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Kinetic Spectrophotometric Determination Of Thiosulfate Based On Its Inhibitory Effect On The Oxidation Of Methyl Red By Bromate

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ABSTRACT

A simple and versatile kinetic spectrophotometric method for determination of thiosulfate is described. The proposed method is based on the inhibitory effect of thiosulfate ion on the oxidation of methyl red (MR) by bromate in the presence of nitrite, which was monitored at 520 nm. The absorbance of the reaction mixture decreases with time and reaches to a minimum in the absence of thiosulfate. The variables affecting the rate of the reaction were investigated and the optimum conditions were established. Under the optimum experimental conditions (0.03 M sulfuric acid, 2×10^{-5} M MR, 2.4×10^{-4} M bromate, 0.45 M nitrate, 1 μg ml^{-1} nitrite and 20°C), thiosulfate can be measured in the range of 0.1 - 9 μg ml^{-1} with a detection limit of 0.095 μg ml^{-1}. This method has been used to determine the trace amounts of thiosulfate ion in tap water samples.

KEYWORDS

Kinetic;
Spectrophotometric;
Methyl Red;
Bromate;
Inhibitory Effect;
Thiosulfate.

INTRODUCTION

Due to the importance of sulfur in chemical, biological and industrial areas, sulfur compounds have been extensively studied for many years, especially the determination of sulfur and its compounds in drugs, cosmetic, food stuffs, natural and petroleum products has received great consideration. Sodium and ammonium thiosulfate are important in chemical industries. The hydrated salt is used as an antichlorine in bleaching in wastewater purification, for reduction of dichromate in chromed leather production, and as a solvent for silver chloride in the chloride roasting of silver containing minerals[1]. There are some reports in the literatures on the determination of thiosulfate microamounts by different techniques, in particular, by spectrophotometric methods[2-5], kinetic method[6-7], differential pulse polarography[8], capillary and capillary zone electrophoresis[9-10], and liquid chromatographic separation and polarographic[11].

In the present work, a detailed study of the appropriate condition for the inhibition effect of thiosulfate on the oxidation of MR in the presence of nitrite was performed. The reaction was monitored (changing in absorbance vs. time) spectrophotometrically at the maximum wavelength of the methyl red (520nm).

EXPERIMENTAL

Reagents

All of the chemicals used were of analytical-regent grade. Sub-boiling, distillated water was used throughout. A 1000 μg ml^{-1}solution of sodium nitrite was prepared and stored in a brown bottle. A few milligrams of sodium hydroxide were added to prevent its decomposition. A potassium bromate solution (0.002 M) was prepared by dissolving 0.0334 g of $KBrO_3$ (Merck) in triply distilled water. 2.75 milliliters of sulfuric acid (98% Merck) were added to bromate solution, and the resulting solution was made up to the mark in a 100ml calibrated flask. A MR solution (0.001 M) was prepared by dissolving 0.0269 g of MR in a mixture of water and 1 ml sulfuric acid 98% in a 100 ml volumetric flask. The solution was stable for at least two months. A thiosulfate solution (1000 μg ml^{-1}) was prepared by directly dissolving 0.1108 g of $Na_2S_2O_3$ and diluted to the mark using triply distilled water in a 100ml calibrated flask.

Apparatus

Absorption spectra were measured on an Agilent UV-Visible 8453 and Chem Station software is applied for data acquisition. A cell of 10 mm optical path was used for all measurements. The temperature of the cell compartment was kept constant by circulating water from a thermostatic bath HAAK D1 model.

Procedure

In to a 3ml quartz cell were placed 225 μl of the $NaNO_3$ solution, 1 ml of 4×10^{-5} M, MR solution, 1 ml of 4.8×10^{-4} M bromate solution and the required volume of the $S_2O_3^{-2}$ solution to obtain a final $S_2O_3^{-2}$ concentration of between 0.1-9 μg ml^{-1}; finally 20 μl of a 100 μg ml^{-1} nitrite solution was added. The variation in absorbance of MR (λ_{max}=520 nm) versus time (for duration 300 s) was started to be measured just after with the addition of nitrite solution. The reaction was monitored by recording the absorbance against water at 520 nm. The ΔA_{23-148} was calculated as the difference between absorbance that corresponds to 23 and 148 sec for each kinetic run and was recorded as an analytical signal.

RESULTS AND DISCUSSION

It was found that bromate ion oxidizes MR very slowly in acidic media. The nitrite ion could catalyze the reaction at trace amounts, so that it proceeded much faster. Thiosulfate decreased the catalytic effect of nitrite on the reaction of the MR–bromate system. The reaction rate of the catalyzed reaction decreased with increasing of the amount of $S_2O_3^{-2}$, and the time required for the absorbance to decrease to a predetermined value increased. As it can be seen from figure 1a, the reaction rate is fast in the presence of nitrate and the absorbance decreasing are clearly observed form successive spectra. Figure 1b shows that the rate of decreasing of the absorption spectra was suppressed by addition of $S_2O_3^{-2}$ to the reaction mixture and that the net absorbance change for successive spectra is very smaller in comparison to the corresponding spectra of the catalyzed reaction.

Effects of variables

To obtain the maximum sensitivity in the determination of thiosulfate, we studied the effect of several variables on the rate of catalyzed and inhibited catalyzed reactions, as follows. The effect of sulfuric acid on the catalyzed and inhibited catalyzed reaction was studied in the concentration range 0.01-0.075 M. The rate of the catalyzed reaction increased with increasing of H_2SO_4 concentrations up to 0.035 M. Then to compromise between the sensitivity and the rate; the concentration of H_2SO_4 has fixed at 0.03 M, as specified in the procedure.

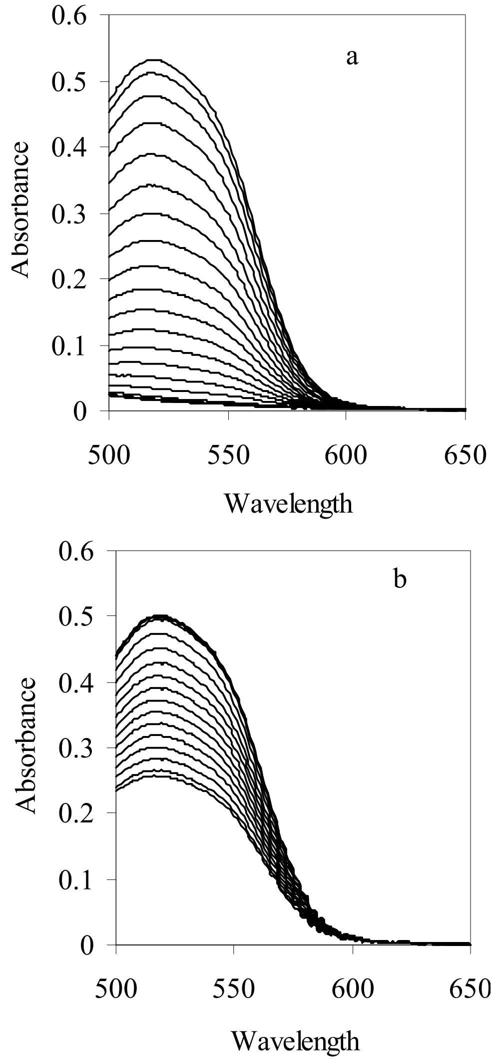

Figure 1: Absorption-spectra changes of methyl red with bromate in acidic media in the presence of the catalyst nitrite and time interval for all spectra is 150 s. (a) in the absence of inhibitor $S_2O_3^{-2}$ and (b) in the presence of inhibitor $S_2O_3^{-2}$

The effect of the bromate concentration on the rate of the catalyzed and inhibited catalyzed reactions were studied in the $1\times 10^{-4} - 3 \times 10^{-4}$ M. The rate of sample reaction increased up to 3×10^{-4} M of bromate concentration. Above 2.4×10^{-4} M of bromate concentration, the reaction rate became too fast; thus the 2.4×10^{-4} concentration was used for the study. The effect of the MR concentration on the catalyzed and inhibited catalyzed reactions rate was studied in the range 1×10^{-5} - 2.4×10^{-5} M MR at the optimum concentrations of others reagents. The inhibition percent at 2×10^{-5} M of MR lead to precise conditions, thus this concentration was chosen as optimum concentration.

The effect of the nitrite concentration on the inhibited catalyzed reaction was studied in the concentration range 0.4 - 3 μg ml^{-1} of nitrite; the best result was obtained at 1 μg ml^{-1} of nitrite. This concentration had the maximum percentage inhibition, as described in the calibration section.

The effect of the temperature on the rate of catalyzed and inhibited catalyzed reactions was studied in the 15 - 40°C range at the optimum reagents concentrations. The results show that 20°C is best, since at higher temperatures the inhibition effect of thiosulfate is decreased; causing increasing in the reaction rate, thus 20°C was used throughout the study.

The effect of the ionic strength on the rate of catalyzed and inhibited catalyzed reactions under the optimum condition was studied using sodium nitrate (4 M).The results show that the maximum of sensitivity could be obtained at 0.45 M of solution with respect to the sodium nitrite.

Calibration

A series of standard solution of thiosulfate was treated according to the recommended procedure. Under these optimum working conditions a calibration curve was prepared, using fixed time method. The ΔA_{23-148} vs. concentration was linear in the range of 0.1- 9 ppm for thiosulfate with detection limit of 0.095 μg ml^{-1}. The equation of the line was ΔA= -

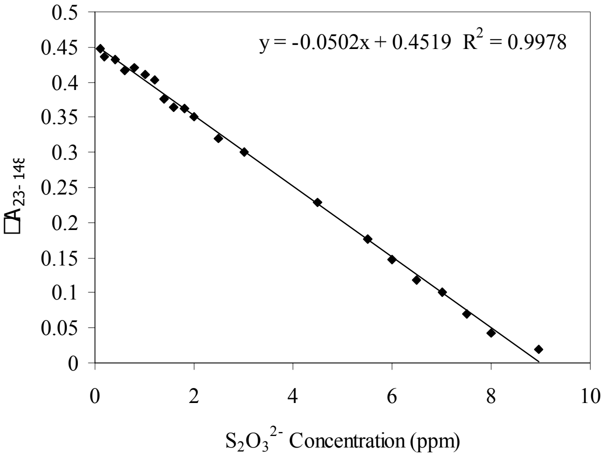

Figure 2: Calibration graph for the determination of the $S_2O_3^{2-}$ by recommended procedure

$0.0502[S_2O_3^{-2}] + 0.4519$ and the squared correlation coefficient was $r^2= 0.9978$. The resulting calibration curve is shown in figure 2. The relative standard deviation for 5 repeated determination of thiosulfate was 0.94% for 2 μg ml^{-1} of thiosulfate. By replicate analysis (n = 5) of the blank reaction, theoretical limit of detection calculated from $S_b = \overline{X} + 3\delta_b$ was 0.095 μg ml^{-1}.

Interference Studies

Under the preferred experimental conditions, to study the selectivity of the proposed method, the effect of various cations and anions on the reaction rate of a 2 μg ml^{-1} solution of $S_2O_3^{-2}$ were tested. The results are summarized in TABLE 1 with maximum tolerance limit for each ion. The tolerance limit was taken as the concentration of diverse ion causing less than 5% relative error. As can be seen, many anions and cations have no considerable effect on the determination of $S_2O_3^{-2}$. However, the presence of , SCN^-, SO_3^-, Br^-, I^-, Hg^{2+} and Ag^+ ions cause serious interferences. The interfering effect of cations was removed by passing the solution from a column containing a strongly acidic H^+-form cations exchanger.

TABLE 1: Influence of foreign ions on the determination of 2 μg ml^{-1} $S_2O_3^{-2}$.

Ion	Tolerance ratio
Mg^{+2},Ca^{+2},Na^+	1000
Mn^{2+},Urea ,Co^{2+}	200
Zn^{2+},Cu^{2+},Ce^{3+},Cd^{2+}	100
Ni^{2+}	50
Hg^{2+},Ag^+	1
SO_4^{2-},CO_3^{2-},PO_4^{3-}	500
Cl^-,F^-	200
IO_3^-	100
I^-,SO_3^-,thiourea	1
SCN^-	0.05

TABLE 2: Determination of $S_2O_3^{-2}$ in tap water and synthetic sample

Sample	Added $S_2O_3^{-2}$ μg ml^{-1}	Found / μg ml^{-1}	RSD %(n = 5)	RE^a
Tap water	2.25	2.359	0.088	-
Synthetic	0.8	0.814	1.92	1.75
Synthetic	1.5	1.510	1.21	0.66
Synthetic	3.25	3.261	0.701	0.34

^{a}Relative Error for proposed method.

Determination of thiosulfate in water

In order to evaluate the applicability of the method to the real sample and synthetic sample, it was applied to the determination of $S_2O_3^{-2}$ in tap water the result show in TABLE 2. The results show that the method is suitable for the analysis of real samples.

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