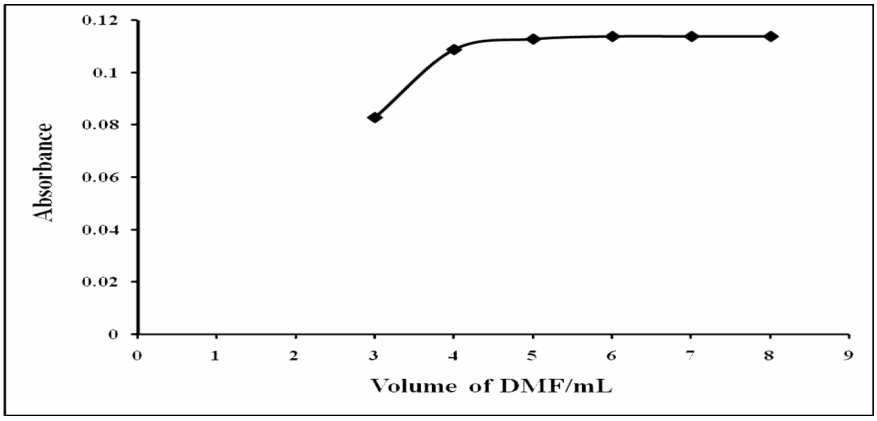


Fig. 2. Effect of solvent (DMF) on the absorbance of Mn(II) -HNA-OPD-HNA system.

3.1.3 Effect of acidity

Of the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied, sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when the 10-mL of solution (1 mg L^{-1}) contained 0.02-0.1-mL of 0.001 M sulfuric acid at room temperature (25±5ºC). Outside this range of acidity, the absorbance decreased Fig. 3. For all subsequent measurements 0.05-mL of 0.001 M sulfuric acid was added.

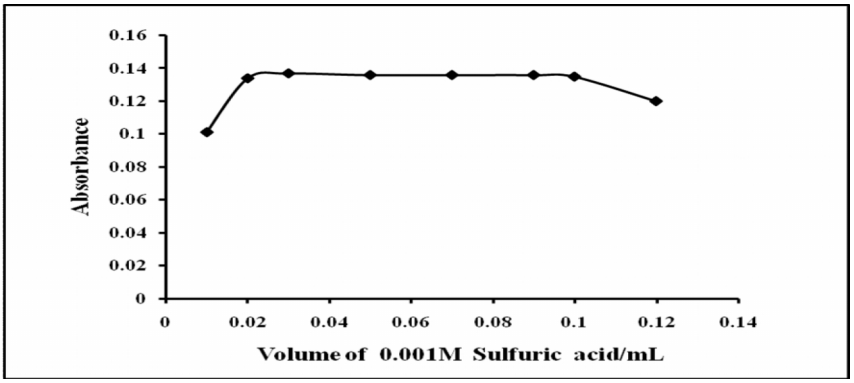


Fig. 3. Effect of acidity on the absorbance of Mn(II)-HNA-OPD-HNA system.

3.1.4 Effect of time

The reaction is instantaneous. The Mn (II)-HNA-OPD-HNA system attained immediately maximum and constant absorbance (within 1 min) after the solution was diluted to the final volume, which then remained strictly unaltered for 24 h.

3.1.5 Effect of reagent concentration

Different molar excesses of HNA-OPD-HNA were added to a fixed metal ion concentration and absorbances were measured according to the standard procedure. It was observed that at 1 mg L^{-1} Mn(II) metal, the reagent molar ratios of 1:100-1:500 produced a constant absorbance of the Mn-chelate. Outside this range of reagent, the absorbance decreased Fig. 4. For all subsequent measurements 1 mL of 2.4 × 10^{-3} M HNA-OPD-HNA reagent was added.

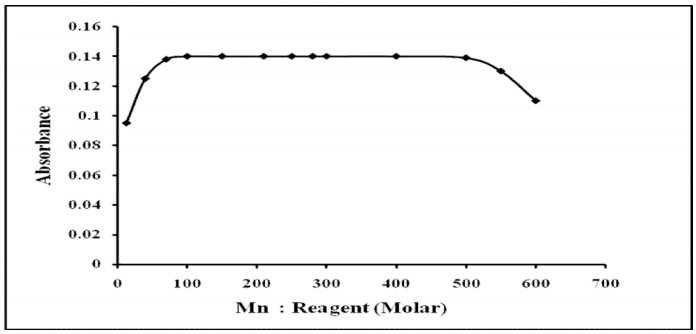


Fig. 4. Effect of reagent on the absorbance of Mn(II)-HNA-OPD-HNA system.

3.1.6 Calibration graph (Beer's law and sensitivity)

The well-known equation for spectrophotometric analysis in very dilute solutions derived from Beer's law. The effect of metal concentration was studied over 0.01-100 mg L^{-1} distributed in four different sets (0.01-0.1, 0.1-1, 1-10 and 10-100 mg L^{-1}) for convenience of measurement. The absorbance was linear for 0.02-25 mg L^{-1} of manganese at 508 nm. Of four calibration graphs, the one showing the limit of the linearity range Fig. 5; the next three were straight-line graphs passing through the origin (R^2 = 0.9998). The molar absorptivity and Sandell's sensitivity [28] were found to be 4.89 × 10^6 L mol^{-1} cm^{-1} and 10 ng cm^{-2} of manganese (II), respectively. The selected analytical parameters obtained with the optimization experiments are summarized in Table 2.

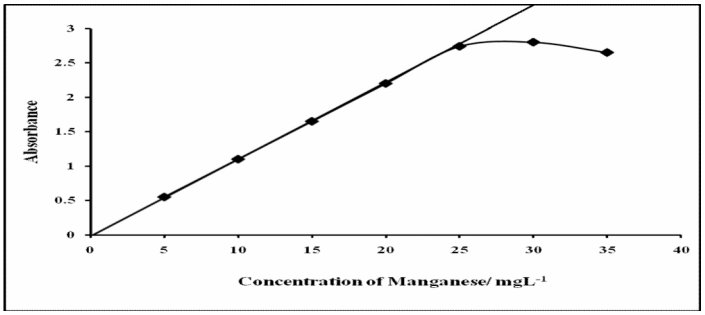


Fig. 5. Calibration graph D: 10 – 25.0 mg L^{-1} of Mn (II)

Table 2. Selected analytical parameters obtained with the optimization experiments

Parameters	Studied range	Selected value
Wavelength / λ_{max} (nm)	200-800	508
Solvent / % N,N-dimethylformamide (DMF)	10-80	50-80 (Preferably 50)
Acidity / M H_2SO_4	0.000001-0.0001	0.000002-0.00001 (Preferably 0.000005)
pH	5.0-2.5	4.25-4.00 (Preferably 4.22)
Time / h	0 - 72	1min-24 h (Preferably 1 min)
Temperature / °C	10-70	15-40 (Preferably 25 ± 5)
Reagent (fold molar excess, M:R)	1:1 - 1:500	1:100 - 1:500 (Preferably 1: 100)
Linear range/mg L^{-1}	0.01-100	0.02- 25
Molar absorption coefficient / L mol^{-1} cm^{-1}	4.52 x 10^6 –5.26 x 10^6	4.89 x 10^6
Sandell's sensitivity/ng cm^{-2}	1-100	10
Detection limit/ µg L^{-1}	0.01-10	1
Reproducibility (% RSD)	0 - 10	0 –2%
Regression Co-efficient (R^2)	0.9992-0.9999	0.9998

3.2 Effect of Foreign Ions

More than 60 anions, cations and complexing agents were studied individually to investigate their effect on the determination of 1 mg L^{-1} of manganese (II). The criterion for interference [29] was an absorbance value varying by more than ± 5% from the expected value for manganese alone. The results are summarized in Table 3. As can be seen a large number of ions have no significant effect on the determination of manganese. The most serious interference was from Co (II) and Cr (III) ions. Interference from these ions is probably due to complex formation with HNA-OPD-HNA.The greater tolerance limits for these ions can be achieved by using several masking agents. In order to eliminate the interference of Co (II) and Cr (III) ions, oxalate and tartrate can be used as masking agents, respectively [30]. A 20-fold excess of Co (II) and Cr(III) ions could be masked with oxalate and tartrate, respectively. During the interference studies, if a precipitate was formed, it was removed by centrifugation. Strong reducing agents such as tin (II), chloride, iron (II), sulfate, hydroxylamine hydrochloride and sodium azide, which would otherwise reduce manganese (VII) had no reducing effect on manganese (II). The amount mentioned is not the tolerance limit but the actual amount studied. However, for those ions whose tolerance limits have been studied, their tolerance ratios are mentioned in Table 3.

3.3 Precision and Accuracy

The precision of the present method was evaluated by determining different concentrations of manganese (each analyzed at least five times). The relative standard deviation (n=5) was 2-0% for 0.2-250 µg of manganese (II) in 10 mL, indicating that this method is highly precise and reproducible Table 2. The detection limit (3s of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for manganese (II) were found to be 1 µg L^{-1} and 10

ng cm^{-2}, respectively. The method was also tested by analyzing several synthetic mixtures containing manganese (II) and diverse ions Table 4. The results for total manganese were in excellent agreement with certified values Table 5. The reliability of our manganese-chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of manganese (II) spike to some environmental water samples was quantitative, as shown in Table 6. The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by AAS Table 7. The results of food analyses by spectrophotometric method were also found to be in excellent agreement with those obtained by AAS Table 11. The results of speciation of manganese (II) and manganese (VII) in mixtures were highly reproducible Table 13. Hence, the precision and accuracy of the method were found to be excellent.

Table 3. Table of tolerance limits of foreign ions[a], tolerance ratio (species (x) / Mn (w/w))

Species x	Tolerance ratiox/Mn(w/w)	Species x	Tolerance ratio x/Mn (w/w)
Ammonium (I)	100	Lithium	200
Arsenic (III)	50	Lead (II)	200
Arsenic (V)	50	Magnesium	200
Aluminium	20[b]	Manganese (VII)	20
Azide	200	Mercury (II)	200
Ascorbic acid	100	Molybdenum (VI)	50[c]
Antimony	50	Nitrate	100
Bromide	50	Nickel	100
Bismuth (III)	50	Oxalate	500
Beryllium (II)	100	Potassium	50
Calcium	200	Phosphate	100
Chloride	50	Selenium (VI)	200
Cobalt (II)	20[c]	Selenium (IV)	200
Cobalt (III)	50	Silver	50
Chromium (III)	20[b]	Sodium	200
Chromium (VI)	50	Strontium	50
Cadmium	200	Sulfate	50
Carbonate	100	Titanium (IV)	100
Cesium	100	Tellurium (IV)	200
Citrate	50	Tartrate	500
Copper (II)	50	Thiocyanate	100
Cyanide	20	Thiourea	100
EDTA	200	Tungsten (VI)	50
Fluoride	100	Tin (II)	20[b]
Iodide	200	Tin (IV)	20
Iron (II)	20	Vanadium (V)	200
Iron (III)	20	Zinc	200

[a]Tolerance limit was defined as ratio that causes less than ± 5 percent interference; [b]with 10 mg L^{-1} tartrate; [c]with 10 mg L^{-1} oxalate.

3.4 Composition of the Absorbent Complex

Job's method [31] of continuous variation method was applied to ascertain the stoichiometric composition of the complex under the optimum conditions Table 2. A Mn (II): HNA-OPD-HNA (1:1) complex was indicated by this method Fig. 6. The molar- ratio method [32] was also

applied to ascertain the stoichiometric composition of the complex. A Mn(II) -HNA-OPD-HNA complex was indicated by both methods and the stoichiometry was also found to be 1:1 (Metal: Ligand).

Table 4. Determination of manganese in some synthetic mixtures

Sample	Composition of mixtures (mg L^{-1})	Manganese(II)/ mg L^{-1}		
		Added	Found[a](n=5)	Recovery ± SD[b] (%)
A	Mn^{II}	0.50	0.49	98±0.5
		1.00	1.00	100±0.0
B	As in A + Na (25) + Ca (25)	0.50	0.50	100 ± 0.0
		1.00	1.02	102 ± 0.8
C	As in B + V^{V} (25) + Cd (25)	0.50	0.49	98 ± 0.5
		1.00	0.99	99 ± 0.3
D	As in C + Mg (25) + Zn (25)	0.50	0.53	106 ± 1.3
		1.00	1.05	105 ± 1.0
E	As in D + Hg^{2+} (25)+ Te^{IV} (25)	0.50	0.54	108 ± 2.0
	+ Tartrate (50)	1.00	1.08	108 ± 1.8

[a] *Average of five analyses of each sample.* [b] *The measure of precision is the standard deviation (s)*

Table 5. Determination of manganese in certified reference materials

Sample	Certified reference materials (Composition, %)	Manganese (%)		
		In C.R.M sample	Found (n=5)	RSD[a]
1	BCS-CRM 163, *Unalloyed Steel* (C=1.2, Mn=0.472, Ni=0.608, Si=0.18, Cu=0.05, Cr=0.03)	0.472	0.471	1.5
2	BAS-CRM-10g, *High-speed Brass* (Cu=60.8, Fe=1.56, Pb=0.23, Ni=0.16, Sn=0.21, Al=3.34, Zn=32.0, Mn=1.36)	1.36	1.35	1.0
3	BCS-CRM-238, *Unalloyed Steel* (C=0.2, Si=0.06, S=0.05, Mn=0.51, Ni=0.06, Cr=0.06 and Cu=0.05)	0.51	0.505	2.0
4	BAS-CRM-1d, *Mild Steel* (C=0.19, Si=0.06, S=0.04, Mn=0.52, P=0.04)	0.52	0.518	2.5
5	BAS-CRM-33b, *Alloy Cast Iron* (Mn=0.64, Cr=0.61, Mo=0.04, Ni=2.24)	0.64	0.632	1.8

[a] *The measure of precision is the relative standard deviation (RSD).*

Table 6. Determination of manganese in some environmental water samples

Sample		Manganese(II)/μg L^{-1}		Recovery ± s (%)	s_r[b] (%)
		Added	Found [a] (n=5)		
Tap water		0	45.0		
		100	145.0	100±0.0	0.00
		500	550.0	100.9±0.1	0.35
Well water		0	30.5		
		100	135.0	99.6±0.5	0.39
		500	530.0	100±0.0	0.00
River water	Karnaphuly (upper)	0	65.0		
		100	165.0	100±0.0	0.00
		500	570.0	100.8±0.6	0.21
	Karnaphuly (lower)	0	70.5		
		100	174.0	102±0.4	0.29
		500	565.0	99±0.5	0.39
	Halda (upper)	0	48.0		
		100	148.0	100±0.0	0.00
		500	550.0	100.4±0.8	0.36
	Halda (lower)	0	50.0		
		100	154.0	102.6±0.7	0.38
		500	550.0	100±0.0	0.00
Sea water	Bay of Bengal (upper)	0	25.0		
		100	125.0	100±0.0	0.00
		500	530.0	100.9±0.3	0.31
	Bay of Bengal (lower)	0	27.5		
		100	128.0	100.3±0.5	0.17
		500	530.0	100.5±0.6	0.27
Drain water	T. S. P. Complex[c]	0	125.0		
		100	225.0	100±0.0	0.00
		500	630.0	100.8±0.5	0.25
	PHP[d]	0	155.0		
		100	255.0	100±0.0	0.00
		500	660.0	100.8±0.6	0.29
	BSRM[e]	0	245.0		
		100	550.0	101±0.8	0.45
		500	740.0	99±0.5	0.23
	K.P.M Water[f]	0	185.0		
		100	285.0	100±0.0	0.00
		500	690.0	100.7±0.6	0.35
	Eastern Refinery[g]	0	265.0		
		100	365.0	100±0.0	0.00
		500	670.0	100.6±0.8	0.53

[a]Average of five replicate determinations of each sample; [b]The measure precision is the relative standard deviation(s_r); [c]T. S. P. Complex Ltd., Patenga, Chittagong. [d]PHP Steel Mills, Kumira, Chittagong; [e]Bangladesh Steel Re-rolling Mills Ltd.(BSRM) , Baizid Bosthami, Chittagong. [f]Karnaphuly Paper Mills, Chandraghona, Chittagong; [g]Eastern Refinery, North Patenga, Chittagong

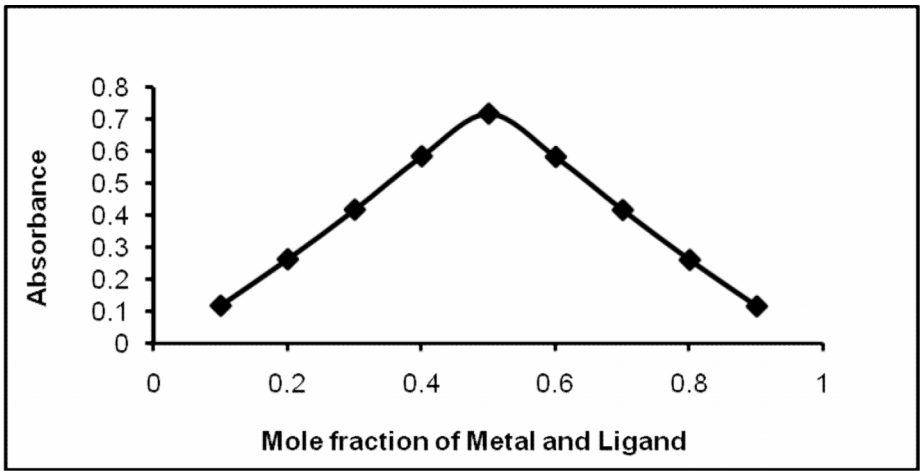


Fig. 6. Job's method for determining the composition of Mn(II) : HNA-OPD-HNA (1 : 1) Complex

4. APPLICATION

The present method was successfully applied to the determination of manganese (II) in a series of synthetic mixtures of various compositions Table 4 and also in a number of real samples e.g. Several Certified Reference Materials (CRM) Table 5. The method was also extended to the determination of manganese in a number of environmental, biological, soil, food, fertilizer and pharmaceutical samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each similar sample were analyzed for manganese content; the recoveries in both the "spiked" (added to the samples before the mineralization or dissolution) and the "unspiked" samples are in excellent agreement Table 6. The results of biological analyses by spectrophotometric method were found to be in excellent agreement with those obtained by AAS Table 7. The results of soil analyses by the spectrophotometric method are shown in Table 8. The results of pharmaceutical samples by the spectrophotometric method are shown in Table 9. The results of vegetable and fruit samples by the spectrophotometric method are shown in Table 10. The results of food analyses by spectrophotometric method were also found to be in excellent agreement with those obtained by AAS Table 11. The results of fertilizer samples by the spectrophotometric method are shown in Table 12.The results of speciation of manganese (II) and manganese (VII) in mixtures are shown in Table 13.

4.1 Determination of Manganese in Synthetic Mixtures

Several synthetic mixtures of varying compositions containing manganese (II) and diverse ions of known concentrations were determined by the present method using tartrate as masking agent. The results were found to be highly reproducible as shown in Table 4. Accurate recoveries were achieved in all solutions.

4.2 Determination of Manganese in Alloys and Steels (Certified Reference Materials)

A 0.1 g amount of an alloy or steel sample containing 0.472 - 1.36% of manganese was

weighed accurately and was placed in a 50 mL Erlenmeyer flask in presence of excess reducing agent following a method recommended by Parker [33]. To it, 10 mL of 20% sulfuric acid was added while carefully covering with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after the addition of 10 mL of concentrated HNO_3 until all carbides were decomposed. Then, 2 mL of 1:1 (v/v) H_2SO_4 was added and the solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen, and then cooled to room temperature (25±5) ºC. After suitable dilution with de-ionized water, the contents of the Erlenmeyer flask were warmed so as to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH in the presence of 1-2 mL of 0.01 % (w/v) tartrate solution. The resulting solution was filtered, if necessary, through a What man No. 40 filter paper into a 50-mL calibrated flask. The residue (silica and tungstenic acid) was washed with a small volume of hot (1 + 99) H_2SO_4, followed by water; the volume was made up to the mark with de-ionized water.

A suitable aliquot (1-2 mL) of the above-mentioned solution was taken into a 10-mL calibrated flask and the manganese (II) content was determined; as described under Procedure using tartrate or oxalate as masking agent. Based on five replicate analyses, average manganese concentration determined by spectrophotometric method was in excellent agreement with the certified values. The results are given in Table 5.

4.3 Determination of Manganese in Environmental Water Samples

Each filtered (with What man No. 40) environmental water sample (500 mL) was evaporated nearly to dryness with a mixture of 5-mL concentrated H_2SO_4 and 10 mL of concentrated HNO_3 to sulfur trioxide fumes in presence of excess sodium azide solution in a fume cupboard, following a method recommended by Greenberg *et al.* [34] After cooling addition of 5 mL of concentrated HNO_3 was repeated and heating to a dense fume continued or until the solution become colorless. The residue was then heated with 10-mL of de-ionized water in order to dissolve the salts. The solution was then cooled and neutralized with dilute NH_4OH solution in presence of 1-2 mL of a 0.01% (w/v) tartrate solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with de-ionized water.

An aliquot (1-2 mL) of this preconcentrated water sample was pipetted into a 10-mL calibrated flask and the manganese content was determined as described under the general Procedure using tartrate or oxalate as masking agent. The results of analyses of environmental water samples from various sources for manganese are shown in Table 6.

Most spectrophotometric methods for determination of manganese in natural and sea-water require preconcentration of manganese [34]. The concentration of manganese in natural and sea water is a few μg L^{-1} in developed countries [35]. The mean concentration of manganese found in U.S. drinking water is greater than 20 μg L^{-1} [35].

4.4 Determination of Manganese in Biological Samples

Human blood (2- 4mL) or urine (10-20 mL) or hair (2-5g) sample was taken into a 100-mL micro-Kjeldahl flask. A glass bead and 10-mL of concentrated nitric acid were added, and the flask was placed on the digester under gentle heating. The sample was digested in the presence of an excess sodium azide solution according to the method recommended by Stahr [36]. When the initial brisk reaction was completed, the solution was removed and

cooled to room temperature. A 1 mL volume of concentrated sulfuric acid was carefully added, followed by the addition of 1 mL of 2.5% sodium azide solution; and heating was continued to dense white fumes, while repeating nitric acid addition if necessary. Heating was continued for at least 0.5 hr and then cooling was applied. The content of the flask was filtered and neutralized with dilute NH_4OH solution in presence of 1-2 mL of a 0.01% (w/v) tartrate solution. The resultant solution was then filtered and transferred quantitatively into a 10-mL calibrated flask and made up to the mark with de-ionized water.

A suitable aliquot (1-2mL) of the final solution was pipetted out into a 10-mL calibrated flask and the manganese content was determined as described under Procedure using tartrate or oxalate as masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are shown in Table 7.

The abnormally high value for the manganism patient is probably due to the involvement of high manganese concentrations with as and Zn. The occurrence of such high manganese contents are also reported in manganism patient from some developed countries [37].

Table 7. Determination results of manganese for human fluids and hair

Serial No.	Sample	Manganese/μg L^{-1}		Sample Source[a]
		AAS (n=5)	Proposed method (n = 5)	
1	Blood	908.2±1.0	910.5±1.2	Manganism (damage of central
	Urine	267.3±1.5	270.5±1.5	nervous system or neurological disorder) patient (Female)
2	Blood	459.3±1.2	465.2±1.5	Leukopenia patient (Female)
	Urine	118.4±1.6	121.5±1.8	
3	Blood	387.5±1.3	391.0±1.5	Liver cirrohosis
	Urine	107.6±1.8	112.2±2.0	patient (Male)
4	Blood	367.4±1.5	372.5±1.8	Pneumonities
	Urine	95.5±1.8	98.5±2.2	(Manganic Pneumonia) patient (Male)
5	Blood	225.6±1.6	228.5±2.0	Hypertension patient (Male)
	Urine	82.9±2.0	85.5±1.8	
6	Blood	102.0±2.2	105.5±2.0	Asthma patient (Male)
	Urine	40.2±1.9	43.5±2.5	
7	Blood	12.5±2.0	12.8±1.5	Normal Adult (Male)
	Urine	3.25±1.2	3.30±1.0	
8	Hair[b]	685.8±1.5	691.5±1.2	Normal human hair (Male)

[a]Samples were from Chittagong Medical College Hospital. [b]Values in ng g^{-1}

4.5 Determination of Manganese in Soil Samples

An air-dried homogenized soil sample (100 g) was accurately weighed and placed in a 100-mL micro-Kjeldahl flask. The sample was digested in the presence of an reducing agent (1mL of 2.5% (w/v) sodium azide solution) following a method recommended by Jackson [38]. The content of the flask was filtered through a What man No.40 filter paper into a 25-mL calibrated flask and neutralized with dilute NH_4OH solution in presence of 1-2 mL of 0.01% (w/v) tartrate solution. The resulting solution was then diluted up to the mark with de-ionized water.

A suitable aliquot (1 mL) of the final solution was pipetted out into a 10-mL calibrated flask and the manganese content was determined as described under Procedure using tartrate or oxalate as masking agent. The manganese content was then determined by the above procedure and quantified from a calibration graph prepared concurrently. The results are shown in Table 8. The average value of manganese in Chittagong region surface soil was found to be 43.29 mg kg^{-1} [39].

Table 8. Determination of manganese in some surface soil

Serial No.	Manganese (mg kg^{-1}) [a] (n=5)	RSD (%)	Sample Source[b]
S_1[b]	2.5±0.5	1.5	Agriculture soil (Chittagong University Campus)
S_2	0.85±0.3	1.3	Marine soil (Bay of Bengal)
S_3	17.5±1.0	1.8	Traffic soil (Kadamtali Bus Terminal)
S_4	85.6±1.2	2.1	Industrial soil (Estern Cables)
S_5	75.8±1.0	2.4	Industrial soil (T.S.P. Complex, Chittagong)
S_6	127.5±1.3	2.5	Industrial soil(Bangladesh Steel Re-rolling Mills Ltd., Chittagong, Bangladesh)
S_7	5.85±0.8	2.1	Road side soil (Dhaka-Chittagong Highway)
S_8	107±1.5	2.0	Paint soil (Elite Paint, Chittagong)
S_9	3.5±0.5	1.6	River soil (River Halda, Chittagong)
S_{10}	6.8±0.8	1.8	River soil (River Karnaphully, Chittagong)

[a]Average of five analyses of each sample. [b]Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu, Mo, Fe, Pb, V, Zn, Mn, Co, NO_3, SO_4 etc

4.6 Determination of Manganese in Pharmaceutical Samples

Finished pharmaceutical samples (each Mn containing 1mg tablet or 5 mL syrup or required weight) were quantitatively taken in a beaker and digested following a method recommended by Ahmed et al. [40]. Add 10-mL of concentrated nitric acid and heated to dryness and then added 10-mL of 20% (v/v) of H_2SO_4 and 1-2 drops freshly prepared azide solution. The volume was reduced to 2.5 mL and then cooled to room temperature. The solution was than neutralized with dilute NH_4OH in the presence of a 1-2 mL of 0.01% (w/v) EDTA or tartrate solution. The resulting solution was then filtrated and quantitatively transferred to a 25-mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2 mL) of this digested sample was pipetted into a 10-mL calibrated flask and then manganese content was determined as described under the general Procedure using tartrate as a masking agent. The results of some pharmaceutical analyses are in excellent agreement with the reported values. The analyses of pharmaceutical samples from several Pharmaceutical Companies for manganese are given in Table 9.

4.7 Determination of Manganese in Vegetable and Fruit Samples

The vegetable and fruit samples collected prior to the determination were pretreated in the following way. Edible portion of samples was first washed clean with tap water followed by rewashing with deionized water. After removing deionized water from the surface of vegetables and fruits, the samples were cut into small pieces and dried at 65°C in oven. An air dried vegetables and fruits samples (10gm) were taken in a 100-mL micro-Kjeldahl flask in presence of reducing agent and digested following a method recommended by Stahr [36].

A glass bead and 10 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled at room temperature. 1 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 2 mL of concentrated HF, and heating was continued for at least ½ hr and then cooled. The content of the flask was reduced from manganese (VII) to manganese (II) by using freshly prepared sodium azide solution (2.5% w/v) and excess of azide was removed by boiling and then filtered. The solution of flask then neutralized with dilute ammonia in the presence of 1-2 mL of a 0.01 % (w/v) tartrate or EDTA solution. The resultant solution was then transferred quantitatively into a 25-mL calibrated flask and made up to the mark with deionized water [41].

A suitable aliquot (1-2 mL) of the final solution was pipetted into a 10-mL calibrated flask and the manganese content was determined as described under the Procedure using tartrate as masking agent. High value of manganese for *Allium cepa* (onion) is probably due to the involvement of high manganese concentration in the soil [41]. The results are shown in Table 10.

4.8 Determination of Manganese in Food Samples

The food samples used were rice, wheat and tea and these were used as dry condition. Each sample was first ground in a mortar. Tea samples (0.1g) or rice and wheat samples (1.0 g) were weighed accurately and placed in a porcelain crucible and charred in an electric furnace; the sample was ashed at 555ºC in a muffle furnace in presence of excess reducing agent following the method recommended by Stahr [36], 2.0 mL of HCl and 10 ml of water were added to the ash. The mixture of each foodstuff was heated below the boiling point for a moment. The solutions were cooled and neutralized with NH_4OH in presence of 1-2 mL of 0.01% (w/v) tartrate or EDTA solution and filtered. The resulting solution was quantitatively transferred into 25-mL calibrated flask and mixed well and made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted out into a 10-mL calibrated flask and the manganese content was determined as described under Procedure using tartrate as masking agent. The results of food analyses by the spectrophotometric method were also found to be in excellent agreement with those obtained by AAS. The results are shown in Table 11.

High value of manganese for *Camellia sinensis* (Green tea) is probably due to the involvement of high manganese concentration in the soil.

Table 9. Determination of manganese in some pharmaceutical samples

Pharmaceutical samples	Brand name	Trade name	Manganese/μgg^{-1} or mgL^{-1}		RSD (%)
			Reported (Claimed) value	Found (n=5)	
Tablet	Square Pharmaceuticals Ltd.	Mulvit plus (Multivitamin-mineral) /μgg^{-1}	100.5	102.5	2.5
	Eskayef Bangladesh Ltd (SK+F)	Ostocal M (calcium, vitamin D & minerals) /μgg^{-1}	180.5	183.2	1.5
	Beximco Pharmaceuticals Ltd (BPL)	Bextram Gold (A to Z) (Multivitamin-mineral) /μgg^{-1}	200.5	205	2.5
Syrup	The ACME Laboratories Ltd.	Nutrum Junior (Multivitamin-mineral) / mgL^{-1}	150.0	152	2.0
	Finecure Pharmaceuticals Ltd.	Menuvit Syrup (Multivitamin-mineral) / mgL^{-1}	160.0	158.5	1.5

Table 10. Determination of manganese in some vegetable and fruit samples

Serial No.	Sample	Manganese/mg kg^{-1} Found[a] ± s (n=5)	Sample source
1	White Cabbage *(Brassica oleracea cupitata)*	20.8±1.0	Local Market, Chittagong
2	Radish *(Raphanus sativus)*	28.5±1.5	Local Market, Chittagong
3	Tomato *(Lycopersicon esculentum)*	12.75±1.3	Local Market, Chittagong
4	Potato *(Solanum tuberosum)*	7.25±1.2	Local Market, Chittagong
5	Cauliflower *(Brassica oleracea)*	45.5±1.5	Local Market, Chittagong
6	Garlic *(Allium sativum)*	49.8±1.4	Local Market, Chittagong
7	Onion *(Allium cepa)*	75.5±1.5	Local Market, Chittagong
8	Coriander seeds *(Coriandrum sativum)*	39.5±2.0	Local Market, Chittagong
9	Olive *(Olea europaea)*	1.85±0.5	Local Market, Chittagong
10	Banana *(Musa acuminate*)	0.19±0.05	Local Market, Chittagong

[a]*Average of five replicate analyses of each sample*

Table 11. Determination of manganese in some food samples

Sample[a]		Manganese/μgg^{-1}			
		AAS (n=5)		Proposed method (n=5)	
		Found	RSD[b] (%)	Found	RSD[b] (%)
Tea *(Camellia sinensis)*	Muskan Tea	278.5	1.5	283.8	1.8
	Ispahani Tea	271.8	1.8	275.0	1.5
	Taza Tea	185.5	1.2	182.8	1.3
	Green tea	290.5	2.0	287.5	1.8
Rice *(Oryza sativa)*		1.65	1.0	1.64	1.2
Wheat *(Triticum aestivum)*		2.68	1.5	2.65	1.4

[a]*Samples were from Local market, Chittagong.* [b]*The measure of precision is the relative standard deviation (RSD)*

4.9 Determination of Manganese in Fertilizer Samples

1 gm finely grounded TSP (Triple Super Phosphate), MOP (Muriate of Potash) or Urea fertilizer was dissolved in 10 mL concentrated HNO_3 in a 100 mL conical flask in presence of excess reducing agent by gentle heating [42]. Then it was made up to the mark with doubly distilled water. The solution was neutralized by NH_4OH solution in presence of 1-2 mL of 0.01% (w/v) tartrate or EDTA solution and filtered. The digested solution was quantitatively transferred into 25-mL calibrated flask and made upto the mark with deionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted out into a 10-mL calibrated flask and the manganese content was determined as described under Procedure using tartrate or EDTA as masking agent. The results are shown in Table 12.

Table 12. Determination of manganese in some fertilizer samples

Sample	Fertilizers	Concentration / (mg kg^{-1})	
		Found (n=5)	RSD (%)
1	Urea	685.0±1.5	2.0
2	T.S.P (Triple Super Phosphate)	232.5±1.8	2.5
3	MOP (Muriate of Potash)	145.8±1.9	2.8

4.10 Determination of Manganese (II) and Manganese (VII) Speciation in Mixtures

Suitable aliquots (1-2 mL) of manganese (II + VII) mixtures (preferably 1: 1, 1: 5, 1:10) were taken in a 25-mL conical flask. A few drops (2-3drops) of 4 M H_2SO_4, 3-4 mL of a freshly prepared sodium azide solution (2.5% w/v) was added to reduce the heptavalent manganese to divalent manganese and heated gently with the further addition of 5 mL of water, if necessary, for 5 min to drive off the excess azide cooled to room temperature. The reaction mixtures was neutralized with dilute NH_4OH and transferred quantitatively into a 10-mL volumetric flask.1ml of 2.4 x 10^{-3}M HNA-OPD-HNA reagent solution was added followed by the addition of 0.05 mL of 0.001 M H_2SO_4 and 5 mL DMF. It was made up to the mark with de-ionized water. The absorbance was measured after 1 min at 508 nm against a

reagent blank. The total manganese content was calculated with the help of a calibration graph prepared concurrently.

An equal aliquot (1-2 mL) of the above manganese (II+ VII) mixture was taken into a 25-mL beaker. Neutralize the solution with dilute NH_4OH in presence of 1-2 mL of 0.01% (w/v) tartrate solution. After, the content of the beaker was transferred quantitatively into a 10-mL volumetric flask, 1ml of 2.4 x 10^{-3} M HNA-OPD-HNA reagent solution was added, followed by the addition of 0.05 mL of 0.001 M H_2SO_4 and 5 mL DMF. It was made up to the mark with de-ionized water. After 1 min the absorbance was measured at 508 nm against a reagent blank, as before. The manganese concentration was calculated in mg L^{-1} or µg L^{-1} with the aid of a calibration graph. This gives a measure of manganese (II) originally present in the mixture. This value was substracted from that of the total manganese to get the manganese (VII) present in the mixture. The results were found to be highly reproducible. The occurrence of such reproducible results is also reported for different oxidation states of manganese [43]. The results of a set of determination are given in Table 13.

Table 13. Determination of manganese (II) and manganese (VII) in mixtures

Serial No.	Mn(II):Mn(VII)	Mn, taken (mg L^{-1})		Mn, found (mg L^{-1})		Error (mg L^{-1})	
		Mn(II)	Mn(VII)	Mn(II)	Mn(VII)	Mn(II)	Mn(VII)
1	1: 1	1.00	1.00	0.98	0.99	0.02	0.01
1	1: 1	1.00	1.00	1.00	1.02	0.00	0.02
1	1: 1	1.00	1.00	0.97	0.99	0.03	0.01
Mean error : Mn(II) = ± 0.017; Mn(VII) = ± 0.017 Standard deviation : Mn(II) = ± 0.015; Mn(VII) = ± 0.011							
1	1: 5	1.00	5.00	0.98	4.98	0.02	0.02
1	1: 5	1.00	5.00	0.99	4.99	0.01	0.01
1	1: 5	1.00	5.00	0.98	4.98	0.02	0.02
Mean error : Mn(II) = ± 0.0167; Mn(VII) = ± 0.017 Standard deviation : Mn(II) = ± 0.0058; Mn(VII) = ± 0.006							
1	1:10	1.00	10.00	0.99	9.98	0.01	0.02
1	1:10	1.00	10.00	0.98	9.99	0.02	0.01
1	1:10	1.00	10.00	0.98	9.98	0.02	0.02
Mean error : Mn(II)= ± 0.0167; Mn(VII) = ± 0.017 Standard deviation : Mn(II) = ± 0.015; Mn(VII) = ± 0.015							

5. CONCLUSIONS

A new simple, sensitive, and inexpensive method with the manganese (II)-HNA-OPD-HNA complex was developed for the determination of manganese in some real, environmental, biological, soil, food, fertilizer and pharmaceutical samples, for continuous monitoring to establish the trace levels of manganese in different samples matrices. Compared with other methods in the literature Table 1, the proposed method has several remarkable analytical characteristics:

1. The proposed method is highly sensitive with molar absorptivity of the complex of 4.89×10^6 L mol^{-1} cm^{-1}. Thus, amount of ng g^{-1} of manganese can be determined without pre-concentration;
2. The proposed method is very simple, rapid, and stable. The reaction of manganese (II) with HNA-OPD-HNA is completed rapidly in 1 min at room temperature so it does

not involve any stringent reaction conditions and offer the advantages of high complex stability (24h).
3. The method has added the advantage of determining individual amounts of Mn(II) and Mn(VII). With suitable masking agents, the reaction can be made highly selective.

The proposed method using HNA-OPD-HNA in aqueous solutions not only is one of the most sensitive methods for the determination of manganese but also is excellent in terms of selectivity and simplicity. Therefore, this method will be successfully applied to the monitoring of trace amounts of manganese in real, environmental, biological, soil, food, fertilizer and pharmaceutical samples.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. WHO, Manganese and its compounds: environmental aspects, Geneva: World Health Organization; 2004.
2. Sidorovitch E, Rupasova G, Zubkova J, Ignatenko V, Kuharenik T. The physiological fundamentals of plant nutrition, Agrochemistry. 1987;6:72-136.
3. Udintseva E, Hodorovski J, Zulikova A. The entering of Mn into plants from different soil, Agrochemistry. 1981;9:119-126.
4. Hesse PR. A Text Book of Soil Chemical Analysis. Chemical Publishing Co. Inc., New York; 1972.
5. Geber GB, Leonard A, Hantson P. Crite Carcinogenicity, mutagenecity and tatratognecity of manganese compounds. Rev Oncol Hemat. 2002;25:42-49.
6. Takeda A. Manganese action in brain function. Brain Research Reviews. 2003;41:79-87.
7. Underwood EJ. Trace Elements in Human and Animal Nutrition. Academic Press New York. 1977;170-183.
8. Hurley LS. Trace Element Analytical Chemistry in Medicine and Biology. Bratter P and Schramel P (eds.) vol. 3, Walter de Gruyter, Berlin; 1984.
9. Kazi TG, Afridi HI, Kazi N, Jamali MK, Arain MB, Jalbani N, Kandhro GA. Biol Copper, Chromium, Manganese, Iron, Nickel and Zinc Levels in Biological Samples of Diabetes Mellitus Patients. Trace Elem Res. 2008;122:1-18.
10. Finley JW, Cindy D. Manganese deficiency and toxicity. Are high or low dietary amounts of manganese cause for concern? Bio Factors. 1999;10:15-24.
11. Singh I, Poonam Mrs. Spectrophotometric determination of Mn(II) with 1-(2-quinolylazo)-2,4,5- trihydroxybenzene and microdetermination of Mn in foodstuffs. Talanta. 1984;31(2):109-112.
12. Yamane T. Determination of Manganese at Trace Levels in Natural Waters with Continuous Flow System Utilizing On- Line Cation-Exchange Separation and Catalytic Detection. Analytical Sciences. 1986;2:191-195.

13. Mutftchiev K, Tzachev K, Alexander A. Catalytic spectrophotometric determination of manganese (II) in human blood serum. Bulletin of the Chemists and Technologists of Macedonia. 1999;18:37-40.
14. Dogutan M, Filik H, Apak R. Preconcentration of manganese (II) from natural and sea water on a palmitoyl quinolin-8-ol functionalized XAD copolymer resin and spectrophotometric determination with the formaldoxime reagent. Analytica Chimica Acta. 2003;485:205-212.
15. Ishii H, Hidemasa K, Satoh K. A spectrophotometric method for the determination of manganese using α, β, γ, δ-tetrakis(4-carboxyphenyl)porphine (T(4-CP)P) Analytica Chimica Acta. 1982;136:347-354.
16. Sedaira H. Simultaneous determination of manganese and zinc in mixtures using first- and second-derivative spectrophotometry. Talanta. 2000;51:39-48.
17. Mghimi M, Ahmed Al-okab R, Ahmed SA, Taghartapeh MR. Spectrophotometric determination of manganese (VII) in water, soil and food materials using phenoxazine (PNZ) as a chromogen and 3-methyl-2-benzothiozolinone hydrazone hydrochloride hydrate (MBTH), amiloride (ALR) and acyclovir (AYR) as electrophilic coupling reagents. IPCBEE. 2011;1:337-343.
18. Aguilar-Islas M, Joseph RA, Kenneth BW. Catalytically enhanced spectrophotometric determination of manganese in seawater by flow-injection analysis with a commercially available resin for on-line preconcentration. American Society of Limnology and Oceanography Limnol. Oceanogr. 2006;105-113.
19. Mutaftchiev KL. Determination of Manganese in Some Medicinal Plants and their Water Extracts by a Kinetic Spectrophotometric Method. Chem. Pap. 2002;56:194-198.
20. Maniasso N, Zagatto AGE. Flow-injection spectrophotometric catalytic determination of manganese in plants exploiting the aerial oxidation of diphenyl carbazone. Analytica Chimica Acta. 1998;366:87-92.
21. Bermejo F, Branas G. Spectrophotometric determination of manganese (II) with gluconic acid. Microchimica Acta. 1971;59:489-493.
22. Chapin PT, Johnson SK, Coale HK. Rapid determination of manganese in sea water by flow-injection analysis with chemiluminescence detection. Analytica Chimica Acta. 1991;249:469-478.
23. Sacconi L. Acylhydrazones of O-Oxy and O-Aminoaldehydes and ketones as tridentate complexing agents. J Am Chem Soc. 1954;75:5434-5450.
24. Salam MA, Chowdhury DA, Hossain SMA. Preparation and characterization of Schiff base reagent. Bull of Pure and Appl Sci. 1995;14:129-136.
25. Jeffery GH, Bassett J, Mendham J, Denney RC, editors. Vogel's Textbook of Quantitative Chemical Analysis. 5th ed. Bath Press Ltd., London; 1994.
26. Mukharjee AK. Analytical Chemistry of Zirconium and Hafnium. 1st ed. Pergamon Press New York; 1970.
27. Pal BK, Chowdhury B. Triazene-N-oxides as new type of fluorimetric reagents II; Determination of niobium with 3-(2-hydroxyphenyl)-1-phenyltriazene-N-oxide. Mikrochim Acta. 1984;11:121-131.
28. Sandell EB. Colorimetric Determination of Traces of Metals, 3rd ed., 269 Interscience. New York; 1965.
29. Bosch C, Ojeda A, Torres G, Rojas FS, Pavon JMC. Fluorometric determination of trace amount of gallium in biological tissues. Analyst. 1987;112:1499-1507.
30. Pal BK, Singh KA, Dutta K. Spectrofluorimetric determination of molybdenum in some real and environmental samples. Talanta. 1992;39:971-975.
31. Job P. Stability constant of coordination compounds. Ann Chim Paris. 1928;9:113-116.

32. Yoe JA, Jones AL. Stability constant of coordination compounds. Ind Eng Chem Anal Ed. 1944;16:11-16.
33. Parker GA. Analytical Chemistry of Molybdenum. Springer-verlag Berlin; 1983.
34. Greenberg AE, Clesceri LS, Trussell RR. Eds. Standard Methods for the Examination of Water and Wastewater. 18th ed. American Public Health Association, Washington D C. 1992;3.
35. WHO Guidelines for drinking water quality. 2nd ed. Volume 1 Recommendations. Geneva: WHO; 1993.
36. Stahr HM. Analytical Methods in Toxicology. 3rd Edn. John Wiley & Sons. New York; 1991.
37. American Conference of Governmental Industrial Hygienist (ACGIH); 1996.
38. Jackson ML. Soil Chemical Analysis Prentice Hall. Englewood Cliffs. 1965;326.
39. Page AL, Chang AC, El-Amany M. In Lead, Mercury, Cadmium, Manganese and Arsenic is the Environment. T. C. Hutchinsm and K. M. Mccma, John Wiley and Sons Ltd., New York. 1987;119.
40. Ahmed MJ, Hoque MR, Shahed ASMH, Bhattacharjee SC. A simple Spectrophotometric Method for the Determination of Aluminium in some Environmental, Biological, Soil and Pharmaceutical Samples Using 2-Hydroxynaphthaldehydebenzoylhydrazone. Eurasian J Anal Chem. 2010;5:204-211.
41. Beck HP, Kostova D, Zhang B. Inst Inorg Anal Chem Radiochem. Saarbrucken, D-66123. Germany, Agronomy Research. 2006;4:493-498.
42. Delgadillo LF, Silva GH, Martinez RA, Vermeerch MM. Total contents of cadmium, copper, manganese and zinc in agricultural soil, Rev. Int Contam Ambient. 1992;8:37-46.
43. Pierre A, Karine D, Franck D, Gwenaelle C. Speciation, oxidation state, and reactivity of particulate manganese in marine sediments. Chemical Geology. 2005;218:265-279.

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