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Determination of ultra trace amount manganese (II) with kinetic spectrophotometric method

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ABSTRACT

A new kinetic spectrophotometric method for the determination of trace amount manganese (II) in Tea real samples has been described based on its catalytic effect on the oxidations of barium diphenylaminesulfonate by potassium bromate in sulfuric acid. The reaction is followed spectrophotometrically by measuring the decrease in the absorbance at 547.5 nm. Under the optimum conditions of 0.2 mol l⁻¹ sulfuric acid, 10⁻⁴ mol l⁻¹ bariumdiphanylaminesulfonate, 0.011 mol l⁻¹ potassium bromate at 35°C, calibration graph in the rang of 0.001-0.06 µg l⁻¹ manganese (II). Concentration was obtained with detection limit of 0.2303 g ml⁻¹ by the fixed-time method of 3.5 min. The relative standard deviation for 0.05 µg l⁻¹ manganese (II) is %0.9. No serious interference was identified. The applicability of the method was demonstrated by the determination of the manganese (II) in real samples. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Kinetic spectrophotometric method;
Barium
diphenylaminesulfonate;
Manganese (II);
Potassium bromate.

INTRODUCTION

Manganese is an essential microelement for the human body. In normal conditions it plays an important role in bone and tissue formation (normal growth), normal reproductive functions, and carbohydrate and lipid metabolism. The diet is the basic source of the metal. A daily dietary intake of 2 to 5 mg is estimated to be adequate for adults. Manganese deficiency in humans is related to delayed blood coagulation and hypercholesterolaemia. The metal may be considered toxic when dietary intake is significantly higher^[1]. Hence, sensitive and selective methods for determination of manganese in foodstuffs, drinking waters and drinks are of great interest.

There have been numerous spectrophotometric methods for the determination of manganese. The oxidation of manganese to permanganate and a measurement of the absorption of the charge-transfer band of permanganate at 528 nm has long been used as a standard method for manganese determination; 1, 2 however, this method suffers from low sensitivity. Spectrophotometric methods based on complex formation with chromogenic reagents provide good sensitivity, but have showed serious interferences from many cations and anions despite the high detection limit of 0.05 µg ml⁻¹[2,3].

Numerous kinetic methods have been reported based on the catalytic effect of Mn²⁺ on the oxidation of organic compounds with suitable oxidants. Although

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these methods have shown good sensitivity, they are time-consuming and irreproducible, since it is difficult to control the timing of the reaction, which is variable from one experiment to another^[4-13] Some recent enhancements of the method using a flow injection technique have been reported^[14-16] However, if the reaction time is longer than the flow rate, the method will not be efficient and still irreproducible. Several efforts to increase the reaction rate by temperature have been reported; however, either the sample degrades or airbubbles will develop that hinder the flow rate^[17-23].

In this work, the catalytic effect of manganese (II) on the oxidation of barium die phenyl amino sulfonate with potassium bromide in the presence of barium die phenyl amino sulfonate was investigated. A catalytic kinetic spectrophotometric method for the determination of manganese (II) was developed. The proposed method is extremely sensitive, with higher selectivity and is a simpler procedure than the three methods mentioned above. The method was applied successfully to the determination of total manganese in real sample.

EXPERIMENTAL

Apparatus

A Shimadzu UV-Vis 160 spectrophotometer was used to measure the absorbance of solutions. A Metrohm 691 pH/Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. The evaluation of ions content were carried out on a Shimadzu 680 A atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector, at respective resonance line using an air-acetylene flame. A NBE ultrathermostat (VEB Prüfgerätek-Werk, Medingen, Germany) was used to control the temperature.

Reagents and materials

All chemicals, except barium die phenyl amino sulfonate, were prepared of the analytical grade purchased from Merck Company, solution (Merck, Darmstadt, Germany). The solutions were prepared with doubly distilled water. The concentrations of the stock solutions were as follows: barium die phenyl amino sulfonate, 10^{-4} mol l⁻¹, potassium bromide, 0.1 mol l⁻¹ sulfuric acid, 3 mol l⁻¹ manganese (II) sulphate, 1000

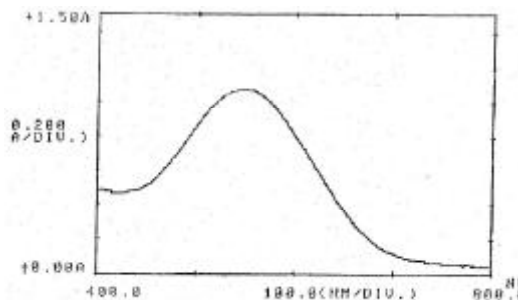


Figure 1: The absorption spectra oxidation of product barium diephenyl amino sulfurnate

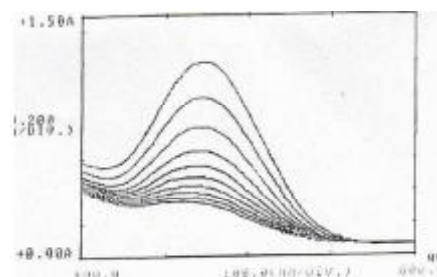


Figure 2: The absorption spectra oxidation of product barium diephenyl amino sulfurnate in each 20min

mg l⁻¹.

Procedure

A typical kinetic spectrophotometric method experiment required the following steps: 1 ml of Mn (II) solution equated to 0.01 ml grams was added to the 10 ml volumetric flask. Then 1 ml gram of potassium bromide (0.1 mol l⁻¹) and 1 ml of sulfuric acid solution (3 mol l⁻¹) was added. By adding the first drop of 1 ml barium diephenyl amino sulfurnate to the volumetric flask, the time of the reaction beginning is recorded, after 5 sec the solution is mixed for 30 sec, and then it is volume by adding the distilled water, a sufficient amount of the solution was added to a 1 cm cell, the difference between the quantities of the absorption in a wavelength equal to 547.5 nm in a time interval equal to 1-4.5 min was measured by mean of spectrophotometer (ΔA_s). All these steps would be repeated for a non catalytic reaction without the presence of Mn (II) as the catalyst element (ΔA_b), finally $\Delta(\Delta A) = \Delta A_{\text{blank}} - \Delta A_{\text{sample}}$ Δ is calculated. Barium die phenyl sulfonate oxidation is traced in the acidic medium by potassium bromide, which its wavelength is 547.5 nm. The absorption spectra in an aqueous solution are shown in figures 1 and 2.

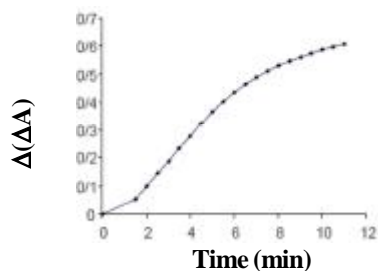


Figure 3: The effect of time on the reaction rate

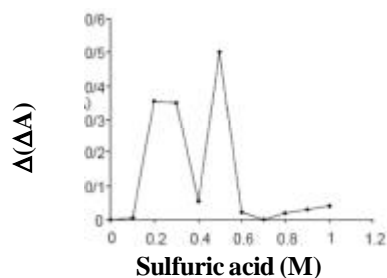


Figure 4: The effect of sulfuric acid concentration on the rate of reaction

Pretreatment of real samples

water sample

Analysis of waste water sample for determination of Mn (II) content was performed as following: 400 ml of sample was poured in a beaker and 8 ml concentrated HNO_3 and 3 ml of H_2O_2 of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. In all of real and synthetic sample amount of Mn (II) ion was found by standard addition method.

Blood

Blood sample 20 ml was weighed accurately and in a 200 ml beaker was digested in the presence of an oxidizing agent with addition of 10ml concentrated HNO_3 and 2ml HClO_4 70% was added and heated for 1 h. The content of beaker was filtered through a Whatman no. 40 filter paper into a 250 ml calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. In all of real and synthetic sample amount of Mn (II) ion was found by standard addition method.

Vegetables

All vegetable samples were purchased from Gachsaran Iran. Afterwards, they were taken in small mesh. A 40 g vegetable sample was heated in silica

crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650°C . The residue was cooled, treated with 10.0 ml concentrated nitric acid and 3 ml 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 ml concentrated hydrochloric acid and 2-4 ml 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. In all of real and synthetic sample amount of Mn (II) ion was found by standard addition method^[24].

RESULTS AND DISCUSSION

The effect of time on the reaction rate

As it was expressed in the method, to obtain optimum time of the reaction, 1 ml Mn (II) 0.01 mg l^{-1} solution, 1 ml potassium bromide 0.1 mol l^{-1} , 1 ml sulfuric acid solution 3 mol l^{-1} and 1 ml barium die phenyl amino sulfunato $10^{-3} \text{ mol l}^{-1}$ are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solutions was measured in the 0-11 min interval of time. The above mentioned operation was repeated for blank solution (the solution without Mn (II)). Changes in absorption based on the time at 30 centigrade degrees temperature are shown in figure 3. 4.5 min was selected as the optimum time.

The effect of sulfuric acid concentration on the rate of reaction

As it was expressed in the method, to obtain optimum sulfuric acid concentration of the reaction, 1 ml Mn (II) mg l^{-1} solution, 1 ml potassium bromide 0.1 mol l^{-1} , 1 ml sulfuric acid solution 0.1 to 1 mol l^{-1} , and 1 ml barium die phenyl amino sulfunato $10^{-3} \text{ mol l}^{-1}$ are added to the volumetric flask 10ml and by adding distilled water. Absorption of solutions was measured after 4.5 min. The above mentioned operation was repeated for blank solutions (the solution without Mn (II)). As it is shown in figure 4, the 0.2 molar concentration of sulfuric acid has the most changes in the absorption, so that, it was selected as the optimum concentration of the acid.

The effect of barium die phenyl amino sulfunato on the reaction rate

To inspecting The effect of barium die phenyl amino

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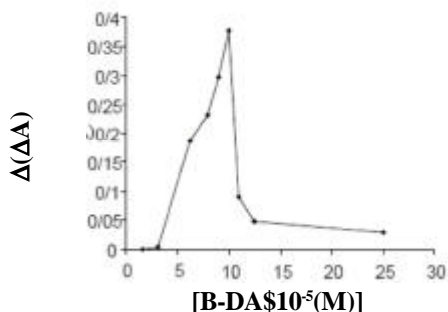


Figure 5: The effect of barium die phenyl amino sulfonate on the reaction rate

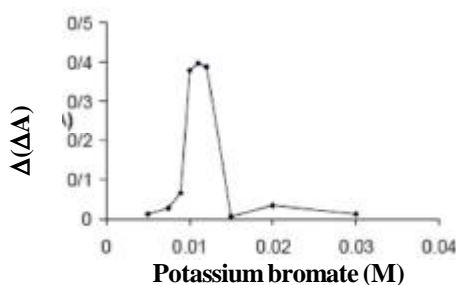


Figure 6: The effect of barium die phenyl amino sulfonate on the reaction rate

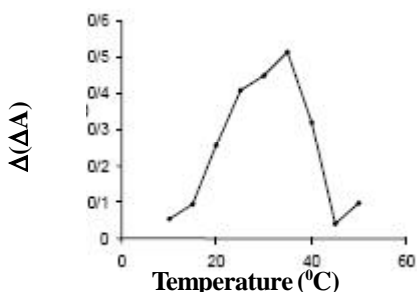


Figure 7: The effect of temperature on the reaction rate

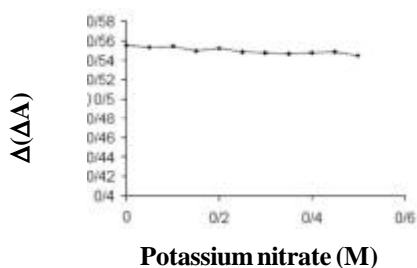


Figure 8: The effect of Ionic power on the reaction rate

sulfonate on the reaction rate, 1 ml Mn (II) 0.01 mg l⁻¹ solution, 1 ml potassium bromide 0.1 mol l⁻¹, 1 ml sulfuric acid solution 2 mol l⁻¹ and 1 ml barium die phenyl amino sulfonate at different concentrations 25×10⁻³ to 1.56×10⁻⁴ are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solutions was

measured after 4.5 min. The above mentioned operation was repeated for blank solutions (the solution without Mn (II)). The results are shown in and figure 5, based on those results 1×10⁻⁴ was selected as the desired concentration.

The effect of potassium bromide concentration on the reaction rate

To inspecting the effect of potassium bromide concentration, 1 ml Mn (II) 0.01 mg l⁻¹ solution, 1 ml potassium bromide at different concentrations 0.05 to 0.3 mol l⁻¹, 1 ml sulfuric acid solution 2 mol l⁻¹, and 1 ml barium die phenyl amino sulfonate 1×10⁻³ mol l⁻¹ are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solutions was measured after 4.5 min. The above mentioned operation was repeated for blank solutions (the solution without Mn (II)). Results are shown in figure 6, based on that results, potassium bromide at a concentration of 0.011 mol l⁻¹ was selected as the desired concentration.

The effect of temperature on the reaction rate

At first put the cells including: Mn, potassium bromide, sulfuric acid, barium die phenyl amino sulfonate, distilled water and volumetric 10 ml flasks in the thermostat to reach to the desired temperature. After they go to the equilibrium temperature, 1 ml Mn (II) 0.01 mg l⁻¹ solution, 1 ml potassium bromide 0.11 mol l⁻¹, 1 ml sulfuric acid solution mol l⁻¹, and 1 ml barium die phenyl amino sulfonate 1×10⁻³ mol l⁻¹ are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solutions was measured after 4.5 min. The above mentioned operation was repeated for blank solutions (the solution without Mn (II)). As it is shown in figure 7, 35 centigrade degree was selected as the desired temperature.

The effect of ionic power on the reaction rate

The effect of ionic power of the medium was also inspected; potassium bromide and potassium nitrate were used for this purpose. 1 ml Mn (II) 0.01 mg l⁻¹ solution, 1 ml potassium bromide 0.11 mol l⁻¹, 1 ml sulfuric acid solution 2 mol l⁻¹, and 1 ml barium die phenyl amino sulfonate 10⁻³ mol l⁻¹ are added to the volumetric flask 10ml and by adding distilled water. Absorption of solutions was measured after 4.5 min. as we can see in figure 8 results show that the effect of ionic power on

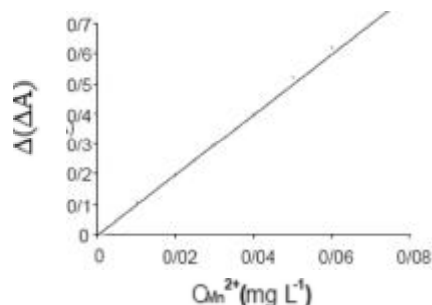


Figure 9: Calibration graph for manganese (II)

TABLE 1: Specification of method at optimum conditions for manganese (II)

Parameter	Mn (II)
Linear range ($\mu\text{g mL}^{-1}$)	0.001-0.06
Detection limit ($\mu\text{g mL}^{-1}$)	0.23
RSD %	0.9

TABLE 2 : Effect of foreign ions on the determination of manganese (II)

Foreign ion	Maximum tolerable ion amount
$\text{CO}^{2+}, \text{Ca}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$	
$\text{Mg}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{K}^{+}$	
$\text{Al}^{3+}, \text{Cr}^{3+}, \text{NH}_4^+, \text{NO}_3^-$	1000
$\text{PO}_4^{2-}, \text{F}^-, \text{NO}_2^-, \text{Cl}^-$	
$\text{CO}_3^{2-}, \text{BrO}_3^-, \text{CH}_3\text{COO}^-, \text{S}_2\text{O}_5^{2-}$	
$\text{Na}^+, \text{W}^{6+}, \text{Ni}^{2+}, \text{SO}_4^{2-}$	750
$\text{Ba}^{2+}, \text{Fe}^{3+}, \text{SO}_4^{2-}, \text{IO}_4^-$	500
$\text{Ag}^+, \text{I}^-, \text{Br}^-$	100
	50

TABLE 3 : Recovery studies of manganese (II) in real samples (N=3)

Sample	Added	Found	RSD %	Recovery %
River water	0	64.1	1.9	-
	100	164.3	1.1	100.2
Tap water	0	61.8	1.3	-
	100	161.9	1.1	100.1
Waste water	0	103.3	1.8	-
	100	203.8	1.2	100.5
Vegetable	0	127.4	1.7	-
	100	228.2	2.7	100.8
Blood	0	67.4	1.7	-
	100	169.6	2.3	102

the reaction rate is neglectable, and can be ignored.

Calibration graph and reproducibility

Reaching to the standard curve of Mn (II) in the reaction, the system went into the desired condition. So different volumes of Mn (II) ($100 \mu\text{g mL}^{-1}$), 1 ml potassium bromide 0.11 mol l^{-1} , 1 ml sulfuric acid solution 2 mol l^{-1} , and 1 ml barium di phenyl amino sulfonate $10^{-3} \text{ mol l}^{-1}$ are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solutions was measured after 4.5 min. the above mentioned operation was repeated for blank solutions. The examination/test was done at 35 centigrade degrees. Results are shown in TABLE 1 and figure 8.

Effect of foreign ions

In order to assess the potential analytical applications of the proposed kinetic reaction, the influence of foreign ions on the determination of manganese (II) was investigated. The tolerated limits for the ions assayed are shown in TABLE 2 (with relative errors less than 5%). As can be seen, the proposed method is highly selective.

Application

The proposed method was applied to the determination of total manganese in water, blood, and Vegetables samples. In TABLE 3 the results obtained are shown, and compared with those obtained by atomic absorption spectrophotometry.

CONCLUSION

The proposed method is very simple, highly selective, sensitive and reproducible for the determination of manganese. The method also exploits low-cost instrumentation and overcomes the problems associated with previously reported spectrophotometric methods for the determination of manganese. The method tolerates most foreign ions more than any other method.

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