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Kinetic Spectrophotometric Determination of Nanogram Levels of Manganese (II) by Azo Dye – Potassium Periodate – 1,10-Phenanthroline System

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The catalytic effect of manganese (II) on the oxidation of 3 - Methyl - 6 - (2 - hydroxyethoxy) - 2 - [2 - methoxy - 4 - N (N,N - diethylamino) phenylazo] benzothiazolium methylsulphate (MHMDPBM), with potassium periodate in the presence of 1,10-phenanthroline in weakly acidic media was studied. The reaction was followed spectrophotometrically by measuring the decrease in the absorbance of the dye at 560 nm. Under the optimum conditions ($4x10^{-5}$ mol dm^{-3} MHMDPBM, $4x10^{-4}$ mol dm^{-3}potassium periodate, $1x10^{-4}$ mol dm^{-3} 1,10-phenanthroline, 0.1 mol dm^{-3} buffer – pH 3.0, 70°C, 8 min), manganese (II) in the range 0.05-5 ng cm^{-3} can be determined by the fixed-time method with a detection limit of 0.015 ng cm^{-3}. The influence of foreign ions on the accuracy of the results was investigated. The developed method is extremely sensitive, selective, and simple. The method was applied successfully to the determination of total manganese in strawberries, raspberries and bilberries. The results showed good agreement with those obtained by atomic absorption spectrophotometry.

Key Words: manganese (II), kinetic determination, azo dye oxidation, berries

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.

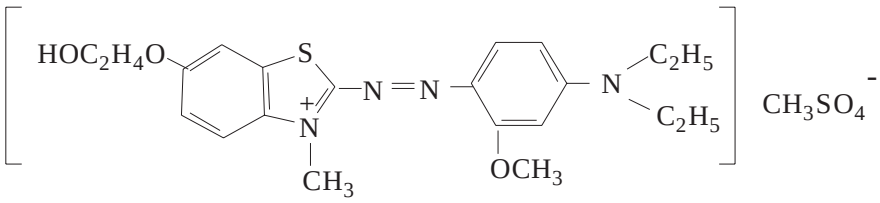
Many kinetic methods have been reported for the determination of manganese (II), based on its catalytic effect on the oxidation of organic compounds most frequently with hydrogen peroxide and the periodate ion [2–12]. However, most of these methods lack sufficient sensitivity for determining manganese (II) at or below ng cm^{-3} levels. Among the most sensitive methods described so far are: (a) the method

of Bartkus and Nauekaitis (detection limit of 0.014 ng cm^{-3}) [13], whose application is limited because Fe^{3+}, Pb^{2+}, and I^- interfere at the same manganese (II) level; (b) the method of Rubio et al. (detection limit of 0.050 ng cm^{-3})[14], in which some ions such as Co^{2+}, Fe^{2+}, Cu^{2+}, and Ni^{2+} interfere, and this necessitates the use of various masking agents; (c) the flow injection method of Kolotyrkina et al. (detection limit of 0.010 ng cm^{-3}) [15], which is relatively sensitive and interference free, but it requires a separation – preconcentration step in order to remove the sea-water matrix effect, and to increase the precision of the determination of manganese.

In this work, 3 - Methyl - 6 - (2 - hydroxyethoxy) - 2 - [2 - methoxy - 4 - N (N,N - diethylamino) phenylazo] benzothiazolium methylsulphate (MHMDPBM), was employed for the first time in a kinetic system. The catalytic effect of manganese (II) on the oxidation of MHMDPBM with potassium periodate in the presence of 1,10-phenanthroline (Phen) was investigated. A catalytic kinetic spectrophotometric method for the determination of manganese (II) was developed. It can be used for the determination of manganese (II) in the range 0.05-5 ng cm^{-3} by the fixed-time method with a detection limit of 0.015 ng cm^{-3}. 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 strawberries, raspberries, and bilberries. This is the first attempt to apply a kinetic method to determine manganese levels in these berries.

Experimental

Synthesis of the Dye



3 - Methyl - 6 - (2 - hydroxyethoxy) - 2 - [2 - methoxy - 4 - N (N,N - diethylamino) phenylazo] benzothiazolium methylsulphate

This benzothiazolic cationic azo dye was synthesised according to the procedure described by Deligeorgiev and Simov [16]. 2-amino-6-(2-hydroxyethoxy) benzothiazole (0.02 moles) was dissolved in 25 cm^3 50% sulphuric acid and the liquor was cooled in an ice-salt bath to 0°C. The diazotisation was carried out with 0.02 moles sodium nitrite dissolved in 5 cm^3 water.

The coupling reagent 3-methoxy-N,N-diethylaniline (0.02 moles) was dissolved in 200 cm^3 1% hydrochloric acid, and the diazo liquor was added to the solution. The precipitate of disperse dye was filtered, washed with water and air dried. To a mixture of 0.01 mole disperse azo dye and 50 cm^3 chlorobenzene, a solution of 0.022 moles dimethylsulphate in 5 cm^3 chlorobenzene was dropped in at 70°C, with stirring, over a period of 30 min. After cooling, the precipitated cationic dye was filtered, washed with diethyl ether and air dried. The dye was purified by double recrystallisation from ethanol + diethyl ether (4 + 1, v/v).

Reagents

All chemicals, except MHMDPBM, were of analytical-reagent grade and the solutions were prepared with doubly distilled water. The concentrations of the stock solutions were as follows: MHMDPBM, $5x10^{-4}$ mol dm^{-3}; potassium periodate, 0.01 mol dm^{-3}; Phen, 0.01 mol dm^{-3}; manganese (II) sulphate, $1.82x10^{-2}$ mol dm^{-3}. Buffer solutions: 0.15 mol dm^{-3} ethanoic acid – potassium dihydrogen orthophosphate (2.33 + 1, v/v) buffer (PHOP) of pH 3.0; 0.04 mol dm^{-3} ethanoic acid – boric acid – orthophosphoric acid and 0.2 mol dm^{-3} sodium hydroxide (UB), in volume proportions respective to the required pH [17].

Apparatus

Absorption spectra were recorded on a Specord-UV-Vis spectrophotometer (Carl Zeiss Jena, Germany), using 1-cm quartz cells. Absorbance measurements were made on a Specol 11 spectrophotometer (Carl Zeiss Jena, Germany) in a 1-cm glass cell. A NBE ultrathermostat (VEB Prüfgeräte-Werk, Medingen, Germany) was used to control the temperature. Decomposition of samples was carried out in a Perkin-Elmer Autoclave-3 (Überlingen, Germany). For comparison measurement, a model Perkin-Elmer 3110 atomic-absorption spectrophotometer, equipped with a standard air-acetylene burner head and a deuterium background corrector (Überlingen, Germany) was used.

Decomposition of Samples

The samples (0.5 g of strawberry, 0.5 g of raspberry, and 0.1 g of bilberry) were treated with 7 cm^3 of conc. HNO_3 and H_2SO_4 mixture (5 + 2, v/v) for 20 min at 150°C in the Autoclave-3. The digest was diluted to the mark: in a 50-cm^3 standard flask (strawberry), and in a 100-cm^3 standard flask (raspberry and bilberry).

General Procedure

In a 10 cm^3 tube place 0.40 cm^3 of MHMDPBM solution and 0.5 cm^3 of sample solution containing 0.25-25 ng of manganese (II). To this add 4.10 cm^3 of a mixture of Phen, potassium periodate and PHOP buffer solution (prepared just before use in volume proportions 1 + 4 + 77). Place the tube in the thermostat at 70°C for 8 min. Then cool it quickly with ice-water to terminate the reaction. Transfer the solution into the spectrophotometer cell and measure the absorbance at 560 nm against a reagent blank. Manganese (II) is determined according to the absorbance A.

Results and Discussion

The oxidation of MHMDPBM by potassium periodate in weakly acidic media results in the decoloration of the solution. Figure 1 shows the absorption spectra of solutions of MHMDPBM, MHMDPBM + KIO_4, MHMDPBM + KIO_4 + Phen, MHMDPBM + KIO_4 + Mn (II), and MHMDPBM + KIO_4 + Phen + Mn (II) after heating at 70°C for 8 min according to the general procedure. Figure 1 indicates that the oxidation of MHMDPBM by potassium periodate is catalysed by the presence of small amounts of manganese (II). The oxidation reaction was also accelerated by Phen, and the acceleration effect was greater when manganese (II) was present in the system. The mechanism of this accelerative reaction is not clear. MHMDPBM has an absorption maximum at 560 nm, which was chosen for subsequent studies.

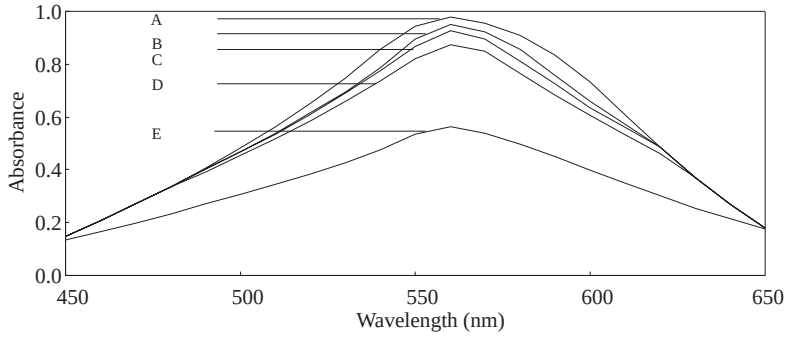


Figure 1. Absorption spectra against water: A, MHMDPBM; B, MHMDPBM + KIO_4; C, MHMDPBM + KIO_4 + Phen; D, MHMDPBM + KIO_4 + Mn (II); E, MHMDPBM + KIO_4 + Mn (II) + Phen. MHMDPBM, 4 x 10^{-5} mol dm^{-3}; KIO_4, 4 x 10^{-4} mol dm^{-3}; Mn (II), 2 ng cm^{-3}; Phen, 1 x 10^{-4} mol dm^{-3}; pH, 3.0; temperature 70°C; and time, 8 min.

Optimum Conditions

The oxidation of MHMDPBM was influenced by the concentrations of MHMDPBM, potassium periodate, Phen and buffer, and by the pH buffer and temperature. The effect of each of these on the catalysed and uncatalysed reactions was studied.

The effect of the MHMDPBM concentration was investigated in the range 1x10^{-5} mol dm^{-3} – 1x10^{-4} mol dm^{-3}. The results showed that the absorbance of the blank was very high when significantly more MHMDPBM was used (> 6x10^{-5} mol dm^{-3}), and the linear range for manganese was too narrow if a small amount of MHMDPBM was used (< 2x10^{-5} mol dm^{-3}). Considering these two factors, 4x10^{-5} mol dm^{-3} was chosen, while the absorbance of the blank was less than 1.0.

The effects of the concentrations of potassium periodate and Phen were also investigated, and the results are shown in Figures 2 and 3, respectively. Concentrations of 4x10^{-4} mol dm^{-3} potassium periodate and 1x10^{-4} mol dm^{-3} Phen were chosen as the optimum.

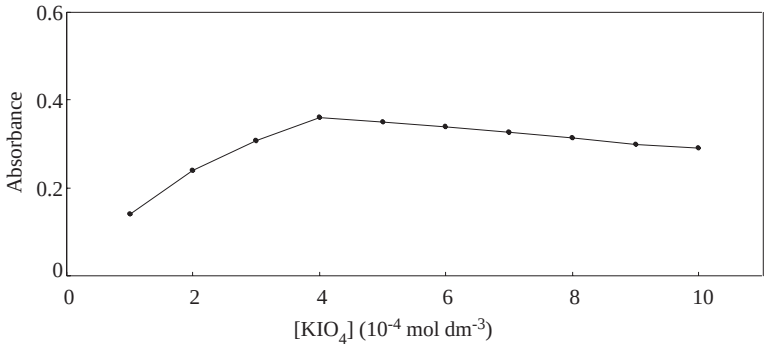


Figure 2. Influence of KIO_4 concentration. Other conditions as in Figure 1.

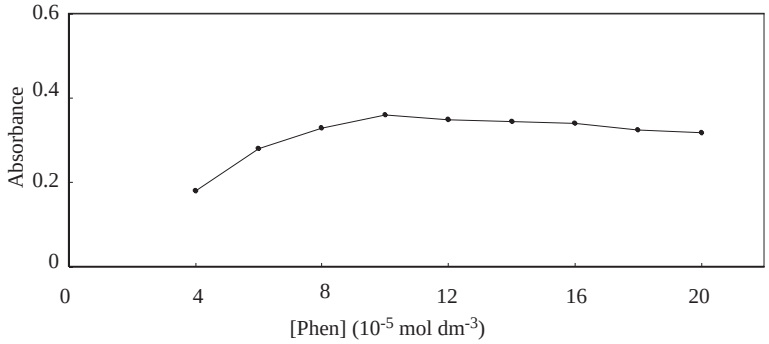


Figure 3. Influence of Phen concentration. Other conditions as in Figure 1.

The influence of pH was studied in the range 2.6 – 5.0 by adjusting the pH with ethanoic acid – boric acid – orthophosphoric acid and sodium hydroxide. The results are shown in Figure 4. A pH value of 3.0 was chosen as the optimum. The influence of several buffer solutions at pH 3.0 were tested. The slope of the calibration graph decreased when sodium citrate – hydrochloric acid or potassium hydrogen phthalate – hydrochloric acid buffer solutions were used. The slope increased when UB or PHOP were used, but, with the latter, better results were obtained and its preparation is easier. The effect of the PHOP concentration was investigated in the range 0.05 mol dm^{-3} – 0.2 mol dm^{-3}. A concentration of 0.1 mol dm^{-3} was chosen as the optimum, because the slope of the calibration graph was maximum.

The dependence of the reaction rate on temperature was investigated between 30 and 80°C (Figure 5). A temperature of 70°C was chosen as the optimum.

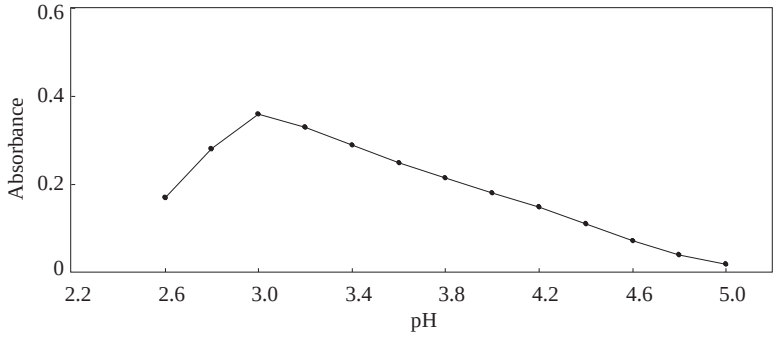


Figure 4. Influence of pH. Other conditions as in Figure 1.

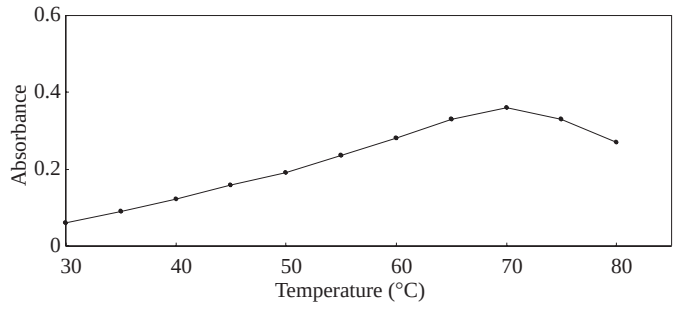


Figure 5. Influence of temperature. Other conditions as in Figure 1.

The effect of reaction time was studied in the range 4-10 min. The optimum reaction time was 8 min. If the reaction time was shorter or longer, the slope of the calibration graph was lower.

Calibration Graph

Under the optimum conditions, a linear calibration graph was obtained for manganese (II) from 0.05 to 5 ng cm^{-3}. The regression equation of the calibration graph was A = 0.010 + 0.175C, where C is concentration (ng cm^{-3}) and the correlation coefficient was 0.998. The method yields a relative standard deviation of 2.2% for 10 determinations of 2 ng cm^{-3} of manganese (II). The detection limit was 0.015 ng cm^{-3}, calculated as three times the standard deviation of the blank divided by the slope of the calibration graph.

Study of Interferences

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 1 (with relative errors less than 5%). As can be seen, the proposed method is highly selective. Only Fe^{3+} and Co^{2+} interfere when their concentrations are in a 200-fold and 170-fold excess over manganese (II), respectively.

Table 1. Effect of foreign ions on the determination of 2 ng cm^{-3} of manganese (II)

Tolerated ratio/ ng of ion per ng of Mn (II)	Foreign ion
$> 10^5$	Na^+, K^+, NO_3^-, SO_4^{2-}, CO_3^{2-}, BO_3^{3-}, PO_4^{3-}, acetate
3 x 10^4	Ca^{2+}, Mg^{2+}, F^-, Cl^-, Br^-
2 x 10^3	Cd^{2+}, Al^{3+}, $C_2O_4^{2-}$, citrate, tartrate
1200	Pb^{2+}, Ni^{2+}, Cr^{3+}, Cr (VI)
500	Cu^{2+}
300	Zn^{2+}
200	Fe^{3+}
170	Co^{2+}

Application

The proposed method was applied to the determination of total manganese in strawberry, raspberry, and bilberry samples. In Table 2 the results obtained are shown, and compared with those obtained by atomic-absorption spectrophotometry.

Table 2. Determination of manganese in strawberries, raspberries, and bilberries

Sample	Manganese found* / μg g^{-1}		
	Kinetic method	AAS method	Relative error (%)
Strawberries	2.40 ± 0.06^a	2.35 ± 0.04$^{a'}$	2.1
Raspberries	5.50 ± 0.12^b	5.60 ± 0.10$^{b'}$	- 1.8
Bilberries	36.25 ± 0.83^c	36.85 ± 0.63$^{c'}$	1.6

* Average values of 7 separate determinations and their standard deviations.
The assessment by Student's t-test and Fischer's F-test did not show a statistically significant difference between: a and a'; b and b'; c and c' (P > 0.05).

Conclusion

This method is highly sensitive, selective and simple (no separation-preconcentration step or masking agents are required), and the precision is very acceptable for the determination of low ranges of manganese (II). The method can be applied for the determination of total manganese in berries, other fruits, and various other foodstuffs.

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