Determination of ultra trace amount manganese (II) in water samples with the 1-(2-PyridylAzo)-2-Naphthol, (PAN) by the bromate ion in sulfuric acid with kinetic spectrophotometric method

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ABSTRACT

A new kinetic spectrophotometic method for the determination of trace amount manganese(II) in Tea real samples has been described based on it s the catalytic effect on the oxidations of 1 - (2 – Pyridyl Azo) - 2 - Naphthol, (PAN), by potassium bromated 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 $molL^{-1}$ sulfuric acid, 1.0×10^{-4} $molL^{-1}$, 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1mL of potassium bromate 0.11 $mol\ L^{-1}$ at 35°C, calibration graph in the rang of 0.001-0.06 $\mu g\ mL^{-1}$ manganese (II). Concentration was obtained with detection limit of 0.23 $ng\ mL^{-1}$ by the fixed-time method of 4.5 min. The relative standard deviation for 0.05$\mu g\ mL^{-1}$ manganese(II) is %90. No serious interference was identified. The applicability of the method was demonstrated by the determination of the manganese (II) in Water, Vegetables and blood samples.

Keywords: Manganese (II); Kinetic; 1-(2-PyridylAzo)-2-Naphthol, (PAN); Determination; Spectrophotometic

INTRODUCTION

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 hyper cholesterolaemia. The metal may be considered toxic when dietary in take is significantly higher [1]. Hence, sensitive and selective methods for determination of manganese in foodstuffs, drinking waters and drinks are of great interes. 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-transfe band of permanganate at 528 nm has long been used as a standard method for nickel

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determination; 1, 2 how ever, 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 ng mL^{-1}[2,3]. Numerous kinetic methods have been reported based on the catalytic effect of Mn^{2+} on the oxidation of organic compounds with suitable oxidants. Although 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 – 9], The sophisticated techniques, such as inductively coupled plasma- mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), electro chemical analysis, spectrophotometry, neutron activation analysis and atomic absorption spectrophotometry (AAS), been adopted for sensitive assays for both oxidation states of manganese. These methods have disadvantage of cost and instruments used in regular analysis. AAS often has low sensitivity due to the matrix effect of samples such as salinity [10,11]. Environment samples at low levels and has matrix effects with detection limit of lead [12]. Some recent enhancements of the method using a flow injection tech- nique have been reported [13 – 15]. However, if the reaction time is longer than the flow rate, the method will not be efficient and still irreproducible. Several efforts increase the reaction rate by temperature have been reported; however, either the sample degrades or air bubbles will develop that hinder the flow rate [16-20]. The azo-dye PAN (1-[2-pyridylazo]-2-naphthol) is a well-known metallochromic indicator for the quantitative and qualitative determination of variety of metal ions.

PAN has many characteristic required an ionophore. This ionophore reacts highly colored complexes. The complexes can be reversed to form again the ionophore over a large number of repetitions [21]. In this work, the catalytic effect of manganese (II) on the oxidation of 1 – (2 – PyridylAzo) – 2 - Naphthol, (PAN), with potassium bromide in the presence of 1 – (2 – PyridylAzo) – 2 - Naphthol, (PAN), 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 (II) in real sample.

EXPERIMENTAL

Apparatus
All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the equipment were established according to the manufacturer's recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution. A NBE ultrathermostat (VEB Prufgerate – WerkMedingen, Germany) was used to control the temperature.

Reagents and materials

All chemicals, except barium die phenyl aminosulfunate, 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: 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1}, potassium bromide, 0.1 mol L^{-1} sulfuric acid, 0.2 mol L^{-1} manganese(II) chloride, 1000.

Pretreatment of real samples
Water samples

Analysis of water samples for determination of Mn(II) ion content was performed as following: 200 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. After adjustment of samples pH to desired value the were performed according to general described procedure [22].

Blood sample

Homogenized 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 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70 % was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 42 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 [23].

Vegetable sample

Spinach sample was bought from Dashtestan, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 hours on a hot plate and the charred material was transferred to furnace for overnight heating at 650 $^{\circ}C$. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3mL30% H_2O_2 again kept in furnace for2 hours at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL hydrochloric acid and 2-4 mL70% perchloric acid and evaporated to fumes, so all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 7.0 made up to 10 mL by addition of KOH [24].

Procedure

A typical kinetic Spectrophotometric method experiment required the following steps: 1 ml of manganese solution equated to 0.01 ml grams was added to the 10 ml volumetric flask. Than 1 ml gram of potassium bromide (0.11 mol L^{-1}) and 1 ml of sulfuric acid solution (0.2 mol L^{-1}) was added. By adding the first drop of 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN) 1.0×10^{-4} mol L^{-1}, 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 equalto 1-4.5 min was measured by mean of spectrophotometer (A A_s). All these steps would be repeated for a non catalytic reaction without the presence of manganese as the catalyst element (AA_b), finally (AA)AAblank-AAsample is calculated. 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), oxidation is traced in the acidic medium by potassium bromide, which its wavelength is 547.5 nm. The absorption spectra in an aqueous solution
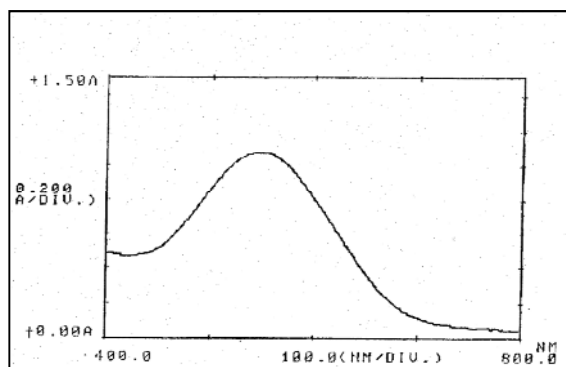
are shown in figures 1 and 2.

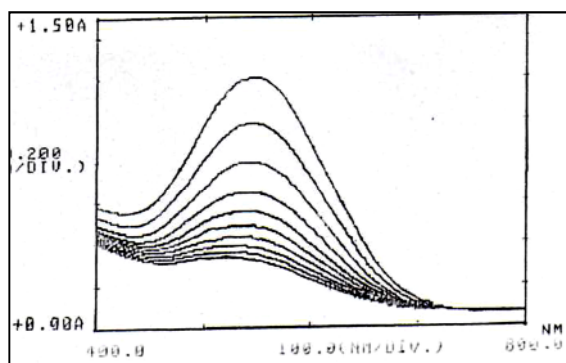**Fig. 1.** The absorption spectra oxidation of product 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN).

Fig. 2. The absorption spectra oxidation of product 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 20min mg L^{-1}.

RESULTS AND DISCUSSION

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 0.2 mol L^{-1} and 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of so lutions was measured in the 0-11 min interval of time. The above mentioned operation was repeated for biank 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.
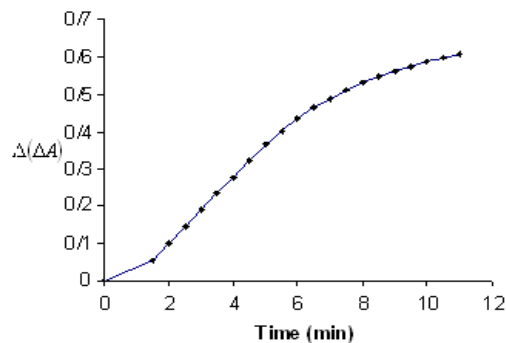

Fig. 3. The effect of time on the reaction rate.

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) mgL^{-1} solution, 1 ml potassium bromide 0.11 mol L^{-1}, 1 ml sulfuric acid solution 0.1 to 10 mol L^{-1} and 1 ml, 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1}are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Mn (II)). As it is shown in figure 4, the o.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.
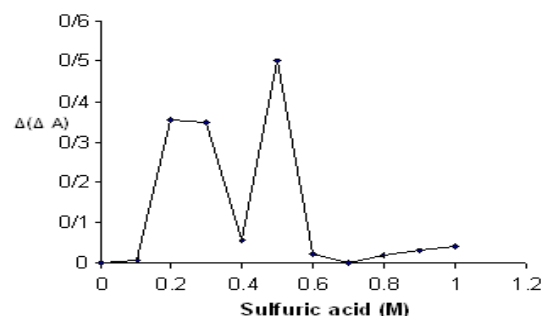

Fig.4. The effect of sulfuric acid concentration on the rate of reaction.

Effect of 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN) on the reaction rate

To inspecting The effect of 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), on the reaction rate, 1 ml Mn (II) 0.01 mg L^{-1} solution, 1 ml potassium bromide 0.11 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml, 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.56×10^{-5} to 2.5×10^{-3} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution, the solution without Mn (II). The results are shown in and figure 5, based on those results 1.0×10^{-4} mol L^{-1} was selected as the desired concentration.
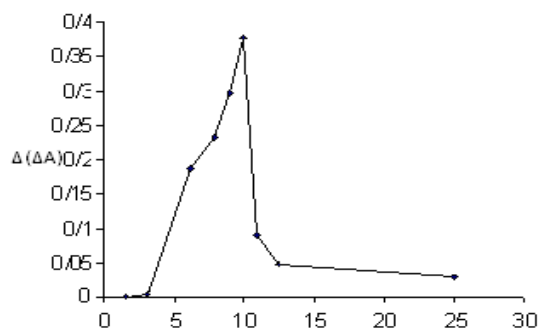

Fig. 5. The effect of 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), on the reaction rate.

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 concentration 0.05 to 0.3 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1}are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution the solution without Mn(II). Results are shown in figure 6, based on that results, potassium bromideat a

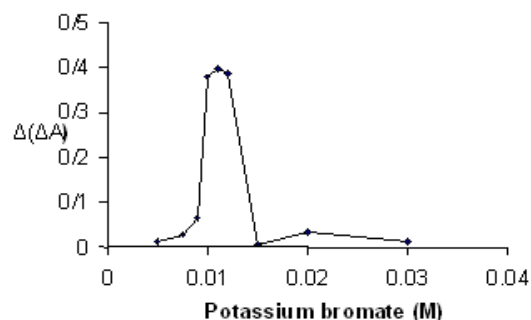concentration of 0.011 mol L^{-1} was selected as the desired concentration.

Fig. 6. The effect of 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), on the reaction rate.

Effect of temperature on the reaction rate

At first put the cells including: Mn (II), potassium bromide, 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 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 sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1}are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Mn (II)). As it is shown in figure 7, 35 centigrade degree was selected as the desired temperature.
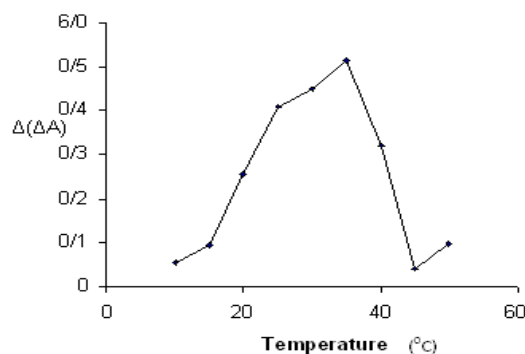

Fig. 7. The effect of temperature on the reaction rate.

Effect of ionic power
Potassium bromide and potassium nitrate were used for this purpose. 1 ml Mn (II) 0.01 mgL^{-1} solution, 1 ml potassium bromide 0.11 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. as we can see in figure 8 results show that the effect of ionic power on the reaction rate is neglectible, and can be ignored.
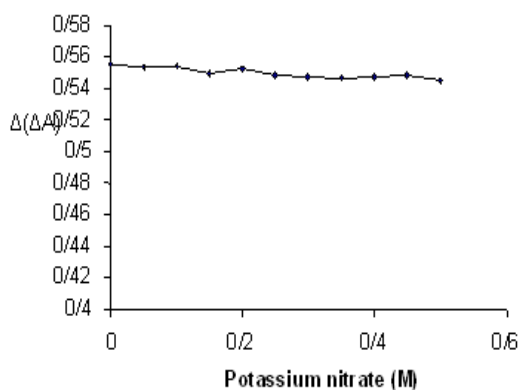

Fig. 8. The effect of Ionic power on the reaction rate.

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 1mL Mn (II) 0.01 mgL^{-1}, 1 ml potassium bromide 0.11 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1 - (2 - PyridylAzo) - 2 - Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution 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 figure 9.
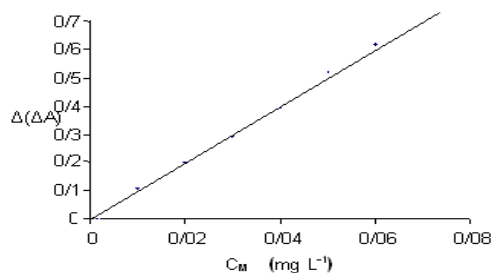

Fig. 9. Calibration graph for Mn (II).

Effect of foreign ions
The accuracy and reliability of this method was evaluated by comparing the results obtained for the same samples by an AAS method. The results estimated by AAS and spectrophotometry are shown in Table 4. The results estimated by spectrophotometry are much less as compare to results obtain by AAS. It may be attributed to the interference of foreign ions in the determination of manganese. The interfering ions. These ions may interfere with manganese (II). 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 [25-28]. The tolerated limits for the ions assayed are shown in Table1, (was relative errors less than 5%). As can be seen, the proposed method is highly selective.

Application
To assess the applicability of the method to real samples with different matrices, containing various amounts of diverse ions were used. For accuracy and reliability of proposed method, spiking experiments and independent analysis were used. The proposed method was applied to the determination of total manganese (II) in water, blood, and Vegetables samples. In Table 2, the results obtained are shown, and compared with those obtained by atomic absorption spectrophotometry. The level of the analyte ions were found below

the detection limit of related element. The results of replicate three analyses of each sample show that the ions recoveries are almost quantitative with a low RSD. The recovery of spiked samples is satisfactory reasonable and was confirmed using standard addition method, which indicate the capability of the proposed method for the determination of trace amounts of these elements in different samples.

Table 1. Effects of the matrix ions on the recoveries of the examined manganese (II) ion (N=6)

Ion	Added As	Tolerance Limit, mg L^{-1}
Cl$^-$, K$^+$, Na$^+$	KCl, NaCl	1000
Mg^{2+},Ca^{2+} Cu^{2+}	chloride & Nitrate salts	800 700
HCO$_3$$^-$ SCN$^-$	NaHCO$_3$ KSCN	1000 1000
PO$_4$$^{3-}$	Na$_3$PO$_4$	400
Fe^{3+}	Nitrate salts	300
CO$_3$$^{2-}$	Na$_2$CO$_3$	500
Cr^{3+}	Nitrate salts	150

Table 2. Recovery of trace manganese (II) from water, vegetables and blood sample after application of presented procedure (N=6)

sample	Added (ng L^{-1})	Founded (ng L^{-1})	RSD %	Recovery %
Tap water	0 100	103.3 161.9	1.1 1.8	--- 103
River water	0 100	61.8 164.3	1.1 1.3	--- 95.3
Veget-ble	0 100	67.4 228.2	1.7 2.7	--- 100.8
Blood	0 100	64.1 169.6	1.9 2.3	--- 102

CONCLUSION
The proposed method is very simple, highly selective, sensivite and reproducible for the determination of manganese (II). The method also exploits low–cost instrumentation and overcomes the

problems associated with previously reported spectrophotometic method for the determination of manganese [29-32]. The method is simple, accurate can be applied for the determination of analytes in environmental samples [33, 34].

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