Catalytic Kinetic Determination of Silver through its Catalytic Effect on Congo Red-Peroxodisulphate Reaction

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ABSTRACT: *A kinetic-spectrophotometric procedure is reported for determination of trace amounts of Ag(I). This method is based on catalytic effect of silver ion on the oxidation of congo red by potassium peroxodisulphate at pH=3.4 and 30 ^{o}C in the presence of 1,10-phenanthroline as an activator. The reaction was followed spectrophotometrically by measuring the rate of change in absorbance of congo red at 510 nm in the range of 30-330 seconds after initiation of the reaction. Silver can be determined in the range 2-100 and 100-1100 ng/ml with detection limit 1 ng/ml Ten replicate analysis of a sample solution containing 8 ng/ml silver gave a relative standard deviation of 1.0%. This method was used for determination of silver in water and photographic plate samples.*

KEY WORDS: *Silver, Catalytic methods, Congo red, Spectrophotometry*

INTRODUCTION

Silver plays an important role in electronic and photography industries [1] and thus, determination of trace amounts of silver ion is necessary. There are various methods such as electrochemistry [2,3], atomic absorption spectrophotometry [4], fluorimetry [5] and spectrophotometry [6-10] for determination of silver. However, many of these methods have a low sensitivity, a small linear dynamic range and/or are expensive and complex. This work presents a simple, highly selective and sensitive method with very low detection limit for the determination of silver based on the catalytic effect of Ag(I) on the oxidation of congo red by peroxodisulphate using 1,10-phenanthroline as an activator. The precision and detection limit of proposed method is similar to other reported catalytic-kinetic methods. But, this procedure has extends linear range and high tolerance limit for interference ions with respect to other methods [6-12].

EXPERIMENTAL

Reagents

All chemicals were of analytical-reagent grade from Merck Company. Doubly distilled water was used throughout.

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Silver solution (1000 μg/ml) was prepared by dissolving 0.1575 g $AgNO_3$ in water in a 100 ml volumetric flask. Potassium peroxodisulphate solution (0.250 M) was prepared by dissolving 33.7912 g $K_2S_2O_8$ (Merck) in water in a 500 ml volumetric flask and diluted to the mark with water.

Congo red (CR) solution (5.0×10^{-3} M) was prepared by dissolving 0.8708 g of the compound in 250 ml volumetric flask and diluted to the mark with water.

1,10-Phenanthroline solution (0.05 M) was prepared by dissolving 0.9010 g of the compound in 100 ml ethanol in a 100 ml volumetric flask.

Apparatus

Absorption spectra was recorded on a Shimadzu Model 160 UV/Vis Spectrophotometr with a 1-cm glass cell. A Perkin-Elmer Model 35-Spectrophotometr with a 1-cm glass cell was used for absorbance measurements at a fixed wavelength. A thermostated bath (HAAKE-F3) was used to keep the reaction temperature at 30 ^oC. A stopwatch was used for recording the reaction time.

The pH was adjusted by a model 624 Metrohm digital pH meter. A Shimadzu AA-680 atomic absorption spectrophotomer was also used for determination of silver in real samples.

Recommended Procedure

All the solutions were preheated to the working temperature of 30 ^oC in a thermostat bath. A sample solution of containing 20-1000 ng of Ag(I) was transferred into a 10-ml volumetric flask. Then 2.0 ml of the acetate buffer solution of pH=3.4, 2.4 ml of 0.25 M $K_2S_2O_8$, 1.0 ml of 5.2×10^{-4} M 1,10-phenanthroline were added to the flask. Then water was added to make the solution volume up to ca. 8 ml. Then 1.0 ml 3.6×10^{-4} M CR was added into the solution and the solution was diluted to the mark with water. Time was measured just after the addition of the last drop of the CR solution. A portion of the reaction mixture was transferred into a 1-cm cell at 30 ^oC within 30 sec and the reaction was followed by recording the decrease in absorbance at 510 nm at a fixed time of 300 s from initiation of the reaction (ΔA_s). The measurement was repeated in the absence of silver to obtain the values for the uncatalyzed reaction (ΔA_b). The net reaction rate was calculated from the difference in the absorbance change of the two measurements for catalyzed and uncatalyzed reactions (ΔA_s- ΔA_b). For large amounts of silver (0.100-1.100 mg/ml Ag(I)), 2.0 ml of buffer solution with pH=3.4, 1.2 ml of 0.25 M $K_2S_2O_8$, 1.0 ml of 5.2×10^{-4} M 1,10-phenanthroline and 1.0 ml of 6.0×10^{-4} M CR was used to construct the calibration graph.

RESULTS AND DISCUSSION

Congo red (CR) is a dye and is used as an acid-base indicator that can be oxidized by oxidizing agents such as peroxodisulphate in acidic solution. On the other hand, the oxidation of CR by peroxodisulphate is increased in the presence of trace amounts of silver, and 1,10-phenanthroline as an activator. This reaction can be followed spectrophotometrically by monitoring the change in the absorbance at 510 nm. Fig. 1 shows the absorption spectra of CR at different times.

The effect of some N-donor substances previously employed for activation of Ag(I)-catalyzed oxidation reaction was examined, and their efficiency was found to decrease in the order, 1,10-phenanthroline, N-aminopyridine, 2,2-bipyridine and ammonia. Thus, 1,10-phenanthroline was used as an activator for obtaining a higher sensitivity [11,12].

Effect of Variables

The effect of pH, reaction time, concentration of reagents, temperature and ionic strength on the catalyzed and uncatalyzed reactions were studied by the

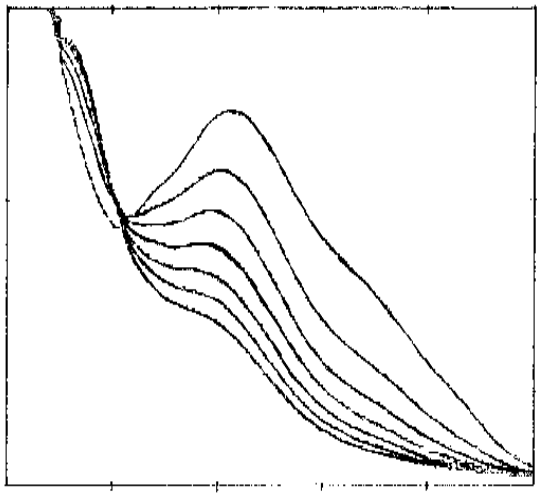

Fig. 1: Absorbance variations of congo red solution in the presence of $K_2S_2O_8$ versus to time.

fixed time procedure. A fixed time interval of 30-330 s from initiation of the reaction was selected for measuring the decrease in absorbance, while resulted in high sensitivity and acceptable analysis time.

Congo red reagent is a acid-base indicator. The structural configuration and its solution absorbance depend on the pH of solution. Therefore, the effect of pH on the reaction rate was studied in the range of 1.3-4.0, using constant values of the other parameters, i.e., 6.0×10^{-5} M CR, 2.6×10^{-5} M 1,10-phenanthroline, 3.75×10^{-2} M peroxodisulphate, 0.1 µg/ml Ag(I) and 25 ^{o}C. As shown in Fig. 2, the reaction rate increases to about pH=3.4, whereas, at greater pH values, the rate of the catalyzed reaction decreases. Thus, a buffer solution (acetic acid and NaOH) with pH=3.4 was used for further studies. After the maximum point in Fig. 2, the suitable form for redox reaction has reduced and the rate of reaction decreases with increasing of pH.

Obviously, the rate of reaction influenced by concentration of CR and peroxodisulphate as reactants. The effect of CR concentration on the reaction rate is shown in Fig. 3. The reaction rate (pH=3.4, 2.6×10^{-5} M 1,10-phenanthroline, 3.75×10^{-2} M peroxodisulphate, 0.1 µg/ml Ag(I) and 25 ^{o}C) increases from 1.0×10^{-5} M CR up to 3.6×10^{-5} M and then decreases with increasing the concentration of CR reagent. In concentrations of CR > 3.6×10^{-5} M, the change in absorbance, in the time interval of 30-330 s after initiation of the reaction, is decreased, which results in lower sensitivity of the measurement. The real limitation of Beer's law influence on the absorbance of solution at higher conentration of the reagent. Thus, the concentration of 3.6×10^{-5} M was selected as an optimum point for CR reagent.

The effect of peroxodisulphate concentration was examined at 3.6×10^{-5} M CR, 2.6×10^{-5} M 1,10-phenanthroline, 0.1 µg/ml Ag(I), pH=3.4 and 25 ^{o}C (Fig. 4). The results show that by increasing the concentration of preoxodisulfate to 0.06 M, the sensitivity increases. At higher concentration of peroxodisulphate > 0.06 M, the absorbance variation of blank solution is become more than sample solution and sensitivity decreased.

Fig. 5 shows the effect of 1,10-phenanthroline concentration on the reaction rate in the presence of 3.6×10^{-5} M CR, 6.0×10^{-2}M peroxodisulphate, 0.1µg/ml

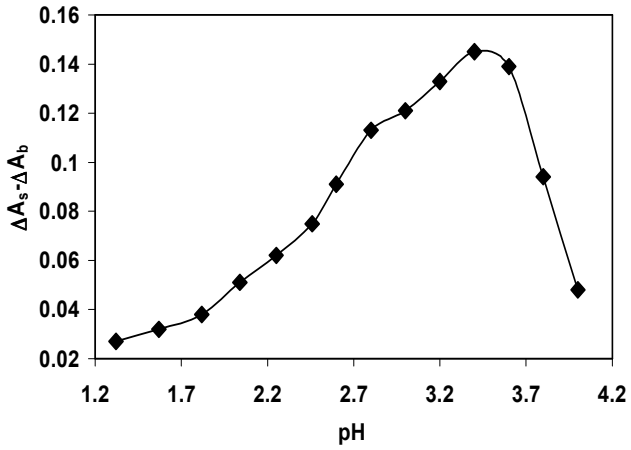

Fig. 2: Effect of pH on the reaction rate

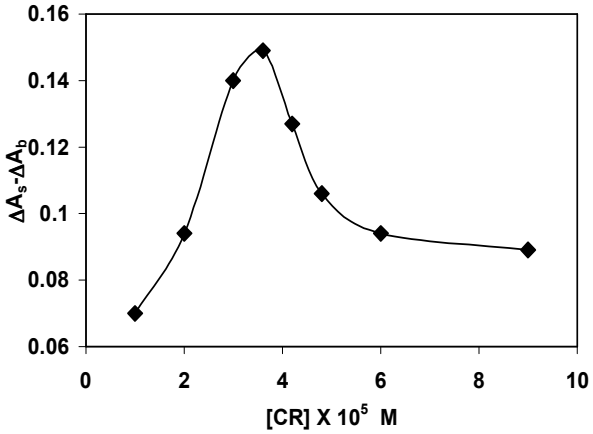

Fig. 3: Effect of congo red reagent concentration on the reaction rate

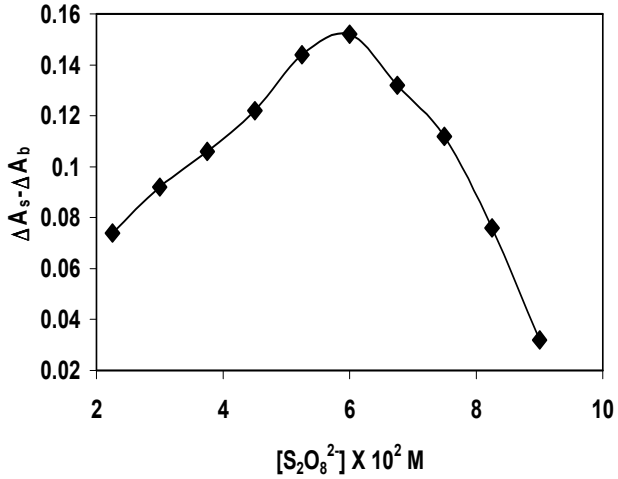

Fig. 4: Effect of peroxodisulphate anion concentration on the reaction rate

Ag(I), pH=3.4 and 25 °C. As it is seen from Fig. 5, with increasing concentration of the reagent up to 5.2×10^{-5} M, the reaction rate increases, whereas, at higher concentration, the rate of catalyzed reaction is decreased. Therefore, 5.2×10^{-5} M 1,10-phenanthroline was chosen as the optimum concentration. In the redox reactions that the Ag(I) acts as a catalyst, the peroxodisulphate oxidize Ag(I) to Ag(II) and the CR reagent was oxidized by Ag(II) ion. 1,10-phenanthroline acts as a ligand for complex formation with silver ions. The its complex with Ag(II) is more stable than Ag(I), thus, the rate of reaction increases with increasing concentration of 1,10-phenanthroline as a stabilizer for Ag(II) ions. At higher concentrations of activator, the amount of Ag(I) was reduced and the rate of reaction decreases.

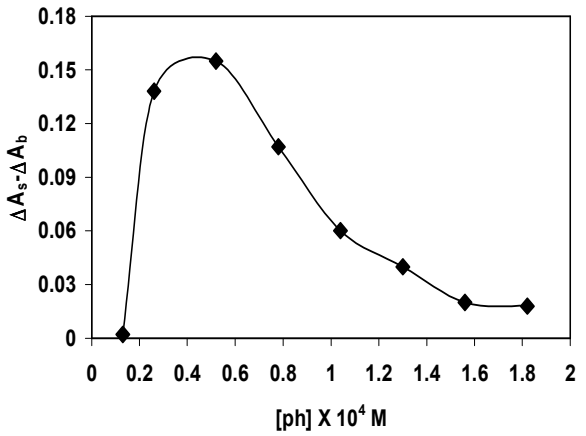

Fig. 5: Effect of 1,10-phenantroline concentration on the reaction rate

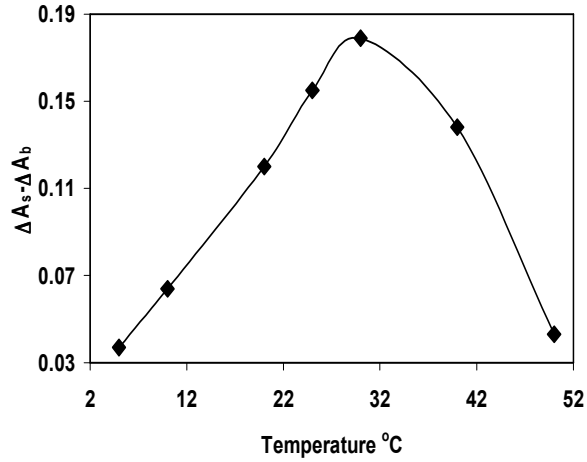

Fig. 6: Effect of temperature on the reaction rate

The sensitivity increased with temperature up to 30°C (Fig. 6) in the presence of optimum reagents concentrations and 0.1 µg / ml Ag (I) and decreased at higher temperatures. This behavior at temperatures higher than 30 °C is due to a higher rate of uncatalyzed reaction with respect to catalytic reaction. Thus, 30 °C was adopted.

The effect of ionic strength also was studied. The results showed that the sensitivity decreased slightly by increasing ionic strength.

Analytical Parameters:

Under the optimum conditions described above and with the fixed-time method in the time interval of 30-330 s from initiation of the reaction, the oxidation rate of CR is a linear function of silver concentration. A linear calibration graph at the optimum conditions was obtained in the concentration range of 0.002-0.100µg/ml with a linear equation of $\Delta A=0.9548[Ag^+]+0.0022$ (r=0.9982). The other calibration curve was obtained in the concentration range of 0.100-1.100 µg/ml with a linear equation of $\Delta A=0.2464[Ag^+]-0.0019$ (r=0.9989) using a 6.0×10^{-5} M CR, 3.0×10^{-2} M peroxodisulphate and other optimum parameters. ΔA is the change in absorbance at the fixed time interval of 30-330 s from initiation of the reaction.

The accuracy and precision of the method is given in Table 1. The limit of detection was 1.6 ng/ml (Detection limit = $3S_b/m$, S_b is standard deviation of ten times measurements of ΔA_b and m is slope of calibration curve in the concentration range of 0.002-0.100 µg/ml silver ion) [13].

Interferences

To study the selectivity of the proposed method, the effect of various cations and anions on the reaction rate of 100ng/ml of silver ion at pH=3.4 was tested. The results are summarized in Table2 with maximum tolerance limit for each ion. Maximum tolerance limit obtains when deviation of absorbance variant in the presence of interfere ion is in the interval of±S (i.e. standard deviation of ΔA_s in the absence of interfere ion with three times measurements). The interference of anions (Cl^-,Br^-,I^-,SCN^-,CN^-,$S_2O_3^{2-}$,BrO_3^-,NO_2^-) can be removed by addition of 1.0ml concentrated nitric acid into 10 ml of the sample solution and heating to dryness.

Table 1: Precision and accuracy for the method

Silvercontent µg/ml	Silver found µg/ml	RSD% N=10	Error%
0.040	0.0396	1.10	-1.0
0.080	0.0804	1.55	0.5
0.100	0.1027	1.37	2.7
0.400	0.3929	2.20	1.8
0.800	0.7919	1.00	-1.0
1.000	1.0100	1.48	1.0

Table 2: Effect of various ions on the determination of 0.1 µg/ml of silver at the optimum conditions

Species	Tolerance limit (µg/ml)
Li^+, Na^+, K^+, NH_4^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Pb(II), Cr(III), Al(III), V(V), Mo(VI), SO_3^{2-}, NO_3^-, $C_2O_4^{2-}$, SO_4^{2-}, HCO_3^-, CH_3COO^-, Phetalat	1000
Mn(II), ClO_4^-, CO_3^{2-}, PO_4^{3-}	800
Cr(II), Zn(II), Fe(III), Co(II), IO_4^-, F^-	500
Hg(II), Cu(II), Ni(II), Fe(II), $^*Br^-$, $^*Cl^-$, $^*I^-$, $^*CN^-$, $^*SCN^-$, $^*S_2O_3^{2-}$, $^*BrO_3^-$, $^*NO_2^-$, $^*HPO_4^-$	200

** after removal of interferences by the proposed method*

Table 3: Determination of silver in real samples

Samples	Silver found		
	Proposed method	RSD% n=10	Standard method
Natural water	5.6 ng/ml	1.70	5.8 ng/ml
Photographic plate	0.0030%	1.80	0.0033%

Determination of Silver in Natural Water and in Developed Panchromatic Plate

For natural water, to a 250 ml water sample, 10 ml of concentrated nitric acid and 1 ml of sulfuric acid was added. Then, the solution was evaporated to dryness, 5 ml of concentrated nitric acid was added and evaporated again. The residue was cooled to room temperature, distilled water was added to dissolve the residue and the solution was made up exactly to 50 ml. Then, a suitable aliquot of the solution was analyzed by the proposed method.

For the developed panchromatic plate, a known amount (0.5757 g) of the plate was treated with 10 ml of 3 M sodium hydroxide until the gelatinous film separated from the rigid support which was discarded after washing. Then, 25 ml of concentrated nitric acid was added and the solution was heated until the silver has dissolved completely. The solution was filtered and the filtrate was made up to volume in a 100 ml volumetric flask with water. A suitable aliquot of the solution was analyzed by the proposed method.

The results of analysis of real samples together with the results obtained by atomic absorption spectrometry (standard addition method) after preconcentration of natural water are shown in Table 3.

CONCLUSION

This method is very sensitive, simple and selective for determination of silver ion at trace levels down to 2 ng/ml without the need for any preconcentration step.

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