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Kinetic Catalytic Spectrophotometric Determination of Thiocyanate Ion Using the Oxidation of Thionine by Bromate

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A new and sensitive kinetic spectrometric method was developed for the determination of ultra free amounts of thiocyanate ion in water samples. The method is based on the inhibiting effect of thiocyanate ion on the oxidation of thionine by bromate in acidic medium. The reaction was monitored spectrophotometrically by 600 nm with a fixed-time method. The decrease in the absorbance of thionine is proportional to the concentration of thiocyanate ion in concentration range 2.0×10^{-4}-2.0×10^{-3} M with a fixed time of 0.5-5 min from initiation of the reaction. The limit of detection is 0.048 ng/mL thiocyanate ion. The relative standard deviation of 0.3 and 1 ppm of thiocyanate ion were 2.13 and 1.36, respectively. The method was applied to the determination of thiocyanate ion in natural water.

Key Words: Thiocyanate, Kinetic spectrophotometry, Thionine.

INTRODUCTION

Thiocyanate ion usually exists in industrial wastewaters and organism metabolites. The presence of low concentration of this ion arise from tobacco smoking. Thiocyanate ion is present as a normal constituent in mammalian tissues and body fluids. If the content of thiocyanate ion is a little higher in the body then it may more into coma[1]. Therefore, the determination of thiocyanate ion at low levels especially in food, biological and water samples is important[2]. Several methods have been developed for the determination of thiocyanate ion. These include application of spectrophotometry[3-5] membrane[6,7] gas chromatography and ion-seleclective electrodes[8], fluorimetric[9], photo kinetic voltammetric method[10], partial least squares regression[11], stopped-flow[12], kinetic methods[12-14], nano-silver coated carbonnanotubes modified glassy carbon electrode[1], liquid chromatography[15].

Most of these methods are laborious to perform and involve the use of harmful reagents. Also, because some of them require more expensive instrument, they cannot be easily popularized. Therefore it is essential to look for a new method with high sensitivity, simplicity and efficiency for the detection of thiocyanate ion.

In this paper, the development of a new method is described for the determination of thiocyanate ion, base on it's inhibiting effect on the reaction was monitored spectrophotometrically at the maximum wavelength of thionine (600 nm) while measuring the change in the absorbance over time.

EXPERIMENTAL

All reagents used were of analytical reagent grade and solutions were prepared in doubly distilled water. A 1000 mg/L stock solution of thiocyanate ion was prepared by dissolving 0.1312 g ammonium thiocyanate ion (Merck) in doubly distilled water and diluting to the mark with water in a 100 mL volumetric flask. A 0.02 M potassium bromate solution was prepared by dissolving 0.334 g of $KBrO_3$ (Merck) in water and diluting to 100 mL in a volumetric flask. A solution of 3.79×10^{-4} M of thionine (Merck) by dissolving 0.01 g of thionine in water and diluting to 100 mL with water. A sulfuric acid solution was prepared by appropriate dilution of concentrated sulfuric acid (Merck). Stock solutions (1000 mg/mL) of interfering ions were prepared by dissolving suitable salts in water. Sulfuric acid or sodium hydroxide solution rinsed with top water soaked in dilute HNO_3 solution (2 % v/v) rinsed with water and dried.

A Shimadzu UV-vis 160A spectrophotometer with 1.0 cm quartz cell was used to measure the absorbance at a fixed wavelength of 600 nm. A thermostat water batch was used to keep the reaction temperature at 30 ºC.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 20 ºC for 20 min for equilibration before starting the experiment. An aliquot of the solution contaning 1 mL of 10 mg/L thiocyanate ion was transferred in to a 10 mL volumetric flask and then 0.7 mL of 2 M H_2SO_4 was added followed by 0.7 mL of 3.79×10^{-4} M of thionine solution. The solution was diluted to 0.8 mL with water and 0.6 mL of 0.02 M bromate solution was added and diluted to the mark with water. A portion of the solution was transferred to a 1.0 cm glass cell within 20 s measurement of the variation in absorbance over time. The reaction was followed by measuring the decrease in absorbance of the solution against water at 600 nm for 0.5-5 min from initiation of the reaction. This signal was labeled as ΔA_s. The same procedure was repeated without addition of thiocyanate ion solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of bromate solution.

RESULTS AND DISCUSSION

A slow reaction is linked to a fast one by the reaction product of the former the effect may be shown as follows:

$$A + B \xrightarrow{k_1} P_1$$

$$P_1 + L \xrightarrow{k_2} Y_1$$

where $k_2 > k_1$ since the second reaction is faster than the first, its product (p) be detected once L has disappeared completely as a result of the second reaction.

Thionine undergoes oxidation with bromate in acidic medium to form a colourless product at low rate. It is found that this reaction rate is sharply increased by addition of trace amount of thiocyanate ion. This process was monitored, spectrophotometrically by measuring the decrease in absorbance of the characteristic band of thionine (600 nm) (Fig. 1).

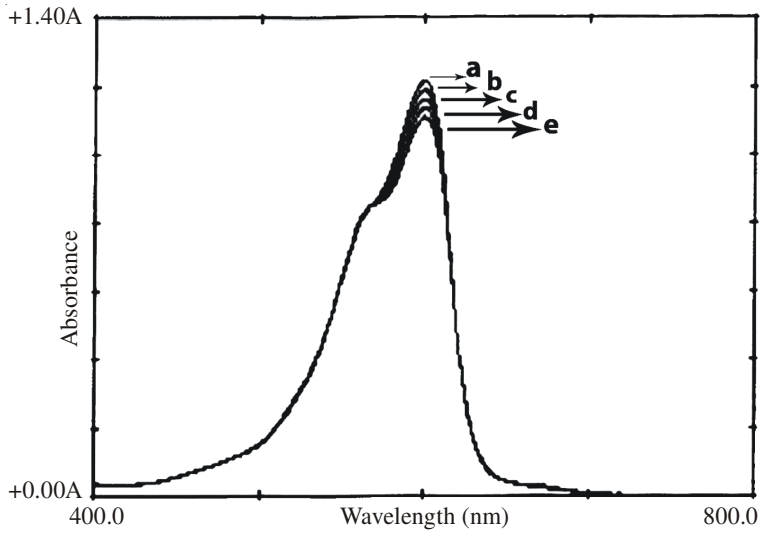

Fig. 1. Variation of thionine, bromate, thiocyanate ion system with time (a) 30 s, (b) 60 s, (c) 90 s, (d) 120 s, (e) 150 s. Condition: 0.14 M H_2SO_4; temperature 25 ºC, 12×10^{-4} M, bromate, 2.94×10^{-5} M thionine, 1 mg/L thiocyanate ion

Influence of variable: Various experimental parameters were studied in order to obtain an optimized system. These parameters were optimized by setting all parameters constant and optimized one at a time. The effect of acid concentration, thionine and bromate concentration and rate of catalyzed and uncatalyzed reaction was studied.

The effect of the sulfuric acid concentration on the rate of reaction was studied in the range of 0.06-0.24 M. Fig. 2 shows that an increase in H_2SO_4 concentration up to 0.16 M and decreases at higher concentrations. This mean that the rate of uncatalyzed reaction increases with sulfuric acid concentration (> 0.16) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions (ΔA_s-ΔA_b) diminishes at higher sulfuric acid concentrations. Therefore, a sulfuric acid concentration of 0.16 M was selected for further study.

Effect of thionine concentration on the sensitivity for the range 4.2×10^{-6} – 42.0×10^{-6} M this sensitivity (net reaction rate) increases with increasing thiocyanine concentration upto 2.94×10^{-5} M and decreases at higher concentration (Fig. 3). This may be due to the aggregation of the dye at higher concentration. Therefore, a final concen-tration of 2.94×10^{-5} M of thionine was selected as the optimum concentration.

The effect of the bromate concentration on the rate of reaction was studied in the range of (2.0×10^{-4}-2.0×10^{-3}) M (Fig. 4). The result show that the net reaction rate increases with increasing bromate concentration up to 1.0×10^{-3} M and decreases at higher concentrations therefore, a bromate concentration of 1.0×10^{-3} M was selected for further study.

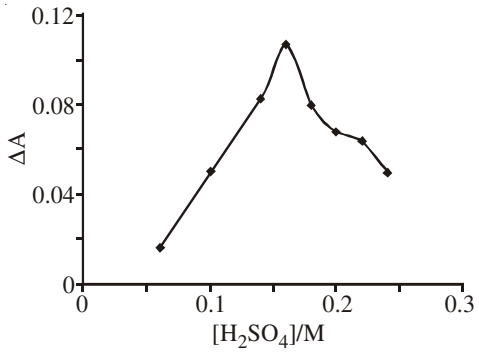

Fig. 2. Influence of sulfuric acid concentration on sensitivity, conditions: 1 mg/L thiocyanate ion, 12×10^{-4} M bromate, 2.94×10^{-5} M thionine and temperature 25 ºC, in fixed time of 0.5-5 min from initiation of reaction

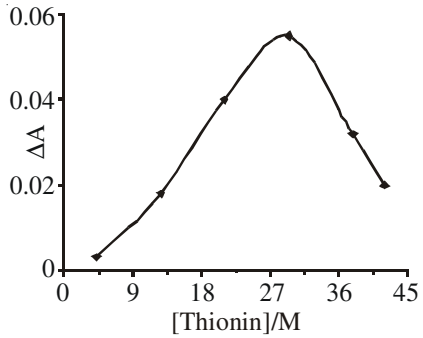

Fig.3. Effect of thionine concentration on the sensitivity, conditions: 1 mg/L thiocyanate ion, 12×10^{-4} M bromate, 0.16 M H_2SO_4 and temperature 25 ºC, in fixed time of 0.5-5 min from initiation of reaction

The effect of the temperature on the sensitivity was studied in range of 10-35 ºC with the optimum of the reagents concentrations. The result showed that as the temperature increases up to 20 ºC the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s - \Delta A_b$). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent and the uncatalyzed reaction occurred at a suitable rate. Therefore, 20 ºC was selected for optimum study.

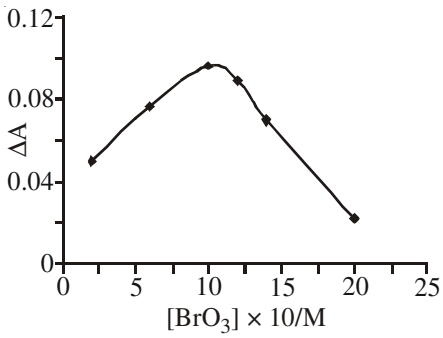

Fig. 4. Effect of bromate concentration on the reaction rate, conditions: 1 ppm thiocyanate ion, 0.16 M H_2SO_4 and 2.94×10^{-5} M thionine. Temperature 25 ºC, in fixed time of 0.5-5 min from initiation of reaction

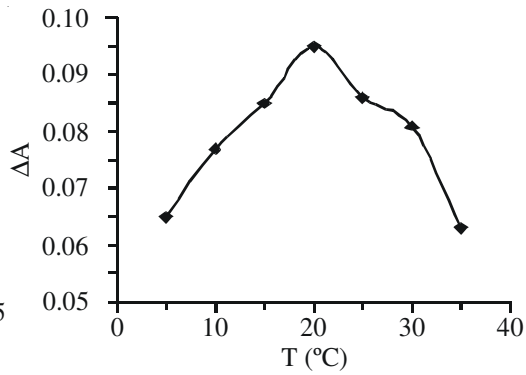

Fig. 5. Influence of temperature on the reaction rate, conditions: 1 mg/L thiocyanate ion, 0.16 M H_2SO_4, 2.94×10^{-5} M thionine and 1.0×10^{-3} M bromate in fixed time of 0.5-5 min from initiation of reaction

Calibration graph, precision and limit of detection: Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an internal of the reaction because it provided the best regression

and sensitivity. Under the optimum conditions described above, a linear calibration 0.1-0.5 and 0.5-1.1 mg/L of thiocyanate ion the equation of the calibration graph were y = 0.1102x-0.003 and y = 0.0223x + 0.0387, respectively (Figs. 6 and 7).

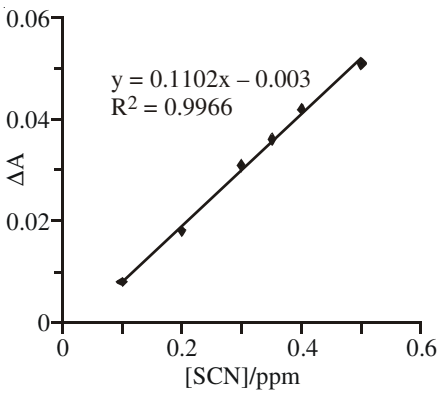

Fig. 6. Conditions: 1 mg/L thiocyanate ion and 0.16 M H_2SO_4, 2.94×10^{-5} M thionine and 1.0×10^{-3} M bromate. Temperature 20 ºC in fixed time of 0.5-5 from initiation of reaction

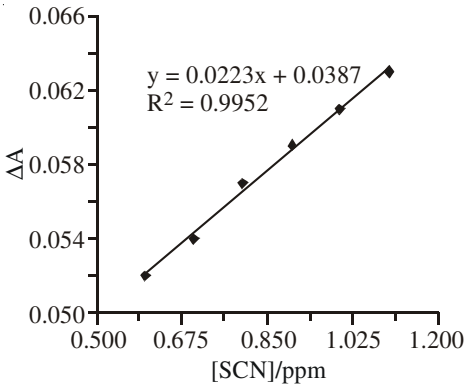

Fig. 7. Conditions: 1 mg/L thiocyanate ion, 0.16 M sulfuric acid, 2.94×10^{-5} M thionine and 1.0×10^{-3} M bromate. Temperature 20 ºC, in fixed time of 0.5-5 min from initiation of reaction

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 1.1 mg/L thiocyanate ion was studied.

The tolerance limit was defined as the concentration of added ions causing a relative error less than ± 3 % (Table-1). Many ions did not interfere, even when they were present in 1000 fold over thiocyanate ion. The results show that the method is relatively selective for thiocyanate ion ion determination.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DELERMINATION OF 1.1 mg/L THIOCYANATE ION ION

Species	Tolerance limit (w_{ion}/w_{thio})
CH_3COO^-, $S_2O_8^{2-}$, $S_2O_3^{2-}$, NO_3^-	1000
K^+, Na^+, Co^{2+}	1000
Cu^{2+}, ClO_3^-	800
ClO_4^-	400
HCO_3^-	300
Ca^{2+}, Mg^{2+}	100
Cl^-	70
Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Ba^{2+}	< 1
NO_2^-, Br^-, I^-	< 1

Sample analysis: In order to evaluate the applicability of proposed method, water samples were analyzed to determine thiocyanate ion contents. The results are

presented in Table-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
DETERMINATION OF THIOCYANATE ION IN SYNHETIC SAMPLES

Samples Water	Added (ppm)	Found (ppm)	Recovery (%)
1	–	–	–
	0.2	0.191	95.50
	0.3	0.292	97.30
	0.4	0.408	102.0
2	–	–	–
	0.8	0.775	96.87
	0.9	0.910	101.11
	1.0	1.040	104.00

The catalytic-spectrophotometry method developed for the determination of thiocyanate ion is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of determination and good precision and accuracy compared to other catalytic procedures. With this method, it is possible to determine thiocyanate ion at levels as low as 0.048 ng/L without the need for any pre concentration step.

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