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Novel analytical reagent for the quantification of Mn(II) in various water systems

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ABSTRACT

Novel, facile, sensitive and selective analytical reagent *(6E,7E)-N^2,N^3*-bis(3-methoxybenzylidene)pyridine-2,3-diamine(BMBPD) was synthesized for the determination of Mn(II) in various environmental samples with spectrometer. The method was based on chelation of Mn(II) with *(6E,7E)-N^2,N^3*-bis(3-methoxybenzylidene)pyridine-2,3-diamine (BMBPD) at pH 4.5 in presence of acetate buffer in 1:2 ratio(M:L) and obtained a orange colored derivative with λ_{max} of 460 nm. The complex obeys Beer's law up to 1.1 mg l^{-1} with an optimum concentration range over 0.15 to 1.2 mg l^{-1}. Sandell's sensitivity of the orange color reaction was calculated to be 0.0012 μg cm^{-2} with molar absorptivity of 5.4×10^4 l mol^{-1} cm^{-1}. Various optimum conditions such as effect of pH, reagent concentration, accuracy, precision and reproducibility for the determination of Mn(II) in different water systems were investigated. The detailed study of various interferences confirmed the high selectivity of the present method. The developed method was applied successfully for the analysis of trace and ultra trace levels of Mn(II) in various water systems and the obtained results were also compared with AAS method.

KEYWORDS

Manganese (II);
(6E,7E)-N^2,N^3-bis(3-methoxybenzylidene)pyridine-2;
3-diamine (BMBPD);
Spectrophotometer;
Water systems.

INTRODUCTION

Manganese is a micronutrient as well as hazardous element to human system and its toxicity depends on the level of concentration of metal present in the living system and environment. It plays vital role in biological systems such as formation of anterior pituitary hormone; production of Vitamin C & B_1 which affects the protein metabolism, oxidation and hematopoiesis. Moreover, manganese regulates many enzymes like phophatase, arginase and dipeptidase. Manganese is an important element which plays significant role in geochemical cycles in sediments and the water columns under the surface water systems. Excessive exposure to manganese (usually in mines and certain industrial plants) causes toxicity and symptoms such as psychiatric abnormalities, neurological disorders and "Parkinson" like symptoms is observed. Therefore, it is necessary to develop facile, sensitive, selective and accurate analytical methods for the determination of manganese in various environmental matrices.

Several analytical methods such as atomic absorption spectroscopy[1], electroanalytical techniques[2], spectrofluorimetry[3] and spectrophotometer[4, 5] were reported for the determination of Mn(II) in different environmental samples. Novel oxidative methods were

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proposed for the quantification of Mn(II) with potassium periodate and ammonium persulfate using spectrophotometer[6-8]. Numerous kinetic spectrophotometric methods were employed for the analysis of manganese by catalytic effects on the oxidation of dye compounds by using different oxidants[9, 10]. At present, more popular catalytic methods[11, 12] for the determination of Mn(II) in water systems have been frequently reported. A new spectrophotometric protocol was developed for the simultaneous determination of soluble Mn(III), Mn(II) and total Mn [sum of soluble Mn(III) and Mn(II)] in sediment pore waters using a water soluble meso-substituted porphyrin [α,ß,γ,δ-tetrakis(4-carboxyphenyl)porphine(T(4-CP)P)][13]. Spectrophotometric methods are particularly useful due to simplicity, sensitivity, stability, comparative low cost and suitability for both automation and field research.

The main objective of the present paper was to develop non-extractive spectrophotometric method for the analysis of Mn(II) after complexation with BMBPD in acetate buffer medium at pH 4.5. Review of literature reveals that *(6E,7E)-N²,N³*-bis(3-methoxybenzylidene) pyridine-2,3-diamine (BMBPD) synthesized in our laboratory was novel and have not been reported so far for the determination of Mn(II). The present method does not require elaborate cleanup procedure and extraction step to extract the Mn(II)-$(BMBPD)_2$ complex into the organic solvents, hence the usage of chloroform and carbon tetrachloride[14] was avoid which are reported as hazardous to the environment[15]. Therefore this method was eco-friendly to the environment.

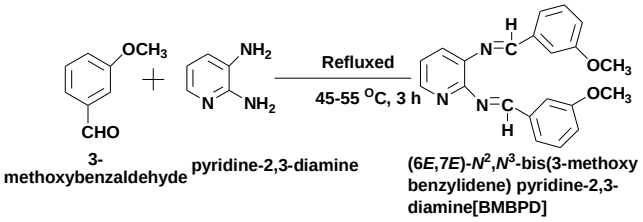
EXPERIMENTAL

Materials and apparatus

All reagents used were of analytical reagent grade and solutions were prepared with deionized distilled water unless mentioned. Stock solution of *(6E,7E)-N²,N³*-bis(3-methoxybenzylidene) pyridine-2,3-diamine (BMBPD) was prepared by dissolving 0. 720 g in deionized distilled water and diluted to 100 ml to get 0.003 M solution. Working solution of BMBPD was prepared by appropriate dilution and the solutions were stable for several months. A stock solution of manganese (II) (1.0 mg ml^{-1}) was prepared by dissolution of $MnSO_4$. H_2O and further dilutions as required were employed. A buffer solution was prepared by adding: 50ml of 0.25M sodium acetate was dissolved in 20ml of 0.1M acetic acid and pH was adjusted to 4.5 with 0.25 M sodium acetate solution and diluted to 100ml in a volumetric flask. A HITACHI model U 3400 UV VIS NIR Spectrophotometer with 10 mm stopped glass cells was used. An ELICO model Li-129 was used for all pH measurements.

Synthesis of (6E,7E)-N², N³-bis(3-methoxy benzylidene)pyridine-2,3-diamine (BMBPD)

(6E,7E)-N², N³-bis(3-methoxy benzylidene)pyridine-2,3-diamine(BMBPD) is not commercially available, and was synthesized according to the method described previously[16]. 3-methoxy benzaldehyde (3-MBD) (2.72 g) was dissolved in 15 ml of deionized distilled water and made up to the 100 ml in volumetric flask. 50 ml of this solution was transferred into the 250 ml round bottom flask and the solution was stirred continuously in a water bath at 5 ^{O}C for 30 min to under go condensation process. Pure form of pyridine-2,3-diamine(PDM) dissolved in methanol (50 ml) was added to the condensed reaction mixture and resulting solution were stirred at 45–55 ^{O}C for 3 h. Finally, the reaction mixture was mixed with deionized distilled water (50 ml) and *(6E,7E)-N²,N³*-bis(3-methoxybenzylidene)pyridine-2,3-diamine (BMBPD) precipitated as a pale yellow colored powder. The yield was 78.50% and melting point of the product is 180–183 ^{O}C. The structure of color forming reagent was shown in Scheme 1.



3-methoxybenzaldehyde pyridine-2,3-diamine (6E,7E)-N²,N³-bis(3-methoxy benzylidene) pyridine-2,3-diamine[BMBPD]

Scheme 1 : Synthesis of (6E,7E)-N²,N³-bis(3-methoxy benzylidene) pyridine-2,3-diamine (BMBPD)

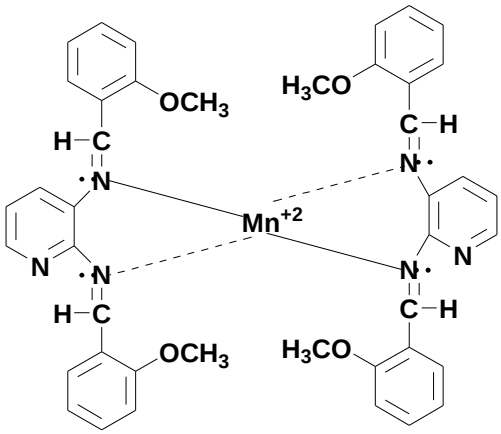
Procedure

An aliquot containing not more than 5.0 –200 µg ml^{-1} of Mn(II) was transferred into 25 ml calibrated flask, 3.0 ml of 0.003 M BMBPD and 5 ml of acetate

buffer solution with pH 4.5 solution were added successively and the mixture was diluted up to the mark with deionized distilled water. The appearance of the color was instantaneous and absorbance was measured at 460 nm against reagent blank solution. The reagent blank was prepared in a similar manner without Mn(II). All measurements were carried out at room temperature. The manganese content in an unknown sample was determined using a calibration graph.

RESULTS AND DISCUSSION

Under the optimal experimental condition, the absorption spectra of BMBPD and Mn(II)–$(BMBPD)_2$ complexes(Scheme 2) were scanned. The absorption maximum of reagent blank (BMBPD) versus reagent blank was measured at 358 nm, where as Mn(II)–$(BMBPD)_2$ complex gave an absorption peak at 460 nm. The difference (bathochromic shift) of the two peaks was 102 nm, and could be obviously distinguished. Thus, the absorption peak at 460 nm was chosen as the determination of wave length for Mn(II)–$(BMBPD)_2$ complex as illustrated in Figure 1.



Scheme 2 : Proposed possible complex structure of Mn(II)-$(BMBPD)_2$ to give orange colored solution

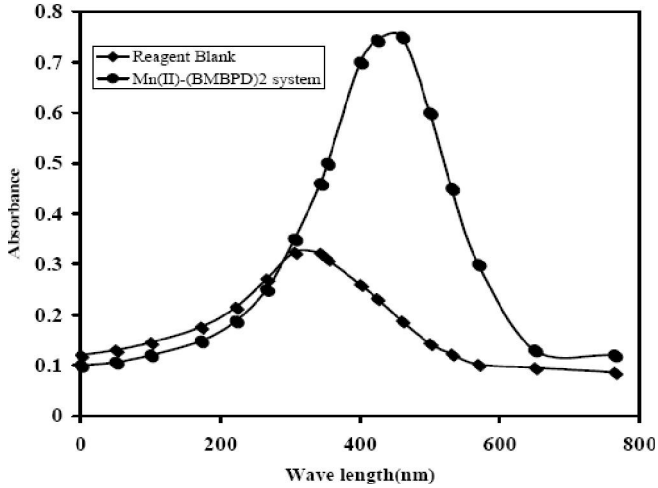


Figure 1 : Absorption spectra of Mn(II)-$(BMBPD)_2$ complex against reagent blank

Effect of pH

pH studies were carried out on the peak height of Mn(II) at various concentrations by fixing 0.03M BMBPD concentration. The pH of acetate buffer was changed over a range of 2.0–7.0 and the peak height were measured for each concentration level of Mn(II). At all concentration levels of Mn(II), maximum peak heights were found between pH 4.0 and 5.0. Therefore, a pH 4.5 for the acetate buffer system was chosen throughout the study as shown in Figure 2.

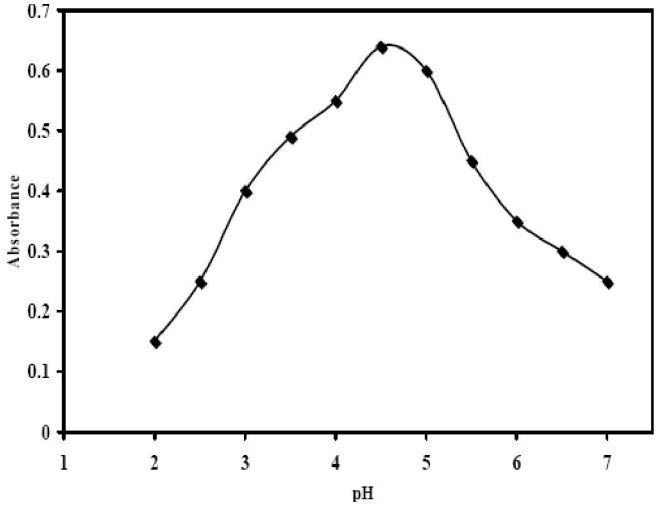


Figure 2 : Effect of pH on the peak height for the analysis of Mn(II)

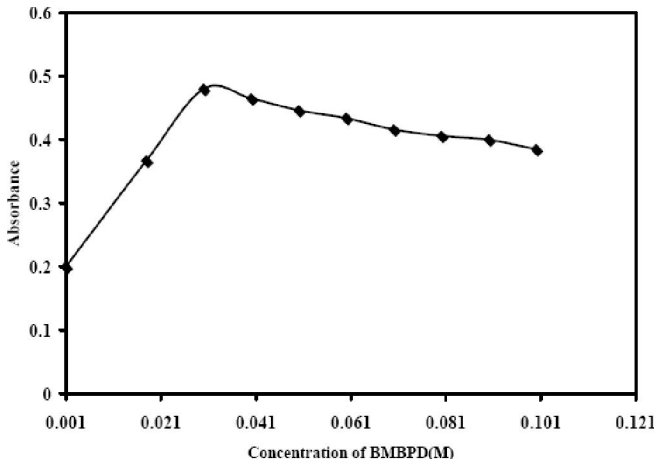


Figure 3 : Effect of BMBPD concentration on the peak height for the analysis of Mn(II)

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Effect of BMBPD concentration on peak height

The effect of concentration of BMBPD, on the peak height was investigated at pH 4.5 in an acetate buffer environment. The concentrations of BMBPD was varied over the range 0.001–0.10 M. Maximum peak height was obtained at a concentration of 0.03 M BMBPD as color developing reagent for lower concentration level of Mn(II) in the sample solution. Further increase in BMBPD concentration, slight decrease in the peak height was observed. Hence, 0.03 M was optimized value for all further studies as represented in Figure 3.

Effect of time and temperature on peak height

The reaction was instantaneous and Mn(II)-$(BMBPD)_2$ system attained maximum and constant absorbance just after the dilution to volume(25 ml in volumetric flask) at room temperature ($32 \pm 5\ ^{O}C$) and remained stable for 36 h.

Analytical parameters

The complex obeys Beer's law up to 1.1 mg l^{-1} with an optimum concentration range between 0.15 to 1.2 mg l^{-1} for Mn(II)-$(BMBPD)_2$ system. The molar absorptivity of complex at 460 nm and at pH 4.5 was calculated as 5.40×10^4 l mol^{-1} cm^{-1}. Sandell's sensitivity of the method was found to be 0.0012 μg ml^{-1}. The correlation coefficient (γ) for the Mn(II)-$(BMBPD)_2$ experimental data was 0.9997. The composition of the complex determined using Job's continuous variation method indicates the formation of 1:2 (M:L) complex. The stability constants corresponding to Mn(II)-$(BMBPD)_2$ was determined and found to be 6.3×10^{15} (1:2, M:L).

Calibration graph

The equation of a typical calibration is $p = 6.30c + 5.31$, $r^2 = 0.9995$ (p, peak height; c, concentration). The calibration graph was obtained at the optimum working conditions: BMBPD concentration 0.03 M at pH 4.50 in acetate buffer medium.

Method evaluation

The proposed method was critically evaluated with regard to reproducibility, accuracy, and detection limit for analysis of Mn(II) in various water systems.

Reproducibility

To test the reproducibility of present method, four repetitive analyses each sample was done. A %S.D. in the range 0.40–1.10 was obtained as summarized in TABLE 3.

Accuracy

The accuracy of the proposed method was evaluated by comparing the results with those obtained by the AAS method. The results shown in TABLE 3 reveals that the good correlation between the two methods indicative of present method almost sensitive to that of AAS method.

Detection limit

Under optimized conditions the detection limit for determination of Mn(II) by using present method (signal to noise ratio = 2) was 0.90 g l^{-1} volume of Mn(II) ion solution.

Effect of excipients

The effect of excipients was also discussed for the determination of Mn(II) [0.30 μ g) by using the developed method. The obtained results were summarized in TABLE 1. The results states that other ions (excipients) commonly encountered in samples solution were tolerated on the whole in relatively high concentration. The sample analysis can be carried out without using masking reagent. Hence, the present method was highly selectivity for the determination of Mn(II) in various water systems.

Applications

To evaluate the applicability of the proposed method, it was applied to the determination of Mn(II) in various water systems.

Determination of Mn(II) in various water systems

Water samples were collected from different areas (Amaraja Batteries, Industrial Estate, Renigunta and Chandragiri, A.P.,India) around Tirupati. The samples were stored at 0 - $5\ ^{O}C$ in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no. 41 and the clean solution was collected into a 100 ml standard flask. The contents were diluted to the mark with distilled water. 10 ml of this solution was further diluted to get working solution for determination of Mn(II) concentration. Spiked water samples were

TABLE 1 : Optical characteristics for the analysis of Mn(II) with BMBPD using spectrophotometer

Optical Characteristics	Values
Color	Orange
λ_{max}[nm]	460
Stability	36 h
Beer's law range [mg l^{-1}]	0.15 - 1.2
Molar absorptivity [l mol^{-1} cm^{-1}]	5.4×10^4
Sandell's sensitivity [µg cm^{-2}]	0.0012
Regression equation (Y^b)	
Slope[a]	0.1671
Intercept[b]	0.0158
Correlation coefficient [r]	0.9997
Relative standard deviation [%][c]	0.585
Range of error (95% confidence level)	±1.142
Detection limit [g l^{-1}]	0.90
% Error	0.129

[a]Experiments performed under optimized conditions (see text), [b]Y = ax + b, where x is the concentration of analyte in µg ml^{-1}, [c] n = 4.

TABLE 2 : Tolerance limit of excipients for the determination of Mn(II)[0.30 µg] with BMBPD in various water systems using spectrophotometer

Excipients	Tolerance Limit(µg)
Cu^{+2}	300
Hg^{+2}	300
Ag^{+}	250
Zn^{+2}	300
Ni^{+2}	300
Pb^{+2}	300
Fe^{+3}	30
Ba^{+2}	50
Cr^{+6}	50
Cd^{+2}	500
Ca^{+2}	250
PO_3^{2-}	300
W^{+6}	200
Al^{+3}	50
Mg^{+2}	50
Co^{+2}	10

TABLE 3 : Analytical data for the determination of Mn(II) in various water systems collected around Tirupati, A.P.,INDIA.

Samples	Present Method					ASS Method	
	Mn(II) [µg l^{-1}]						
	Added	Found	Recovery±SD[d]	*t*-Test[e]	*F*-Test[f]	Found	Recovery±SD[d]
I[a]	1.0	0.96	96.00±0.53	7.70	2.00	0.97	97.00±0.93
	-	0.12	-	-	-	0.14	-
	1.0	0.98	98.00±0.61	2.54	0.31	0.98	98.00±0.62
	-	0.15	-	-	-	0.15	-
	1.0	0.95	95.00±0.40	0.90	1.32	0.96	96.00±0.53
II[b]	2.0	1.97	98.5±0.69	4.42	0.13	1.96	98.00±0.62
	-	0.23	-	-	-	0.24	-
	2.0	1.94	97.00±0.93	5.29	1.05	1.94	97.00±0.93
	-	0.27	-	-	-	0.28	-
	2.0	1.99	99.66±1.05	2.47	0.42	2.00	100.00±1.10
III[c]	3.0	2.92	97.33±0.95	3.98	1.83	2.94	98.00±0.61
	-	0.10	-	-	-	0.10	-
	3.0	2.99	99.66±1.00	2.99	0.38	2.99	99.66±1.05
	-	0.08	-	-	-	0.09	-
	3.0	2.96	98.60±0.71	0.91	1.40	2.97	99.00±0.99

prepared by regular addition of known concentration of Mn(II) into the deionized distilled water and its concentration was measured as per to aforesaid procedure and the results were tabulated in TABLE 3. The obtained results were compared with the ASS methods in terms of Student's *t*-test and *F*-test. The analytical data summarized in TABLE 3 suggest that the percentage of recovery of Mn(II) from different water systems ranges from 95.00 to 100.00% which is more reliable and sensitive to that of ASS method.

CONCLUSIONS

BMBPD was one of the most selective reagent for

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the spectrophotometric determination of Mn(II) ions in different water systems. The newly synthesized color developing reagent was more economical and easy to prepare in a classical laboratories. The present method was facile, selective, sensitive and rapid to that of AAS method. Due to the formation of stable complex [Mn(II)-$(BMBPD)_2$], this investigation made easy to measure the Mn(II) concentration in various environmental samples and may be extended for the routine analysis in commercial laboratories.

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