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CATALYTIC SPECTROPHOTOMETRIC DETERMINATION OF Mn(II) AT TRACE LEVELS USING CELESTINE BLUE-KIO_4-1,10-PHENANTROLINE REDOX REACTION

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ABSTRACT. A new kinetic method has been developed for the measurement of Mn(II) in water samples. The method is based on the catalytic effect of Mn(II) with the oxidation of Celestine blue (CB^+) by KIO_4 using 1,10-phenantroline (Phen) as an activator. The optimum conditions obtained are pH 4.5, 0.1 M acetate buffer solution, 4.0×10^{-4} M KIO_4, 4.5×10^{-5} M CB^+, 1.0×10^{-4} M Phen, reaction temperature 40 °C and reaction time of 4.0 min at 640 nm. Under the optimized conditions, the method allowed the measurement of Mn(II) in a range of 0.1-5.0 μg L^{-1} with a detection limit of 0.023 μg L^{-1}. The recoveries in measuring the standard Mn(II) solutions of 0.5, 2.0 and 4.0 μg L^{-1} were in the range of 97-103%, and the relative standard deviations (RSDs) were in a range of 3.0-0.8%. The method was applied satisfactorily to the determination of Mn(II) in some environmental water samples. The reliability of method was also verified by determining the manganese content of the certified standard reference river water sample, JAC-0031. Compared with the previously published catalytic-kinetic methods and instrumental methods, the method showed fairly good selectivity and sensitivity, low cost, cheapness, low detection limit and rapidity. It can easily and successfully be applied to the natural water samples.

KEY WORDS: Mn(II), Kinetic-spectrophotometry, Catalytic effect, 1,10-Phenantroline, Celestine blue

INTRODUCTION

Manganese is necessary for the proper function of several enzymes and is an essential micro-nutrient for the function of the brain, nervous system and normal bone growth. It optimizes enzyme and membrane transport functions [1-3]. Similar to other essential metals, both excess and deficiency of manganese in the body can cause serious impairment of vital physiological and biochemical processes, excessive intake can cause lesions, headache, psychotic behavior, drowsiness and other related symptoms and/or diseases [4-6].

Manganese(II) is a biometal with low contents in natural waters. Manganese enters living organisms from the environment, in which it is present mainly as hydrated Mn^{2+}. The latter can be oxidized under aerobic conditions to give Mn^{3+} or Mn^{4+}, which form soluble and insoluble compounds. The concentration of manganese in natural water varies from 0.1 μg L^{-1} to 1 mg L^{-1} and may attain 50 mg L^{-1} in contaminated water [7]. The maximum permissible concentration (MPCs) for manganese is 0.01 mg L^{-1} in fresh water and 0.05 mg L^{-1} in sea water [8]. Thus, Mn^{2+} ions present in natural waters always participate into biocycles. Lack of the manganese in the human organism leads to the bones and cartilages deformation and destroys platelet aggregation.

There is an increasing demand towards highly sensitive methods for the determination of trace metals especially in water samples. In spite of the high sensitivities achieved by techniques such as ETAAS, ICP-OES, and ICP-MS, they are relatively expensive and present some limitations due to matrix effects. Flame atomic absorption spectrometry (FAAS) is one of the most widely used instruments for the determination of heavy metals at trace levels due to its simplicity and lower cost than other instruments. However, there are limitations in determining trace amounts of heavy metals in environmental samples FAAS due to insufficient sensitivity of instrument and some matrix interferences. The catalytic kinetic methods are one of the attractive

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procedures for trace metals analysis which offer high sensitivity and simplicity. Ultra-trace levels of metal ions which act as catalyst on an appropriate indicator reaction can be determined with simple instrumentation [9, 10]. The addition of a ligand as an activator can also improve both the sensitivity and selectivity of the reaction.

Many kinetic methods have been reported for the determination of manganese based on its catalytic effects on the oxidation of dye compounds by various oxidants [11-13]. At present, more popular catalytic methods [14-18] for the determination of Mn(II) in water systems have been frequently reported. Catalytic-spectrophotometric methods for Mn(II) using periodate, dissolved oxygen or hydrogen peroxide as the oxidizing agent [19] are not directly applicable to manganese determination in seawater because of possible interferences caused by organic substances and variations in salinity [20]. Although some of these methods are very sensitive, they must be performed at a higher temperature or take a longer time for each analysis.

The aim of the present study was to develop a new precise and accurate catalytic spectrophotometric method for the determination of Mn(II) at trace levels. The method developed is based on manganese catalyzed oxidation of CB^+ by periodate at pH 4.5 in the presence of Phen as an activator.

EXPERIMENTAL

Instrumentation

A spectrophotometer equipped with a 1 cm quartz cell (UV-1800 model, Shimadzu, Kyoto, Japan) was used for absorbance measurements. A thermostatic water bath with good temperature control (Grant LTG-6G model, Shepreth, England) was used. A stopwatch was used for recording the reaction time. A pH meter consisting of a glass-calomel electrode was used to determine pH values of solutions. Two standard buffer solutions of pH 7±0.01 and pH 4±0.01 (Myron L. Company, Carlsbad, USA) were used for the calibration of pH meter. The temperature was maintained constant in the reaction cell by circulating water at appropriate temperature around the cell compartment of the spectrophotometer throughout the experiment. All the solutions were preheated to a working temperature of 40 ^oC with an accuracy of ±0.1 ^oC before the initiation of the indicator reaction. The absorbance measurements were made at a working wavelength of 640 nm for indicator system. In establishment of optimum conditions, the standard micropipettes of 5-50, 50-500 and 10-1000 µL (Volac, UK) were used in distribution of volumes of reagent and working solutions of anionic and cationic interfering ions in interference studies.

Reagents and standards

All the chemicals used were of analytical reagent grade, and doubly distilled water was used throughout experiments. KIO_4 solution (2.0×10^{-3} M) was prepared by dissolving 0.116 g solid reagent (Merck, Darmstadt, Germany) and diluting to 250 mL with deionized water. A stock solution of CB^+ (2.25×10^{-3} M) was prepared by dissolving 0.4093 g of indicator dye (Fluka, Buchs, Switzerland) in 25 mL of 1.00×10^{-3} M NaOH solution and diluting to 500 mL with deionized water. A stock solution of Phen (5.0×10^{-4} M) was prepared by dissolving 0.024 g of pure activator (Sigma-Aldrich, Germany) and diluting to 250 mL with deionized water. The acetate buffer solution, 0.1 M pH 4.50 was prepared by dissolving solid CH_3COONa (Merck, Darmstadt, Germany) at the known amounts with 0.1 M HCl solution and diluting to 100 mL with deionized water. The pH of solution media was controlled by using a pH meter when necessary. Stock solution of Mn(II) (200 mg L^{-1}) was prepared by dissolving 0.154 g of manganese sulfate monohydrate (Merck, Darmstadt, Germany) in water and diluted to 250 mL. The working standard solutions of Mn(II) were obtained by stepwise dilution of the stock solution immediately before use. All stock solutions were stored in polyethylene containers. All

the laboratory ware used for handling solutions were cleaned with detergent solution, soaked in the diluted HNO_3 solution of 2.0% (v/v), followed by vigorous shaking, rinsed thoroughly with deionized water.

General procedure

All the reagent solutions, deionized water and empty volumetric flasks were thermostated, usually at 40 ^oC, in a water bath. A suitable aliquot of a solution containing Mn(II) at trace levels in a range of 0.1-5.0 μg L^{-1} was transferred into a 10-mL volumetric flask. Exactly 2.0 mL of buffer solution (0.1 M pH 4.50 HAc/NaAc) and 2.0 mL of 2.25 x 10^{-3} M CB^+ solution and finally 2.0 mL of 2.0 x 10^{-3} M KIO_4 and 2.0 mL of 5.0 x 10^{-4} M Phen were added to the flask, and the final solution was diluted to the mark with water and thoroughly shaken. The time recording was initiated by the addition of the last reagent. A portion of the solution was transferred into a 1.0-cm cell within 30 s from initiation of the reaction, and the reaction was followed by recording the absorbance changes at 640 nm for a fixed time of 0.5 to 4.0 min (ΔA_C). The same measurements were performed in the absence of manganese and regarded as analyte blank (ΔA_0). The net changes in the absorbance, as a measure of the catalyzed-reaction rate, were calculated from the difference in the absorbance change of the catalyzed- and uncatalyzed-reactions [$\Delta(\Delta A) = \Delta A_C - \Delta A_0$].

Sample preparation

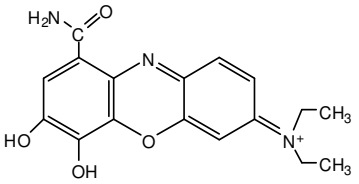
Prior to accurate and reliable kinetic analysis, river and lake water samples were treated as follows: 50 mL of sample was evaporated to about 5 mL in a 100 mL beaker on a hot plate at about 90 ^oC. 1 mL of concentrated HNO_3 and 0.5 mL of H_2O_2 30% (w/w) to preserve pH of sample solution near to 2.0-2.5 and oxidize organic matter such as humic and fulvic acid was added and the contents were heated to dryness at 90 ^oC. After cooling, the digest was diluted to 25 mL with water and adjusted to pH 4.50 using 0.1 M HCl and NaOH by means of pH meter. It was boiled for 5 min to expel the dissolved CO_2. After cooling, the solution was transferred to a 50 mL volumetric flask and diluted to the mark with deionized water, which was ready for analysis. Lake water sample was collected from Hafik Lake (Sivas, Turkey), and river water sample was freshly collected from Kızılırmak river (Sivas, Turkey). The hot- and cold-spring water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and were stored at 4 ^oC in the dark. The tap water samples were collected from different places of Yenişehir district, Sivas, Turkey including intercity bus terminal, taxi stand and the market place. The water samples (1 L) were collected in a clean 2 L beaker and slowly evaporated to about 25 mL. Then, 5 mL H_2O_2 to oxidize organic matter in place of HNO_3/H_2O_2 mixture was added and evaporated up to dryness [21]. It was then dissolved in 2 mL of water and filtered to remove insoluble substance. The filtrate was collected in 100 mL volumetric flask quantitatively and diluted to the mark with distilled water.

RESULTS AND DISCUSSION

Absorption spectra

CB^+ is a basic cationic dye of the oxazin group with a formula of $C_{17}H_{18}N_3O_4^+Cl^-$ containing vicinal hydroxyl groups in 3,4-diol position that undergoes selective oxidation reaction with periodate at pH 4.50 to form a colorless product. It is also known as 1-(aminocarbonyl)-7-diethylamino-3,4-dihydroxyphenoxazin-5-ium chloride (Scheme 1). The acidity is apparently due to its phenolic hydroxyl groups. It was used for the determination of ribavirin in

pharmaceutical formulations [22], and determination of drugs in pharmaceutical formulations by means of a spectrophotometric method based on the reaction of excess KIO_4 with CB^+ in presence of Te(IV) [23]. It was used as excellent electron transfer mediators for amperometric detection of H_2O_2 at nano-NiO/thionine and CB^+ nanocomposite-modified glassy carbon electrodes [24]. In this context, CB^+ was chosen as indicator in the current study due to be cleavage of vicinal diols on phenoxazine skeletal by periodic acid, HIO_4, into two carbonyl compounds, selective of the reaction for vicinal diols, occurred of the reaction via the formation of a cyclic periodate ester and determined of the products by the substituents on the diol.



Scheme 1. The open molecular structure of Celestine blue (CB^+ or HIn^+).

The indicator system was monitored spectrophotometrically by measuring the decrease in absorbance against water in the range of 490-750 nm for the first 4.0 min from the initiation of the reaction. Absorption spectra of the catalytic and non-catalytic systems against water in the range of 490-750 nm are clearly shown in Figure 1. The analytical results have suggested that the absorbance values of different systems reach to a peak at 640 nm, and the oxidation of CB^+ by KIO_4 at pH 4.5 slowly proceeds. In the presence of trace amounts of Mn(II), the oxidation rate of CB^+ evidently has increased. The Mn(II) catalyses the decolorizing oxidation of indicator dye at 640 nm. The absorbance changes are proportional to the Mn(II) concentrations in calibration range, and when Phen as an activator is added to enhance the sensitivity and selectivity of the Mn(II)-catalyzed-indicator reaction, the absorbance of the catalytic system is further reduced. This has shown that the addition of Phen can increase the sensitivity of the indicator reaction. Therefore, the kinetic determination should be carried out at 640 nm for further experimental studies.

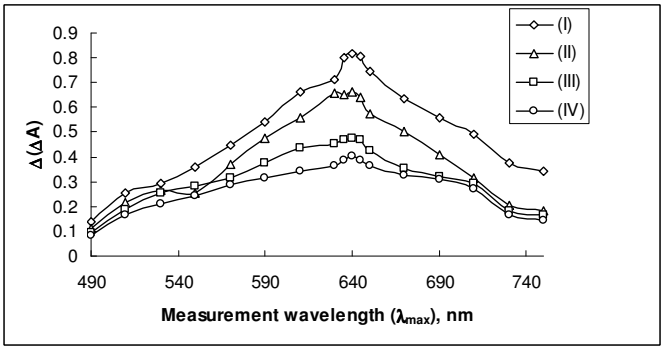


Figure 1. Absorption spectra of indicator systems at optimum conditions ([CB^+]: 4.00 x 10^{-5} M, [Phen]: 1.00 x 10^{-4} M, [KIO_4]: 4.0 x 10^{-4} M, 0.1 M acetate buffer pH 4.50 for the fixed-time of 4.0 min at 640 nm and 40 ^oC in presence of 2.0 µg L^{-1} Mn(II)). System I: CB^+-pH 4.5 acetate buffer. System II: CB^+-pH 4.5 acetate buffer-KIO_4. System III: CB^+-pH 4.5 acetate buffer-KIO_4-Mn(II). System IV: CB^+-pH 4.5 acetate buffer-KIO_4-Mn(II)-Phen.

Optimization of reaction conditions

In order to take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized; providing that the optimum concentration of each component will give the smallest relative standard deviation and its reaction order will be zero according to its relevant species for the kinetic measurements, except for the analyte (where catalyst). The conditions of which the small fluctuations in concentration have not any effect on the initial rate are desired. These conditions should be selected providing that the initial rate will be first order according to the analyte, $\Delta(\Delta A)$: k_C [Mn(II)]. In this context, the optimization data for each analytical variable was repeated at least three times during the kinetic absorbance measurements. The influence of analytical variables such as the pH, reagent concentrations (CB^+ and periodate), Phen as activator, and temperature and ionic strength of environment on the rate of catalyzed and uncatalyzed reaction was studied in detail. Here, any statistical study such as factorial design to identify both synergic effects among them and to make an economy of efforts and reagents was not made. In our further studies a similar study in optimization step before determination of catalytically active species will be considered. In reaction rate-concentration curves according to their tradition in literature the concentration of reactants and inert salt as a measure of ionic strength were taken into consideration. In order to reconcile sensitivity [$\Delta(\Delta A)$] and short analysis time the fixed-time method for the first 4 min due to be proportional of sensitivity to the reaction time in the time interval of 0.5-15 min was adopted as kinetic detection method in the catalytic determination of manganese.

Influence of pH on sensitivity

The influence of pH on sensitivity in presence of 2.0 µg L^{-1}Mn(II) was studied by adjusting the sample pH to a value ranging from 2.0 to 7.0. For this purpose, acetic acid-boric acid-orthophosphoric acid and NaOH solutions, which is also known as universal buffer, were used. Based on the experimental findings, the optimum pH value of 4.5 was selected. The influence of several buffer solutions at pH 4.5 was tested. The best buffer solution was selected using the slope of the calibration graph as the optimization criterion. In the case of sodium citrate-HCl and potassium hydrogen phthalate-HCl buffer solutions, the slope of calibration graph was unsatisfactory. On the other hand, if H_3PO_4-NaOH or NaAc-HCl buffers were used, the slope of calibration graph was higher. However, the best results were obtained for the latter one. Moreover, the preparation of NaAc-HCl buffer is less time-consuming compared to the preparation of H_3PO_4-NaOH buffer solution. Later on, the NaAc-HCl concentration was varied within 0.01-0.25 M in order to discriminate the optimum HAc-NaAc content in samples. The results are presented in Figure 2. It was found that the highest slope of the calibration graph was achieved for the buffer concentration of 0.1 M.

Influence of KIO_4 concentration on sensitivity

The influence of the periodate concentration on the rate of reaction in presence of 2.0 µg L^{-1} Mn(II) was studied in the range of 1.0 x 10^{-4}–1.2 x 10^{-3} M. The results showed that the net reaction rate increases with increasing periodate concentration up to 4.0 x 10^{-4} M and decreases at higher concentrations. As can be seen from Figure 3, the rate of uncatalyzed reaction increases with periodate concentration (>4.0 x 10^{-4} M) to a greater extent and the difference between the rates of catalyzed and uncatalyzed reactions (ΔA_C–ΔA_0) diminishes at higher periodate concentrations as a result of increasing blank signal. Therefore, a periodate concentration of 4.0 x 10^{-4} M was selected for further study.

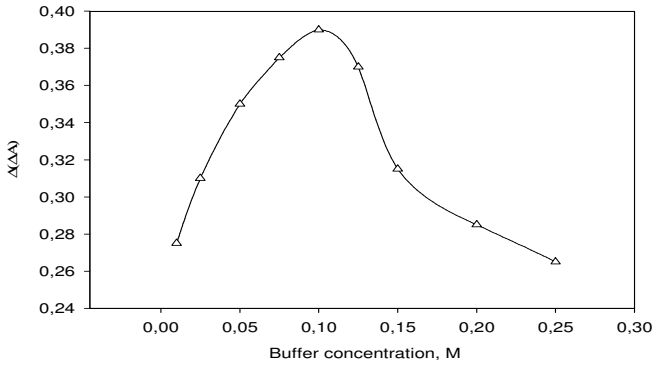


Figure 2. Influence of buffer concentration on analytical sensitivity for the net catalyzed-reaction rate. Conditions: [Phen]: 1.0×10^{-4} M, [KIO_4]: 4.0×10^{-4} M, [CB^+]: 4.0×10^{-5} M and pH 4.50 acetate buffer for the fixed time of 4.0 min at 640 nm and 40°C in presence of 2.0 µg L^{-1}Mn(II)

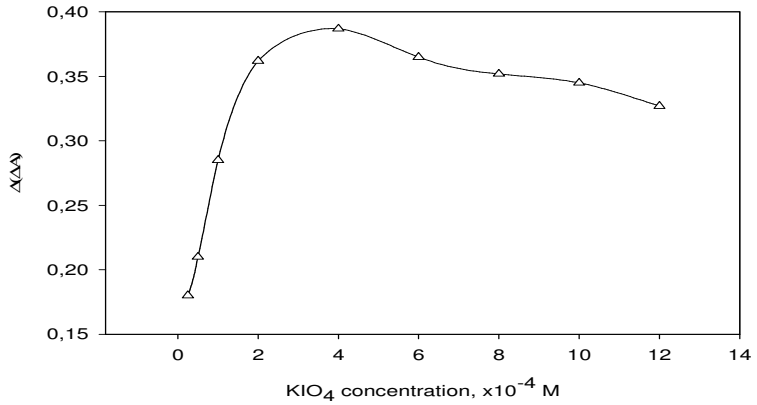


Figure 3. Influence of KIO_4 concentration on analytical sensitivity for the net catalyzed-reaction rate at 0.1 M acetate buffer. Other conditions are same as in Figure 2.

Influence of Celestine blue concentration on sensitivity

Figure 4 shows the influence of CB^+ concentration on the sensitivity for the range of 1.0×10^{-5}-10×10^{-5} M in presence of 2.0 µg L^{-1} Mn(II). This sensitivity (net reaction rate) increases with increasing CB^+ concentration up to 4.5×10^{-5} M and decreases at higher concentrations. This decrease may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of 4.5×10^{-5} M of CB^+ was selected as the optimum concentration.

Influence of activator concentration on sensitivity

The influence of Phen concentration on the rate of net reaction was studied in the range of 5.0×10^{-6}-2.0×10^{-4} M in presence of 2.0 µg L^{-1} Mn(II). As can be seen from in Figure 5, the sensitivity increases with increasing 1,10-phenantroline concentration up to 1.0×10^{-4} M and decreases at higher concentrations. This is due to the ion-pair complex formation with indicator dye in blank solution and change in the activation effect of the activator in the solution.

Therefore, a final concentration of 1.0 x 10^{-4} M was selected as the optimum concentration of Phen.

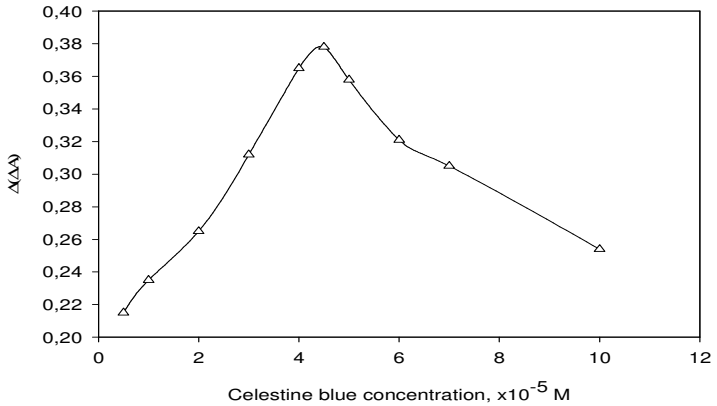


Figure 4. Effect of Celestine blue concentration on analytical sensitivity for the net catalyzed-reaction rate at [KIO_4]: 4.0 x 10^{-4}M. Other conditions are same as in Figure 3.

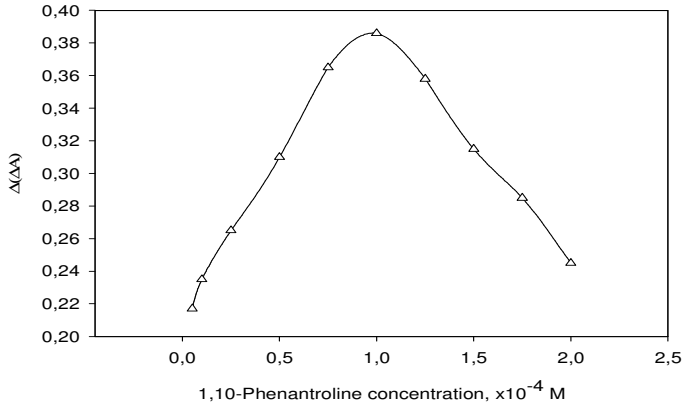


Figure 5. Influence of activator concentration on analytical sensitivity for the net catalyzed-reaction rate at [CB^+]: 4.0 x 10^{-5}M. Other conditions are same as in Figure 4.

Influence of reaction time and temperature on sensitivity

The effect of time on the sensitivity was studied in the range 0.5-15 min at the optimized reagent concentrations in absence and presence of Mn(II) at fixed concentration of 2.0 µg L^{-1}. For the uncatalyzed-reaction the sensitivity, ΔA_0 initially increases approximately up to 12 min, then reaches a plateau and kept constant with a decreasing slope in time interval of 12-15 min. However, for catalyzed-reaction the sensitivity, ΔA_C initially increases with a large slope, and then reaches a plateau and kept constant at higher reaction times than 8.0 min as the time gradually advances up to 8.0 min. In order to achieve higher sensitivities and shorter time, for reasonable signal difference between catalyzed- and uncatalyzed-reaction rates, $\Delta(\Delta A)$: ΔA_C-ΔA_0, a fixed-time of 4.0 min was considered as the optimal time for further studies.

The influence of the temperature on the sensitivity was studied in the range 10–70 °C with the optimum pH and other reagent concentrations in presence of 2.0 µg L^{-1} Mn(II). It can be

seen from Figure 6 that as the temperature increases up to 40 ^{o}C, the net reaction rate increases with increasing slope, and then the sensitivity, $\Delta(\Delta)$: $\Delta A_C - \Delta A_0$ gradually decreases at higher temperatures. This means that the rate of uncatalyzed reaction increases with temperature to a greater extent in the range of 40-70 ^{o}C, and as a result of increasing signal blank the net signal difference is decreased. Another cause may be instability of potassium periodate at high temperatures. Therefore, 40 ^{o}C was selected for further study. To calculate the activation energy, $-\ln[\Delta(\Delta A)/\Delta t]$ was measured over the range of 10–25 °C, the results suggest that $-\ln[\Delta(\Delta A)/\Delta t]$ is linearly related to (1/T) x 10^3, and the calibration curve obeys the following linear regression equations: $-\ln[\Delta(\Delta A)/\Delta t]$: 5.5761 × (1/T) x 10^3–17.5391 (for catalyzed reaction) with a regression coefficient (r^2) of 0.9921. According to the Arrhenius equation, the activation energy of the Mn(II)-catalyzed reaction calculated from the equation mentioned above is 23.3 kJ mol^{-1}. In this study, the catalyzed-reaction is heated during the fixed-time of 4.0 min.

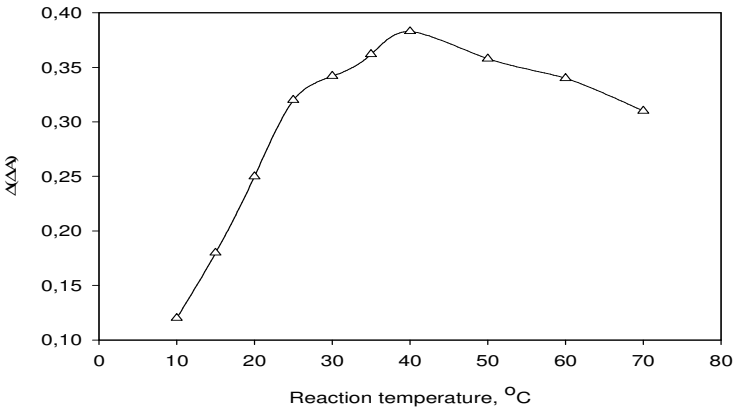


Figure 6. Influence of reaction temperature on analytical sensitivity for the net catalyzed-reaction rate at [Phen]: 1.0 x 10^{-4} M. Other conditions are same as in Figure 5.

Influence of ionic strength on sensitivity

Under optimal conditions selected, the influence of ionic intensity of environment onto the analytical sensitivity, $\Delta(\Delta A)$ was examined in the concentration range of 0.005-0.5 M $NaNO_3$. It was observed that the reaction ratechanged very little with increasing concentration approximately up to 0.07 M, after this concentration exhibited a negative change with increasing inclination. This case predicated that the catalyzed-indicator reaction would give accurate analytical signals for catalyst in real samples with low matrix such as fresh waters. It can be expressed that inert salt effect should be checked at matrix systems with the high salt content such as sea water and wastewaters. Standard addition method can be suggested for analyzing Mn(II) in real samples having high salt content.

The calibration curve, detection limit and precision

Calibration curves were obtained using the fixed-time method. This method was directly applied to the change in absorbance over an interval of 0.5–4.0 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration curve was obtained for Mn(II) in the concentration range 0.1–5.0 µg L^{-1} Mn(II). The equation of the calibration curve is $\Delta(\Delta A) = 0.0047 + 0.176C_{Mn(II)}$ ($r^2 = 0.9978$, n = 10), where *c* is the concentration of Mn(II) in µg L^{-1}.

By ten replicate blank experiment determinations the detection limit (LOD) of the method was calculated to be 0.03 μg L^{-1} Mn(II) according to $3S_{blank}/k$ method (S is the standard deviation of ten blank replicate determinations, k is the slope of calibration curve).

The relative standard deviations of 0.50, 2.00 and 4.00 μg L^{-1} of Mn(II) for five replicate measurements were 3.0, 1.4 and 0.8%, respectively. Table 1 shows the accuracy and precision of the kinetic method developed under the optimum reagents conditions at 640 nm and 40 °C.

Table 1. The accuracy and precision of the proposed kinetic method. Conditions: ([Phen]: 1.0 x 10^{-4} M, [KIO_4]: 4.0 x 10^{-4} M, 2 mL 0.1 M pH: 4.5 acetate buffer, [CB^+]: 4.0 x 10^{-5} M for the fixed time of 4.0 min at 640 nm and 40 °C).

Added Mn(II), μg L^{-1}	Found Mn(II), μg L^{-1} (N = 5)	*RSD % (N = 5)	*RE % (N = 5)	Recovery %
0.5	0.5	3.0	6.0	100
2.0	2.0	1.4	2.5	100
4.0	4.0	0.8	1.5	100

*The relative errors and relative standard deviations of five replicate determinations at the concentration levels of 0.5, 2.0 and 4.0 μg L^{-1}.

Interference studies

In order to assess the analytical application of the proposed method to synthetic samples, the effect of various ions on the determination of 2.0 μg L^{-1} Mn(II) was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 5.0%. The results are summarized in Table 2. Many ions did not interfere, even when they were present in 50–4500 fold excess over Mn(II). A 10-25-fold excess of Cr(III) and Ni(II) showed almost a significant effect on the catalytic signal of Mn(II). However, some reductive ions such as NO_2^- (>7.5 μg L^{-1}), S^{2-} (>10 μg L^{-1}) and Fe^{2+} (>15 μg L^{-1}) could yield serious adverse effects on sensitivity. It is perceptible that these reductive ions may interfere onto the indicator reaction, on which the measurement is based, although they were rarely mentioned and discussed in the previous catalytic kinetic systems. In natural waters in the local area, their concentrations generally range from 20 to 200, 10 to 100, and 5 to 50 μg L^{-1} for NO_2^-, S^{2-}, and Fe^{2+}, respectively [25]. Also, the interfering effect of permanganate ion, MnO_4^- as a manganese species available together with Mn(II) in oxygen-rich surface waters was investigated. It was observed that permanganate ion did not interfered up to a tolerance limit of 60 fold in the optimized conditions. However, at higher tolerance ratios a positive interfering effect was observed. This effect was spectrophotometrically monitored and controlled at 524 nm with a blue shift of 4 nm from 520 nm, which is maximum absorption wavelength of permanganate in presence of excess MnO_4^- ions. It can be explained with increase in concentration of catalytic active species due to the fact that (i) solutions of MnO_4^- are intrinsically unstable, decomposing slowly, but observably in a weak acidic medium:

$$4MnO_4^- + 4H^+ \rightarrow O_2 + 2H_2O + MnO_2 \quad (1)$$

(ii) since MnO_4^- oxidizes Mn^{2+} (E^0: 0.46 V), the product in the presence of an excess of permanganate is MnO_2:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (2)$$

These experimental findings are also important for explanation of catalytic effect of Mn(II) in presence of reagents, KIO_4, CB^+ and Phen at pH 4.5. In order to eliminate their possible potential interferences, water samples were treated with strong oxidizing agents such as HNO_3 and H_2O_2, prior to analysis as described in Section 2. Therefore, no attempt was made to individually avoid the adverse effects from each of the above-mentioned ions. The results show that the method is relatively selective for determination of Mn(II). All the results are averages of three replicate measurements with 1.3–3.5% RSD.

Table 2. Interference study for determination of 2.0 µg L^{-1} Mn(II) in the presence of optimum reagent concentrations: [Phen]: $1.0x10^{-4}$ M, [KIO_4]: 4.0 x 10^{-4} M, 2 mL 0.1 M pH: 4.5 acetate buffer, [CB^+]: 4.0 x 10^{-5} M for the fixed time of 4.0 min at 640 nm and 40 °C.

Interfering species (K^{n+} or A^{m-})*	Tolerance limit ($W_{interfering\ ion}/W_{Mn(II)}$)**
K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+	3000-4500
Ca(II), Mg(II), F^-, HCO_3^-, Cl^-	2000-2750
Cd(II), Al(III), $C_2O_4^{2-}$	1250-2000
Cr(VI), Cu(II), Zn(II)	350-750
Ag^+, Fe(III)	300
V(V), Co(II), Bi(III)	75-250
SO_3^{2-}, V(IV), Mn(VII)	50-75
Cr(III), Ni(II)	25-50
Fe(II)	15
S^{2-}	10
NO_2^-	7.5

* For interfering cationic and anionic species with positive and negative charge. ** Concentration ratios of interfering ions and Mn(II) at fixed concentration of 2.0 µg L^{-1}.

Analytical applications of the developed kinetic method

In order to determine the accuracy and validity of the developed kinetic method, the Mn(II) concentrations were determined by spiking the standard Mn(II) solutions into tap water samples at concentration levels of 1.0, 2.0 and 3.0 µg L^{-1} for analysis separately. The results, which are found by spiking into tap water samples collected from three different sampling points for determining Mn(II) are given in Table 3. All of the results found with three replicate analyses were statistically in 95% confidence interval. The RSDs less than 3.2% were obtained from the analysis of tap water samples for Mn(II) contents ranging from 1.2 to 1.9 µg L^{-1}. Also, the recovery results prove clearly the accuracy and validity of kinetic spectrophotometric method described in the present study.

The proposed method was applied to the determination in some environmental water samples such as river, lake, hot- and cold-spring water. After being collected, the samples were filtered with membrane filter having the pore size of 0.45 µm and the filtrates were acidified at approximately pH 4.5 by adding appropriate volumes of 5.0 M HCl. After pretreatment at suitable dilution ratios, in order to control a possible systematic error, both the calibration curve method and standard addition method were carried out. Applications of standard addition procedure yielded linear calibration curves with the same slopes as that of standard calibration curves and showed reasonably good agreement in Mn(II) concentrations determined by both methods. These results show that the proposed method gives reasonably precise and accurate determinations, especially from the standpoint of trace metal analysis with very simple procedure. In order to validate the present method, the recovery tests were also made by adding two standard Mn(II) solutions at known concentrations. The results are summarized in Table 4.

The recovery values obtained were highly good. In order to test the analytical validation of the newly developed kinetic method, the method was also applied to the determination of manganese in certified standard river water sample. The standard reference material was employed without any pretreatment procedure. For comparison of the results found by using the present method, the standard reference water sample was also analyzed by recoveries of the Mn(II) spiked water samples. It was found that the results obtained by the present method were in agreement with the certified value. To confirm both the accuracy and precision of the kinetic method with the recovery experiments, the known amounts of Mn(II) were added to the certified sample solution as well as using an unpaired t-test to compare the obtained result in the certified sample. The results are shown in Table 4. It was found that the recovery of spiked Mn(II) was

satisfactorily quantitative and the reproducible. It was observed that the result obtained with the proposed method was in good agreement with the certified value, and contained no significant differences at the 95% confidence level. It can be concluded that the proposed kinetic method for determining the trace amounts of manganese available in real samples is a useful and applicable method.

Table 3. Determination of Mn(II) present in tap water samples by using the kinetic method.

***Samples	Concentration, μg L^{-1}		Recovery %	RSD %**
	Added	Found*		
Tap water-I[a]	-	1.2	-	3.0
	1.0	2.2	100	3.0
	2.0	3.2	100	3.0
	3.0	4.1	97	2.0
Tap water-II[b]	-	1.9	-	3.0
	1.0	2.9	100	3.0
	2.0	3.9	100	2.0
	3.0	4.9	100	2.0
Tap water-III[c]	-	1.5	-	3.0
	1.0	2.5	100	3.0
	2.0	3.5	100	3.0
	3.0	4.6	103	2.0

*Average of five replicate determinations. **The RSDs obtained are based on five determinations on separate occasions within 95% confidence level. ***The tap water samples were collected from three different places of Yenişehir district, Sivas, Turkey. (a) Intercity bus terminal (b) Taxi stand (c) Market place.

Table 4. Determination of manganese in certified standard river water (JAC–0031) and some environmental water samples such as river, lake, hot- and cold-spring water.

Samples	Mn added (μg L^{-1})	Mn found* (μg L^{-1})	Mn in sample (μg L^{-1})	Recovery (%)	RSD (%)
River water after dilution of 1:1000 (Kızılırmak, Sivas)	0	2.5±0.02 (2.5±0.02)***	-	–	0.8
	1.0	3.5±0.02	-	100	0.6
	2.0	4.5±0.02	-	100	0.4
Lake water after dilution of 1:250 (Hafik, Sivas)	0	1.3±0.02 (1.4±0.02)	-	–	1.5
	1.0	2.4±0.02	-	110	0.8
	2.0	3.4±0.02	-	105	0.6
Hot-spring water after dilution of 1:250 (Sivas)	0	0.8±0.02 (0.8±0.02)	-	–	2.5
	1.0	1.8±0.02	-	100	1.1
	2.0	2.8±0.02	-	100	0.7
Cold-spring water after dilution of 1:250 (Sivas)	0	1.0±0.02 (1.0±0.02)	-	–	2.0
	1.0	2.0±0.02	-	100	1.0
	2.0	3.1±0.02	-	105	0.7
JAC–0031**	0	0.2±0.02 (0.2±0.02)	0.5±0.02	–	10.0
	1.0	1.2±0.02	-	100	1.7
	2.0	2.2±0.02	-	100	1.0
	3.0	3.2±0.02	-	100	0.6

*Average values plus their standard deviations for four replicate measurements. **After a dilution of 1:2; certified value (μg L^{-1}), 0.46±0.02. ***Values in parenthesis are the results of applying the standard addition method.

The catalytic reaction mechanism

The kinetics of the uncatalyzed- and Mn(II) catalyzed-oxidation of CB^+ or HIn^+ by KIO_4 at pH 4.5 was studied in presence of Phen as an activator. The absorbance of CB^+ at 640 nm was

found to be evidently decreased by the presence of MnO_2 and/or Mn^{3+} as catalytic active species, and the absorption spectrum of oxidation product was the same as that obtained from oxidation of CB^+ by KIO_4 at pH 4.5. The possible catalytic reaction mechanism for the indicator system at pH 4.5 may be postulated by a series of reactions as follows:

$$Phen + H^+ \xleftarrow{pK_a:4.86} PhenH^+ \quad (1)$$

$$Mn^{3+} + e^- \leftrightarrow Mn^{2+}, E^0 : 1.5volt \quad (2)$$

Because of the possibility of coexistence of paraperiodic acid and metaperiodic acid in equilibrium in weak acidic medium as follows:

$$H_5IO_6 \leftrightarrow HIO_4 + 2H_2O \text{ and } HIO_4 + H^+ + 2e^- \leftrightarrow IO_3^- + H_2O$$

$$H_5IO_4 + H^+ + 2e^- \leftrightarrow IO_3^- + 3H_2O, E^0 : 1.6volt \quad (3)$$

Because the pH of catalytic system is 4.5, the predominant species of Phen present in reaction media is relatively $PhenH^+$. In presence of Mn(II) at trace levels, this activating species reacts with Mn^{2+} ions forming the stable $Mn(Phen)_3^{2+}$ complex. In presence of activator, this intermediate Mn(II)-Phen complex participates into the catalytic cycle in the kinetic determination of Mn(II) at pH 4.50.

$$2Mn^{2+} + IO_4^- + 2H^+ \xrightarrow{Rapid} 2Mn^{3+} + IO_3^- + H_2O \quad (4)$$

The produced Mn(III) is quite powerful oxidizing agent and also prone to disproportionation in solution to Mn(II) and Mn(IV) due to its electron donor and electron acceptor properties.

$$2Mn^{3+} + 2H_2O \xrightarrow{Rapid} Mn^{2+} + MnO_2 + 4H^+ \quad (5)$$

$$MnO_2 + HIn^+_{(reducedform)} + 3H^+ \xrightarrow{Rapid} Mn^{3+} + In^+_{(oxidizedform)} + 2H_2O \quad (6)$$

Degradation byproducts

$$Mn^{3+} + HIn^+_{(reducedform)} \xrightarrow{Rapid} Mn^{2+} + In^+_{(oxidizedform)} + H^+ \quad (7)$$

Advanced degradation byproducts

In presence of Phen as stability enhancement agent in indicator system

$$Mn^{2+} + 3Phen \leftrightarrow Mn(Phen)_3^{2+} \quad \text{Or} \quad (8)$$

$$2Mn(Phen)_3^{2+} + IO_4^- + 2H^+ \xrightarrow{Rapid} 2Mn(Phen)_3^{3+} + IO_3^- + H_2O \quad (9)$$

$$Mn(Phen)_3^{3+} + HIn^+_{(\mathrm{Re}\,ducedform)} \xrightarrow{Rapid} Mn(Phen)_3^{2+} + In^+_{(Oxidizedform)} + H^+ \quad (10)$$

$$2HIn^+_{(\mathrm{Re}\,ducedform)} + H_5IO_6 \xrightarrow{Slow} IO_3^- + 2In^+_{(Oxidizedform)} + H^+ + 3H_2O \quad (11)$$

$$2HIn^+_{(\mathrm{Re}\,ducedform)} + H_5IO_6 \xrightarrow{Rapid} IO_3^- + 2In^+_{(Oxidizedform)} + H^+ + 3H_2O \quad (12)$$

In presence of MnO_2 and Mn^{3+} produced by oxidation of Mn^{2+} at trace levels, the net catalyzed-reaction rapidly proceeds in equation (12) as a result of catalytic cycles taking place in equations (5-10) whereas the uncatalyzed-reaction slowly proceeds in absence of catalyst in equation (11). The concentration of colloidal MnO_2 or $Mn(Phen)_3^{3+}$ complex in equation (5) has greatly increased with increase in temperature in the range of 10-40 ^oC, which improved the decolorizing rate of HIn^+ as reduced form of CB^+ (8), thus the reaction rate was effectively enhanced by selective oxidation of HIn^+ by KIO_4. The calculated apparent activation energy (E_A: 23.3 kJ moL^{-1}) was in line with the need for a low reaction temperature of 40 °C.

Table 5. Comparison of the proposed kinetic method with the other Mn(II)-catalyzed kinetic methods reported in the literature.

Indicator reaction	Dynamic range ($\mu g\ L^{-1}$)	Detection limit ($\mu g\ L^{-1}$)	Kinetic parameters and remarks	Ref.
Tropaeolin OO+KIO_4	0.05-2.5	0.02	Phen as activator	[27]
Nile blue A+H_2O_2	6.6-65.9	0.08	Ribavirin as activator and tiazofurin as inhibitor	[29]
Methylthymol blue+H_2O_2	0.2-40	0.64	k: 5.62 x 10^{-4} s^{-1}, E_a: 73.2 kJ mol^{-1}	[30]
Naphtol blue black+KIO_4+Phen	0.08-4	0.025		[31]
1,3-Dimethyl-2 [4-N(N,N-dimethylamino)phenylazo] imidazolium perchlorate+KIO_4	0.1-4.5	0.03	Phen as activator	[32]
2',4'-Dihydroxy-azo-benzen4-sulphonic acid sodium salt	0.1-5.0	0.03	Phen as activator	[33]
Alizarin green+KIO_4	0.4-2.4	0.097	NTA as activator and β-cyclodextrin as sensitizer	[34]
Dahlia violet+KIO_4	0.4-5.6	0.0375	NTA as activator and nonionic microemulsion system k: 1.31 x 10^{-3} s^{-1}, E_a: 10.2 kJ mol^{-1}	[35]
Nile blue+KIO_4	0.4-5.6	0.054	NTA as activator and cetylpyridinium bromide as sensitizer	[36]
Azure II+KIO_4	0.4-2.0; 2.0-6.0	0.053	NTA as activator and dodecyl dimethylamino acetic acid as sensitizer	[37]
Celestine blue-KIO_4	0.1-5.0	0.03	Phen as activator, E_a: 23.31 kJ mol^{-1}	Present method

CONCLUSIONS

The catalytic kinetic method developed for Mn(II) in environmental samples such as river, lake, hot- and cold-spring water as well as tap water samples is inexpensive and readily available and allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and very good precision and accuracy, relation to the other kinetic procedures. The validation of the method was achieved by determination of Mn(II) present in the certified river water sample, JAC-0031 by using the calibration curve and standard addition curve procedures, and the results obtained by using both approaches statistically showed a good agreement with its certified value in view of accuracy and precision. The linear range is wider than some of the previously reported methods and has a lower detection limit [26-28]. Compared with the other catalytic kinetic methods given in Table 5, the proposed kinetic method shows many advantages such as shorter analysis time, low operational temperature, wider linear dynamic range and lower detection limit [30, 32-37]. Moreover, it can easily be adapted for a flow injection system analysis to improve the figures of merit for fast/in situ-monitorization of Mn(II) present in environmental waters.

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