

Kinetic Method for Spectrophotometric Determination of Iron(III) by its Catalytic Effect on the Reduction Reaction of Methyl Red with Potassium Pyrosulfite

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A kinetic spectrophotometric method for the determination of iron(III) is described. The method is based on the catalytic effect of iron(III) on the reduction reaction of methyl red by pyrosulfite. The reaction is followed spectrophotometrically by measuring the change in absorbance at 522 nm using a fixed time method (2.5 min). The effect of different parameters on the reaction was studied to obtain optimum conditions. The calibration curve was linear in the range of 0.4-2.0 $\mu\text{g mL}^{-1}$ of iron(III) and the $3S_b$ detection limit was 0.07 $\mu\text{g mL}^{-1}$. The method was successfully applied to the determination of iron(III) in an iron oral drop and clover plant.

Key Words: Catalytic, Spectrophotometry, Iron(III), Methyl red, Pyrosulfite.

INTRODUCTION

Iron plays an important role in ecological system. Many methods have been reported for the determination of iron. Among them kinetic catalytic methods have high sensitivity and sufficient accuracy without expensive and special instruments¹⁻¹¹. In the determination of catalytic species by kinetic methods different reducing agents have been used to reduce methyl red. Among them sodium hypochlorite¹² and hydrazine¹³ were used for the determination of gold and molybdenum, respectively.

In this work we present a new kinetic method of analysis for iron(III) based on its catalytic effect on the reduction of methyl red by pyrosulfite. The proposed method is rapid and sensitive for the determination of iron(III) in real samples.

EXPERIMENTAL

All chemicals were analytical-reagent grade and double distilled water was used. A stock solution of 1000 mg mL^{-1} Fe(III) was prepared by dissolving 0.3404 g of Fe (NO₃)₃·9H₂O in water, adding 0.5 mL of nitric acid and diluting to 50 mL with water. This solution was standardized by titration with dichromate¹⁴.

A 0.01 mol L⁻¹ solution of methyl red was prepared by dissolving 0.5388 g of the reagent in 8 mL of concentrated sulfuric acid and diluting to 200 mL in a volumetric flask with water. The working solutions were prepared by diluting this solution.

0.6 mol L⁻¹ Potassium pyrosulfite solution was prepared by dissolving 13.4 g of solid powder in water and diluting to 100 mL. More dilute solutions were prepared from this solution whenever needed.

A buffer solution pH = 2.9 was prepared by mixing 95.2 mL of 0.2 mol L⁻¹ of succinic acid with 4.8 mL of 0.2 mol L⁻¹ of borax solution.

A Jasco Model 7850 UV-Visible spectrophotometer was used for recording absorption spectra and a Perkin Elmer model 550 S with 1 cm glass cells was used for absorption measurements. A Galan Kamp BJH-400-0100 thermostate was used for controlling the temperature within $\pm 0.1^\circ\text{C}$. A Metrohm Model 632 with a combined glass electrode measured the pH.

General procedure: An aliquot of standard solution containing 20-100 μg iron(III) was transferred into a 50 mL volumetric flask. Then 5 mL of 2×10^{-4} mol L⁻¹ methyl red, 14 mL succinic acid borax buffer (pH = 2.9) and 1 mL of 0.6 mol L⁻¹ potassium pyrosulfite were added to the flask and make up to the mark with water. The time was measured just after the addition of last drop of pyrosulfite solution. A portion of this solution was transferred into a 1 cm glass cell and the absorbance was measured at 532 nm after 2.5 min. A blank solution is also prepared in the same way without the addition of iron(III).

RESULTS AND DISCUSSION

Methyl red reacts with potassium pyrosulfite in acidic media to form a colourless compound. The formation of colourless product is accelerated by traces of iron(III). Fig. 1 shows absorption spectra of methyl red in the absence and presence of iron(III). The reaction can be followed spectrophotometrically by measuring the change in absorbance at 522 nm at a fixed time.

Effect of variables: The concentration of methyl red, potassium pyrosulfite, temperature and pH of the solution influenced the reduction reaction of methyl red with potassium pyrosulfite. Therefore the effects of these variables on the catalyzed and uncatalyzed reaction were studied.

The effect of potassium pyrosulfite concentration on the absorbance change (ΔA) was studied and the results are shown in Fig. 2. The rate of reaction increases up to potassium pyrosulfite concentration of 0.012 mol L⁻¹ and decreases above this concentration. Thus a concentration of 0.012 mol L⁻¹ was used for further studies.

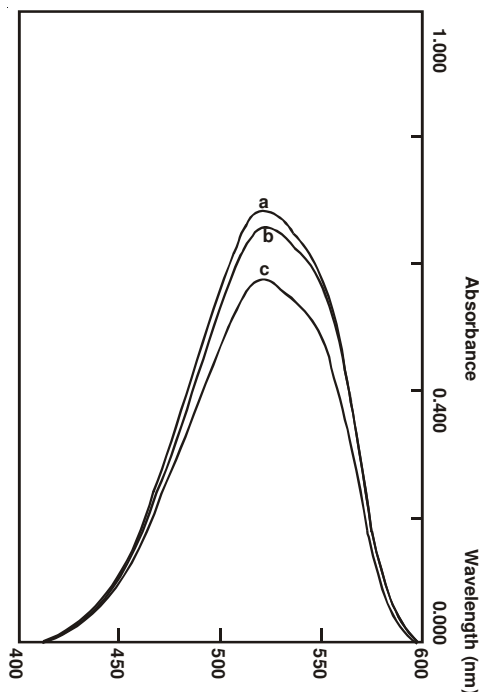


Fig. 1. Absorption spectra of (a) methyl red alone (b) in the absence of pyrosulfite and (c) in presence of pyrosulfite and iron(III)

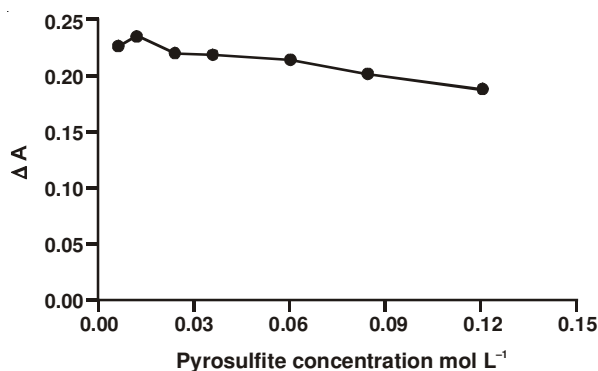


Fig. 2. Effect of potassium pyrosulfite concentration on the absorbance change (ΔA)

The effect of methyl red concentration was also investigated. The results showed that by increasing the reagent concentration up to 2×10^{-5} mol L⁻¹ in the final solution, ΔA was increased (Fig. 3) and decrease with further increase of reagent concentration. Therefore, 2×10^{-5} mol L⁻¹ concentration was chosen as optimum.

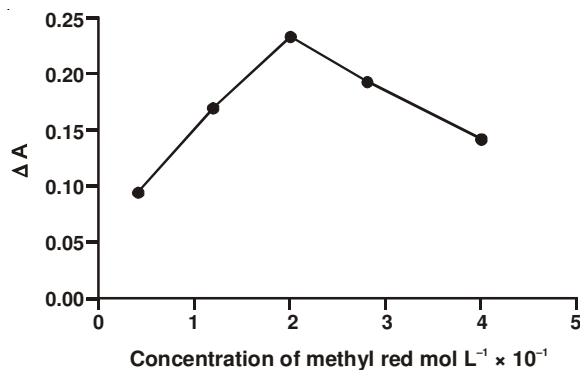


Fig. 3. Effect of methyl red concentration on the reaction

The influence of pH on the reaction was investigated in the pH range of 1.7-3.13. The results are shown in Fig. 4. The rate of reaction increases up to pH value of 2.9 and above that decreases. Thus pH = 2.9 was selected as optimum. Among different buffer systems with pH = 2.9 a borax-succinic acid buffer was selected, because in the presence of this buffer the reaction rate was maximum. The volume of the buffer was also optimized and 5 mL of the buffer solution was used for further work.

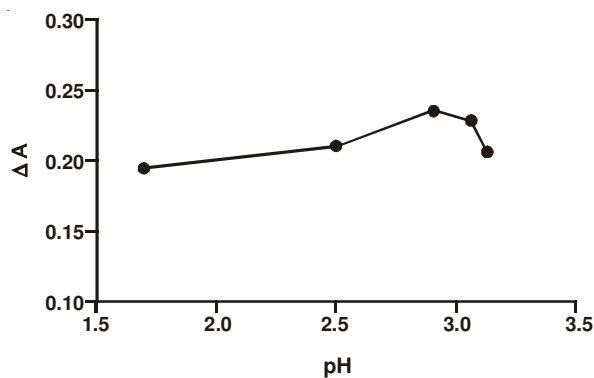


Fig. 4. Effect of pH of the solution on the reaction

The influence of temperature on the reaction rate was studied in range of 15-50°C. It was observed that change in absorbance increased by increasing temperature, but a temperature of 25°C was chosen for convenience. However, using higher temperatures can further increase the sensitivity.

Analytical characteristics: A linear calibration graph for iron from 0.4 to 2.0 $\mu\text{g mL}^{-1}$ was obtained using the general procedure under the optimum conditions. The regression equation of the calibration graph was $\Delta A = -0.0633 + 0.1595C$ where C is concentration of iron in $\mu\text{g mL}^{-1}$ and

the correlation coefficient, $r = 0.9976$. The detection limit of the method calculated from three times the standard deviation of the blank S_b was $0.07 \mu\text{g mL}^{-1}$ and relative standard deviation for eight replicate measurements of $2 \mu\text{g mL}^{-1}$ iron(III) was 1.02 %.

Interference study: The effect of different foreign ions on the determination of $2 \mu\text{g mL}^{-1}$ of iron was examined. The tolerated limit was defined as the concentration of the diverse causing a relative error less than 5 % in the signal. The results shown in Table-1 indicate that most of the ions do not have severe interference.

TABLE-1
EFFECT OF INTERFERING IONS ON THE DETERMINATION
OF $2 \mu\text{g mL}^{-1}$ OF IRON

Interfering ion	Tolerance ratio
K^+ , Na^+ , Mg^{2+} , Ca^{2+} , NO_3^-	2000
NH_4^+ , HCO_3^-	800
CO_3^{2-} , I^-	600
Al^{3+} , SO_4^{2-}	400
CN^-	200
Co^{2+} , Ni^{2+} , Zn^{2+} , PO_4^{3-} , HOP_4^{2-}	100
Mo^{6+}	60
Cr^{3+} , Cd^{2+} , Fe^{2+} , Br^- , SO_3^{2-} , SCN^-	10
V^{5+} , $\text{S}_2\text{O}_4^{2-}$, Ag^+	2

Application: In order to evaluate the applicability of the method, it was applied to the determination of iron in an iron oral drop and clover plant.

1 mL of the iron oral drop was transferred into a 100 mL beaker, 2.5 mL of nitric acid was added and boiled for 5 min, then cooled and transferred to a 100 mL volumetric flask and diluted exactly to the mark with water. An aliquot of this solution was treated under the general procedure. The results are shown in Table-2.

TABLE-2
DETERMINATION OF IRON IN AN IRON ORAL DROP

Iron present (mg mL^{-1})	Iron found by kinetic method (mg mL^{-1})	Relative error (%)
0.70	0.71	1.40
1.80	1.76	-2.22
3.50	3.39	-3.14
5.50	5.58	1.45

5 g of the clover plant was weighed in a porcelain crucible and heated at 80°C for 2 h. Then few drops of water and 25 mL of HCl (6 mol L⁻¹) was added and heated on a water bath for 0.5 h. The solution was transferred to a 100 mL volumetric flask and diluted to mark with water¹⁵. An aliquot of this solution was treated under the general procedure. The results are shown in Table-3.

TABLE-3
DETERMINATION OF IRON IN AN IRON CLOVER PLANT

Iron found by FAAS (mg mL ⁻¹)	Iron found by kinetic method (mg mL ⁻¹)	Relative error (%)
0.72	0.73	1.40
0.96	0.93	-3.10
3.60	3.65	1.40
6.80	6.60	-2.90

REFERENCES

1. A. Zoton and C.C.G.P. Poulos, *Analyst*, **112**, 782 (1987).
2. K. Hirayama and N. Yonehara, *Anal. Chem.*, **60**, 2573 (1988).
3. D. Zhaong and J. Zhi, *Talanta*, **36**, 1107 (1989).
4. S. Abe and M. Endo, *Anal. Chim. Acta.*, **226**, 137 (1989).
5. R. Forteza, J.M. Estela and V. Cerda, *Analyst*, **115**, 749 (1990).
6. T. Tomiyau, H. Sakamoto and N. Yonehara, *Anal. Sci.*, **10**, 761 (1994).
7. S.S. Mitic, G.Z. Miletic and M.V. Obradoric, *Talanta*, **42**, 1273 (1995).
8. S.H. Wang, L.Y. Du, A.M. Zhang and B. Li, *Anal. Lett.*, **30**, 2099 (1997).
9. T. Watanalble, N. Teshima, Sh. Nakano and T. Kawashima, *Anal. Chim. Acta*, **374**, 303 (1998).
10. T. Tomiyasu, N. Yonehara, N. Teshima and T. Kawashima, *Anal. Chim. Acta*, **394**, 55 (1999).
11. J.M.T. Carnerio, A.C.B. Dias, E.A.G. Zagatto and R.S. Honorato, *Anal. Chim. Acta*, **455**, 327 (2002).
12. Z. Jiang, L. Wang, R. Nai and C. Qin, *Huaxue Shijie*, **34**, 267 (1993); *Chem. Abstr.*, **121**, 25815y (1994).
13. Z. Jiang, *Fenxi Ceshi Xuebao*, **12**, 11 (1993); *Chem. Abstr.*, **121**, 147882q (1994).
14. R.B. Fischer and D.G. Peters, *Basic Theory and Practice of Quantitative Chemical Analysis*, edn. 3 (1968).
15. J.B. Jones, B. Wolf and H.A. Mills, *Plant Analysis Handbook*, Micro Marco Publishing, Inc. (1991).

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