CATALYTIC-SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF MANGANESE(II) BY CATALYSIS OF THE OXIDATION OF FERROIN WITH PERIODATE

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ABSTRACT : *A catalytic spectrophotometric method for determination of ultra-trace quantities of manganese(II) is described. The method is based on the catalytic effect of manganese(II) on the oxidation reaction of ferroin by potassium periodate in acidic media. The reaction is monitored spectrophotometrically at 510nm by a slope method and Mn(II) is determinable in the range of 1-1000ngmL^{-1}. The limit of detection is as low as 0.94ngmL^{-1}. The proposed method was applied to the determination of manganese in milk.*

KEY WORDS: *Manganese(II), Catalytic, Spectrophotometric, Ferroin, Periodate.*

INTRODUCTION

Kinetic methods of chemical analysis have some advantages, including high sensitivity, extremely low detection limit, good selectivity, rapid analysis and inexpensive instruments such as a spectrophotometer or spectrofluorimeter. Catalytic determinations are the most widely used of the kinetic methods [1-4].

Numerous catalytic-kinetic methods for the determination of manganese have been described [5-22]. In these methods various redox reactions have been used. The reactions have been monitored by chemiluminescence, potentiometric, oscillopolarographic and thermometric techniques. The methods are either not sensitive

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enough or require complicated and expensive instruments, or are subject to interferences from other ions, suffer from small calibration range, toxicity of the reagents used, or more or less are time consuming.

In this work, a catalytic spectrophotometric method based on the catalytic effect of Mn(II) in oxidation reaction of ferroin with periodate has been introduced for the determination of ultra-trace amounts of Mn(II). The proposed method is rapid, sensitive, relativity selective and is suitable for the determination of as low as 0.94ngmL^{-1} of Mn(II). A wide range of Mn(II) can be determined by changing the periodate concentration.

EXPERIMENTAL

Reagents

All solutions were prepared using reagent grade substances and triply-distilled water. A stock solution of manganese (1000μgmL^{-1}) was prepared by dissolving 0.3073g $MnSO_3 .H_2O$ *(Merck)* in water and diluting to the mark with water in a 100mL volumetric flask. The solution was standardized by titrimetry with EDTA [23]. The solution was diluted further as required. A 0.016M periodate solution was prepared by dissolving 0.3682g of KIO_4 *(Merck)* in water and diluting to the mark in a 100mL volumetric flask. Ferroin solution (1.41×10^{-3}M) was prepared by appropriate dilution of its 0.025M solution *(Merck)* with water.

Apparatus

Absorption spectra were recorded on a *Shimadzu* model UV-256 UV-Visible recording spectrophotometer with a 1-cm glass cell. A *Shimadzu* model UV-120-01 spectrophotometer with a 1-cm glass cell was used for absorbance measurements.

Recommended procedure

All reactants were kept in a thermostated bath at 30.0±0.1°C before the beginning of the reaction.

A suitable aliquot of the sample solution containing 10-500ng Mn(II) was transferred into a 10mL volumetric flask contained 3mL of 0.016M periodate solution. Then 1.5mL of 0.1M sulfuric acid was added. The solution was diluted to ca.8mL with water then 1.0mL of 1.41×10^{-3}M ferroin solution was added to initiate the reaction. The solution was diluted to the mark with triply distilled water and a portion was transferred into a glass cell within 30s for measuring the change in absorbance with time (dA/dt) at 510nm for the first 3.0 minutes after initiation of the reaction.

Higher concentrations of Mn(II) could be determined by decreasing the amount of added potassium periodate. For determination of 100-10000ng of manganese 1mL of 0.002M potassium periodate was added.

RESULTS AND DISCUSSION

Mn(II) catalyzes the oxidation reaction of ferroin with potassium periodate in acidic media (Fig.1).The reaction could be monitored spectrophotometrically by measuring the decrease in absorbance at 510nm (λ_{max} for absorption spectra of ferroin).

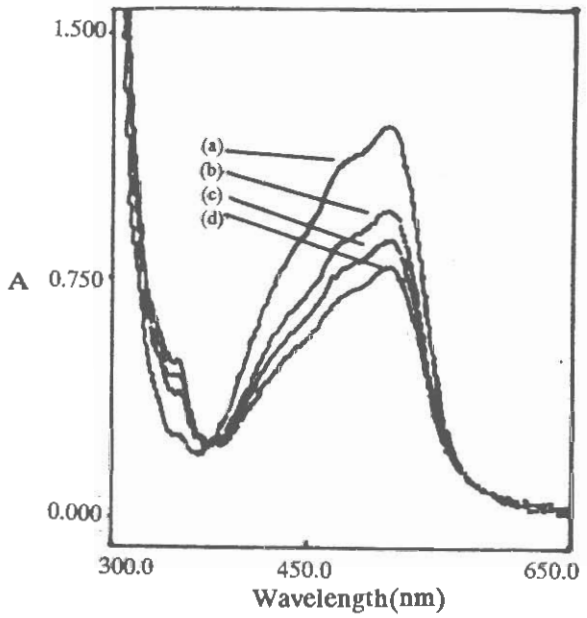

Fig. 1: Absorption spectra of ferroin in the presence of 4.8×10^{-3}M periodate, 0.015M H_2SO_4 and (a) 0.00, (b) 20, (c) 40, (d) 50ngmL^{-1} of Mn(II) at 50 seconds after initiation of reaction.

Optimization of variables

Several variables affecting the catalyzed and uncatalyzed reaction were optimized to establish the most suitable analytical conditions.

The effect of temperature was studied in the range of 5-46°C. As Fig.2 shows, the catalyzed reaction proceeds more quickly at higher temperatures, but the rate of the uncatalyzed reaction also increases. The temperature of 30°C was adopted as the most suitable.

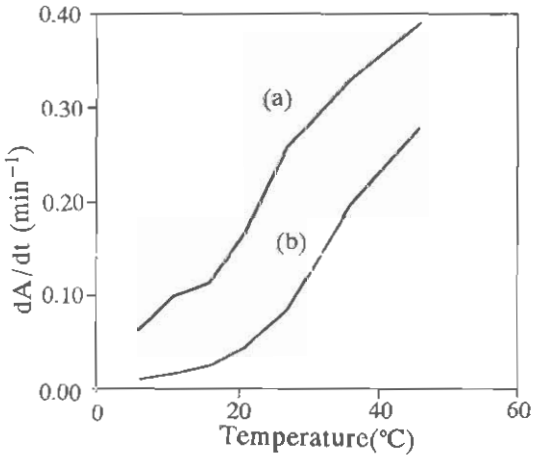

Fig. 2: Effect of temperature on (a) catalyzed and (b) uncatalyzed reaction rate; conditions: Mn(II) 0.05ngmL^{-1}; periodate 4.8×10^{-3}M; H_2SO_4 0.015M; ferroin 1.4×10^{-4}M.

The effect of the concentration of ferroin was examined in the range of 3.5×10^{-5}-1.7×10^{-4}M. The reaction rate of both the catalyzed and uncatalyzed reactions increased by increasing the concentration of ferroin (Fig.3). A 1.4×10^{-4}M ferroin concentration was selected for the sake of high sensitivity.

As mentioned before, the reaction proceeds in acidic media. Various acids were tested and sulfuric acid was found as the best one. The effect of sulfuric acid concentration on the rate of both the catalyzed and uncatalyzed reactions in the range of 0.002-0.10M was also tested. As Fig.4 shows by increasing the concentration of sulfuric acid, the rate of catalyzed reaction increases up to 0.015M, whereas the rate of uncatalyzed reaction, remains almost constant. However the rate of both reactions decreases at higher concentrations. Therefore a final concentration of 0.015M sulfuric acid was selected.

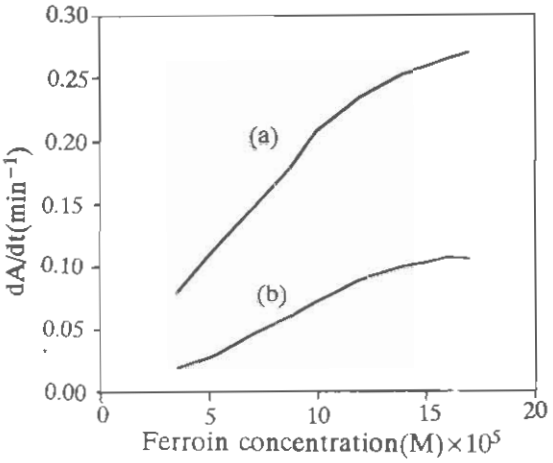

Fig. 3: Effect of ferroin concentration on (a) catalyzed and (b) uncatalyzed reaction rate; conditions: Mn(II) 0.05ngmL^{-1}; periodate 4.8×10^{-3}M; H_2SO_4 0.015M;

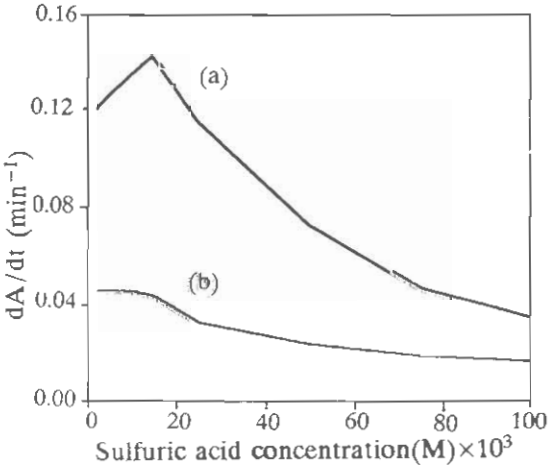

Fig. 4: Effect of sulfuric acid concentration on (a) catalyzed (b) uncatalyzed reaction rate; conditions: Mn(II) 0.05ngmL^{-1}; periodate 4.8×10^{-3}M; ferrion 8.8×10^{-5}M.

The effect of the periodate concentration was studied in the range of 4.0×10^{-4}-6.4×10^{-3}M (Fig.5). The rate of both the catalyzed and uncatalyzed reactions increased by increasing the periodate concentration up to about 4×10^{-3}M and remained constant at higher concentrations. It was observed also that the linear dynamic range for the determination of manganese depends on the concentration of periodate.

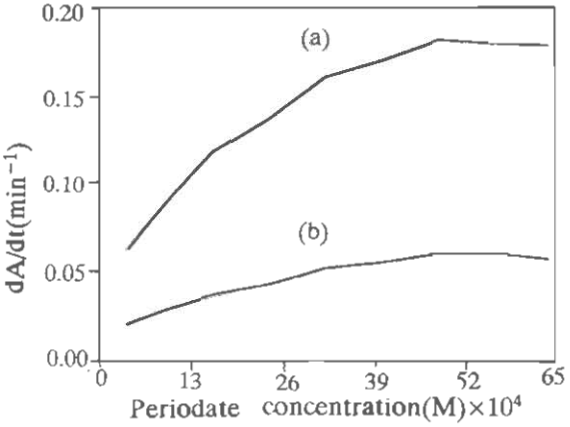

Fig. 5: Effect of periodate concentration on (a) catalyzed and (b) uncatalyzed reaction rate; conditions: H_2SO_4 0.015M; Mn(II) 0.05ngmL^{-1}; ferrion 8.8×10^{-5}M.

Therefore the concentration of periodate was selected according to the concentration range of manganese under study.

Analytical parameters

The calibration graphs were obtained under the optimum conditions. The linearity range of the calibration graph was dependent on the periodate concentration (Table 1).

The reproducibility of the measurements was satisfactory. Relative standard deviations of 1.54 and 0.88% were obtained for ten determinations of 5 and 25ngmL^{-1} manganese respectively.

For final concentration of 4.8×10^{-3}M periodate, the limit of detection (3×noise) of

Table 1: Linear regression of calibration data for manganese at different concentrations of KIO_4

KIO_4 (M)	Slope (mL/ng.min)	Intercept (min^{-1})	Correlation Coefficient	Detection Limit (ngmL^{-1})	Calibration range (ngmL^{-1})
4.8×10^{-3}	3.2×10^{-3}	0.0667	0.9997	0.94	1-50
2.0×10^{-4}	1.32×10^{-4}	0.0177	0.9996	9.0	10-1000

Table 2: Effect of various ions on the determination of 70ngmL^{-1} of Manganese(II).

Ion	Tolerance ratio of ion to Manganese
CN^-, NO_3^-, ClO_4^-, CH_3COO^-, Cl^-, Ca(II) NH_4(I), Ni(II), Na(I), Mg(II), Li(I), K(I), Sr(II)	1000
Zn(II),Ba(II),Pb(II),Cd(II),$H_2PO_4^-$, Br^-,IO_3^-,F^-	500
Hg(II)*, Ag(I)*	100
Co(II), Mo(V), Cr(III), Citrate	50
$S_2O_3^{2-}$, I^-, V(V), Se(IV)	10
Cu(II), Ce(III)	1
SCN^-	0.02

* *After elimination of their interferences as described in text.*

the method was 0.94ngmL^{-1}.

Selectivity

In order to assess the possible analytical applications of the proposed method, the influence of foreign ions on the determination of 70ngmL^{-1} manganese was examined. The results are summarized in Table 2. The tolerance limit was taken as the amount required to cause less than ±2% error in Mn(II) recover.

As Table 2 shows most of the ions tested did not interfere, even when present in concentrations 500-1000 fold over that of manganese.

Cu(II) and Ce(III) and SCN^- showed negative interference effects. Hg(II) and Ag(I) interfered when present in 30 and 0.3 fold over manganese, respectively. Their interfering effects were removed by addition of CN^- to the solution.

Applications

The proposed method was applied to the determination of manganese in a sample of milk.

A known amount of sample was heated to dryness at 100°C, and then heated in a porcelain capsule in a furnace at 500°C for 24h.

The ash was moistened with water and 5mL of perchloric acid was added. The sample was digested in a sand-bath until dry. 5mL of hydrochloric acid was then added and the sample was again evaporated to dryness. It was then dissolved in 5mL of hydrochloric acid and the clear solution transferred into a 50mL volumetric flask. After proper dilution, the manganese content of the sample was determined by proposed method and atomic absorption spectroscopy. The amount of manganese was found to be 9.9±0.3μg/100g (n=5) by the proposed method that was in satisfactory agreement with that obtained from atomic absorption spectroscopy (10.1±0.2μg/100g).

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