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Direct spectrophotometric determination of manganese(II) with N,N'-Bis (2-amino-benzoyl) triethylenetetramine in aqueous medium

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ABSTRACT

A new, simple, sensitive and rapid spectrophotometric method is proposed for the determination of trace amounts of manganese(II). The method is based on the reaction at pH 11.5 between the synthesized reagent, N,N'-Bis (2-aminobenzoyl) triethylenetetramine (BABTT) and manganese (II) forming a brown coloured water soluble complex. The brown coloured Mn(II) – BABTT complex shows maximum absorbance at 400nm. At this wavelength, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence, the analytical study are carried out at 400nm at pH 11.5. Beer's law is valid over the concentration range 1.20-16.86µg mL⁻¹, with molar absorptivity of 0.684x10³Lmol⁻¹cm⁻¹. The tolerance limits for interfering ions are discussed. All variables were studied in order to optimize the reaction conditions. Though, a number of spectrophotometric methods have been reported for the determination of manganese, however, no reagent exhibits outstanding performance for direct spectrophotometric determination of manganese(II) in aqueous medium. The efficacy of the proposed method is shown by the successful determination of traces of manganese in its pure form, natural samples, alloys and industrial effluents. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Manganese(II) determination;
N,N'-Bis (2-aminobenzoyl)
triethylenetetramine (BABTT);
Spectrophotometry;
Natural samples;
Alloys;
Industrial effluents.

INTRODUCTION

A large number of industries discharge metal containing effluents into air and water resources without adequate treatment and one such metal that happens to be the current area of concern contaminating the environment is manganese. Although manganese^[1] is an essential micronutrient, it is also a respiratory irritant and a slow systemic poison when inhaled (as oxides) in excessive amounts. Manganese also occurs in domestic waste water and receiving systems. Manganese is an essential trace element which is used in manufacture of

dry battery cells, alloys, electric coils etc. Manganese is a co-factor in many enzymatic reactions involved in phosphorylation. Fertilisers containing manganese cause air and water pollution. At higher doses it accumulates in the kidneys, liver and bones and causes manganese psychosis which is an irreversible brain disease characterized by uncontrollable laughter, euphoria, mutation producing agent for bacterium E-coli and T4 bacteriophage. The increasing use of the metal necessitates development of rapid and sensitive methods for the determination of minute quantities of the metal. And, also new accurate and reliable methods for analysis of vari-

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ous objects containing traces of manganese should be searched for this element.

There are several methods available for manganese (II) determination including atomic absorption spectroscopy (AAS), flow injection analysis (FIA), spectrofluorimetry^[2] and spectrophotometry. In routine analysis, spectrophotometric methods are versatile and economical. The oxidants, such as potassium periodate and ammonium persulphate are commonly used for determination of manganese(II) by spectrophotometry^[3-7]. Existing methods are complicated, require oxidation, heating^[8], are time consuming and are frequently characterized by poor sensitivity. Catalytic kinetic methods have received considerable attention because of the significant advantages in the determination of many analytes at trace levels. At present, catalytic methods^[9-13] for determination of manganese(II) in water systems have been frequently reported. Catalytic- Spectrophotometric methods for manganese(II) using periodate, dissolved oxygen or hydrogen peroxide as the oxidizing agent^[14] are not directly applicable to manganese determination in seawater because of the possible interferences caused by organic substances and variation in salinity^[15]. Therefore, there is a need to develop new analytical procedures for manganese determination and keeping this in mind and in our continuation of the development of suitable methods for the determination of metals, especially in natural samples^[16-18], a simple, very sensitive and accurate spectrophotometric method has been proposed for the determination of manganese(II) in its pure form, natural samples, alloys and industrial effluents. Though a number of spectrophotometric methods have been reported for the determination of manganese^[19-24], however, no reagent exhibits outstanding performance for direct spectrophotometric determination of manganese(II) in aqueous medium. The use of *N,N'*-Bis (2-aminobenzoyl) triethylenetetramine (BABTT) as a reagent for the sensitive and selective determination of manganese(II) is reported in the present work.

EXPERIMENTAL

Instruments

The absorbance and pH measurements were made on a Shimadzu UV-Visible spectrophotometer fitted with 1.0cm Quartz cells and Systronics digital pH meter

equipped with combined glass electrode respectively. The pH meter has reproducibility of measurement within ± 0.01 pH.

Reagents and chemicals

Triethylenetetramine and isatoic anhydride were taken from Sigma Aldrich, Co., Ltd. and Manganous sulphate monohydrate was taken from E - Merck, India. All chemicals and solvents used were of analytical reagent grade, and doubly distilled water was used for preparation of all solutions and experiments. The working solutions were prepared daily by diluting the stock solution to an appropriate volume.

Solution of *N,N'*-Bis (2-aminobenzoyl) triethylenetetramine (BABTT) (1×10^{-2} M) was prepared by adding triethylenetetramine to a hot methanolic solution of isatoic anhydride in 1:2 molar proportion until a clear solution was obtained^[25]. Lower concentrations were prepared by diluting the appropriate volume of the reagent solution.

Manganese(II) solution was prepared by dissolving manganous sulphate monohydrate (~ 0.46 g) in sulphuric acid (5mL, 0.1N) and then making up the solution to mark in a standard flask (250mL) with distilled water. The solution was standardised by titrimetric method using EDTA^[26].

Buffer solution

The buffer solution was prepared by dissolving 3.8g of trisodium orthophosphate (0.01M) in 1 L distilled water (pH 11.5). The pH of the solution was checked with the above mentioned pH meter.

Determination of manganese(II)

To measured aliquots of manganese(II) ($0.06-0.36$ mgmL⁻¹) solution placed in a standard flask, buffer solution (2mL) and the reagent (BABTT) (3mL, 1×10^{-2} M) was added and the resulting brown coloured solution was quantitatively diluted (25mL) with distilled water. The absorbance of the coloured solution was measured at 400nm against a reagent blank prepared in the same manner.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectrum of manganese-BABTT complex was recorded in the range of 300–700nm and

the results showed a maximum absorbance at 400nm, where the absorption of the reagent blank is almost negligible and hence all the absorbance measurements were carried out at 400nm.

Stability of the complex

The formation of manganese-BABTT complex is instantaneous and the absorbance of the brown coloured complex is stable for more than 12 hours.

Effect of pH

Keeping the concentration of manganese(II) constant, the complexation reaction between manganese-BABTT was studied over the pH range 1.0-14.0. A constant and maximum value of absorbance was obtained in the pH range of 11.0 - 11.5. Hence, the pH was fixed at 11.5 for further analysis, by use of trisodium orthophosphate buffer solution.

Analytical characteristics

The absorbance is a linear function of concentration of manganese(II) in the range of 1.20-16.86 $\mu\text{g mL}^{-1}$ at 400nm. The determinations for manganese(II) were carried out in the range 2.41–14.45 $\mu\text{g mL}^{-1}$ of solution. The results of the determinations are given in TABLES 1 and 2. The apparent molar absorptivity value obtained 0.684 $\times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. The standard deviation and co-efficient of variation calculated for six replicate measurements are in good agreement with the standard method. It was found that the order of addition of reactants has no effect on the formation of the complex.

Effect of diverse ions

The effect of diverse ions on the determinations of manganese(II) was studied and the results are shown in TABLE 3. The selectivity of the proposed method has been determined by the analysis of samples containing known amount (9.63 $\mu\text{g mL}^{-1}$) of manganese(II) in the presence of various amounts of diverse ions. The results showed that the studied anions and most of the cations do not interfere with the determination of manganese(II). The main interferences were shown by iron(III), cobalt(II), copper(II) and nickel(II) solutions and they were effectively masked by using suitable masking reagents. Iron(III) was masked by the use of sodium fluoride (1% w/v, 5mL) solution, Cobalt(II) with ammonium hydroxide(1% w/v, 5mL), Copper(II) was masked us-

ing thiourea (1% w/v, 5mL) solution and Nickel(II) with the use of sodium tartarate (1% w/v, 5mL) solution.

TABLE 1 : Determination of manganese(II).

Sl. No.	BABTT method				Persulphate method ^[27]		
	Mn(II) taken ($\mu\text{g mL}^{-1}$)	Mn(II) found ($\mu\text{g mL}^{-1}$)	recovery (%)	error (%)	Mn(II) found ($\mu\text{g mL}^{-1}$)	recovery (%)	error (%)
1.	2.41	2.42	100.4	0.4	2.39	99.2	0.8
2.	4.82	4.80	99.6	0.4	4.77	99.0	1.0
3.	7.22	7.20	99.7	0.3	7.17	99.3	0.7
4.	9.63	9.70	100.7	0.7	9.55	99.2	0.8
5.	12.04	12.06	100.2	0.2	11.97	99.4	0.6
6.	14.45	14.41	99.7	0.3	14.38	99.5	0.5

TABLE 2 : Statistical comparison.

Sl. No.	method	av. error* (%)	S.D* (%)	C.V* (%)
1.	N, N'-Bis(2-aminobenzoyl) triethylenetetramine(BABTT)	0.38	0.411	0.411
2.	Ammonium persulphate	0.73	0.160	0.161

*6 replicates

TABLE 3 : Effect of diverse ions on the determination of manganese (II) Amount of manganese (II) taken–9. 63 $\mu\text{g mL}^{-1}$.

Diverse ions	Tolerance limit ($\mu\text{g mL}^{-1}$)
Molybdate, iodide, bicarbonate and bromate	1500
Nitrite, citrate and fluoride	1300
Tartarate and thiosulphate	1050
Hydroxide, oxalate, thiocyanate, sodium and acetate	600
Potassium(I) and tin(II)	500
Sulphate, tungstate, nitrate, chloride, zinc(II), silver(I), nickel(II) ^a and copper(II) ^b	250
Tertaborate, ammonium(I), iron(III) ^c and mercury(II)	150
Barium(II), strontium(III) and lead(II)	100
Carbonate, cadmium(II), cobalt(II) ^d and calcium(II)	80

^amasked with sodium tartarate(1%w/v, 5mL); ^bmasked with thiourea(1%w/v, 5mL); ^cmasked with sodium fluoride(1%w/v, 5mL); ^dmasked with ammonium hydroxide (1%w/v, 5mL)

APPLICATION

Water and effluent samples

Water samples were collected from a bore well, effluent samples from a tannery and dyeing unit. All

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samples were filtered before analysis and known amounts of manganese(II) were added, as none of the samples contained any amount of manganese(II). The samples were analysed for manganese(II) by the proposed method and the recoveries are shown in TABLE 4 and 5. A close examination of the table reveals that the presently developed method can be applied for de-

TABLE 4 : Determination of manganese(II) in natural water sample.

Sl. No.	Mn(II) added ($\mu\text{g mL}^{-1}$)	Mn(II) found ($\mu\text{g mL}^{-1}$)	recovery (%)
1.	2.41	2.44	101.2
2.	4.82	4.87	101.0
3.	7.22	7.28	100.8
4.	9.63	9.70	100.7
5.	12.04	12.15	100.9
6.	14.45	14.57	100.8

TABLE 5 : Determination of manganese(II) in effluent samples (Tannery and Dyeing unit).

Sl. No.	Mn(II) added ($\mu\text{g mL}^{-1}$)	Tannery		Dyeing Unit	
		Mn(II) found ($\mu\text{g mL}^{-1}$)	recovery (%)	Mn(II) found ($\mu\text{g mL}^{-1}$)	Recovery (%)
1.	2.41	2.43	100.8	2.45	101.6
2.	4.82	4.85	100.6	4.89	101.4
3.	7.22	7.26	100.5	7.31	101.2
4.	9.63	9.68	100.5	9.72	100.9
5.	12.04	12.12	100.7	12.20	101.3
6.	14.45	14.49	100.3	14.58	100.9

TABLE 6 : Determination of manganese(II) in alloys.

Sample composition (%)	Sl. No.	Alloy taken ($\mu\text{g mL}^{-1}$)	Amount of Mn(II) found ($\mu\text{g mL}^{-1}$)	Amount of Mn(II) found (%)	Av. of Mn(II) Found(%)	S.D	C.V (%)
manganin (Cu*-82, Ni-3, Mn-15)	1.	40.00	5.80	14.50	14.94	0.23	1.54
	2.	60.00	9.17	15.28			
	3.	80.00	11.97	14.96			
	4.	100.00	14.98	14.98			
	5.	120.00	17.87	14.89			
	6.	140.00	21.01	15.01			
Manganese Bronze (Cu*-95, Mn-5)	1.	20.00	1.14	5.70	5.10	0.27	5.28
	2.	28.00	1.38	4.93			
	3.	36.00	1.78	4.94			
	4.	44.00	2.21	5.02			
	5.	52.00	2.60	5.00			
	6.	60.00	3.02	5.03			

*masked with thiourea

termination of manganese(II) in these samples with a high degree of accuracy and precision.

Alloy samples

The method was applied for the determination of manganese(II) in manganin and manganese bronze by the presently developed method and the results are shown in TABLE 6. The result show that the recoveries are in good agreement with the certified values, indicating that the proposed method can be used in routine analysis of the metal in these alloys.

CONCLUSION

From the above discussions, it can be concluded that BABTT is a potential reagent for the spectrophotometric determination of manganese(II). An exhaustive search through the literature revealed that only limited methods are available for the direct quantitative determination of manganese, therefore the developed method attains high importance as it is direct, sensitive, accurate, selective, specific, non-extractive, reproducible and simple. The results of the investigations were highly fruitful with a considerably high value of molar absorptivity, accuracy and precision and it is hoped that this method can be suggested for the routine analysis of manganese(II) in free state, environmental sample, effluent samples and alloys.

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