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Catalytic Spectrophotometric Determination of Trace Amounts of Ag(I) using the Oxidation of 1,8-Dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic Acid Trisodium Salt with Peroxodisulfate

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A simple and sensitive kinetic spectrophotometric method for determination of ultra trace amounts of silver(I) has been proposed. It is based on the oxidation of 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt (SPADNS) by peroxidisulfate in acetate buffered solution at pH 3.5 and in the presence of 1,10-phenanthroline as an activator at 35ºC. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of SPADNS at 510 nm in time period of 0.5-5.5 min from initiation of the reaction. The method allows the determination of silver concentration in the range 2.0-100.0 ng/mL, with the detection limit of 0.26 ng/mL. The relative standard deviation for ten replicate determinations of 0.040 and 0.10 μg/mL Ag(I) is 1.9 and 2.3%, respectively. The method has been applied to determination of silver in photographic solution and water.

Key Words: Spectrophotometric determination, Silver(I), 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt.

INTRODUCTION

Silver is widely distributed in nature and is a major compound of a wide range of minerals. The most important application of silver compounds are in photography, structure of batteries and semiconductors, electroplating for both decorative and industrial applications. However, silver has been recognized as a toxic element in marine environment[1]. Thus, the determination of traces of silver is important.

Among the most important kinetic methods, catalytic methods are very well known because of their simplicity, sensitivity and selectivity. Many workers have reported the use of catalytic reaction for determination of silver. Ag(I) is a good catalyst for the oxidation of various organic dyes[2] by $S_2O_8^{2-}$ and by[3] H_2O_2 in the presence or absence of an activator[4]. For

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example, piperazine acts as an activator in oxidation of *p*-nitrodiazo aminobenzene[5], 1,10-phenanthroline was used as an as activator for the oxidation of bromopyrogallol red[6] and for the oxidation of Brilliant Cresyl Blue. 1,10-phenantroline was also used as an activator in the oxidation of certain azo dyes[7-10]. Ethylendiamine and triethylenetetramine have also been studied as activators[11]. However, many of these methods suffer from poor selectivity.

This paper describes a simple, precise, selective and sensitive method for determination of silver using its catalytic effect on the oxidation of 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt (SPADNS) by peroxodisulfate in the presence of 1,10-phenanthroline as an activator.

EXPERIMENTAL

Absorption spectra were recorded on a Perkin Elmer model Lambda 2 UV-VIS spectrophotometer with a 1.0 cm glass cell. A model 2501 CECIL spectrophotometer with 1.0 cm glass cell was used to measure the absorbance at a fixed wavelength of 510 nm. A thermostated bath (HAAKE-F3) was used to keep the reaction temperature at 35°C. A stopwatch was used for recording time. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 %) (v/v), rinsed with water and dried.

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. A silver stock solution (1000 μg/mL) was prepared by dissolving 0.1575 g of $AgNO_3$ (Merck) in water and diluting to the mark in a 100 mL flask.

SPADNS solution (7.36×10^{-4} M) was prepared by dissolving 0.0419 g of the reagent (Merck) in water and the solution was diluted to the mark in a 100 mL volumetric flask. Peroxodisulfate solution (0.10 M), was prepared by dissolving 0.2703 g of its potasium salt (Merck) in distilled water and diluting to 100 mL flask. 1,10-Phenanthroline solution (1.48×10^{-3} M) was prepared by dissolving 0.0267 g of the compound in ethanol and the solution was diluted to the mark with ethanol in a 100 mL volumetric flask.

Stock solutions (1000 μg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

Recommended procedure: All of the solutions and distilled water were kept in a thermostated water bath at 35ºC for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.020-1.0 μg/mL Ag(I) was transferred into a 10 mL volumetric flask and then 2 mL of buffer solution (pH = 3.5, acetate 0.2 M), 1 mL SPADNS 7.36×10^{-4} M and 2 mL 1.48×10^{-3} M 1,10-phenanthroline solutions were added to the flask. The solution was diluted to *ca.* 5.5 mL with water, then 4 mL 0.10 M peroxodisulfate solution was added and the solution was diluted to the mark with water. The solution was mixed and a portion of the solution was transferred to the spectrophotometric cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 510 nm for 0.5-5.5 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of Ag(I) solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of peroxodisulfate.

RESULTS AND DISCUSSION

SPADNS undergoes an oxidation reaction with peroxodisulfate to form a colourless product at slow rate. This reaction rate is sharply increased by addition of trace amount of Ag(I), especially in the presence of 1,10-phenanthroline as an activator. The rate equation of the catalyzed reaction is:

$$\text{Rate} = -d[\text{SPADNS}]/dt = K[\text{Ag(I)})][\text{SPADNS}]^m[S_2O_8^{2-}]^n \qquad (1)$$

where k is the rate constant. Because $[S_2O_8^{2-}] >> [\text{SPADNS}]$, $[S_2O_8^{2-}]$ can be considered to be constant and m was found to be 1. By integration of eqn. 1 and by incorporating Beer's law, we obtain the final expression:

$$\Delta A = K[\text{Ag(I)}]t \qquad (2)$$

where t is the reaction time.

There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 510 nm. Fig. 1 shows the relationship between A and reaction time ‘t’. It was found that the rate of reaction is proportional to the Ag(I) concentration. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of SPADNS at 510 nm (Fig. 1). The presence of 1,10-phenanthroline as an activator increased the rate of this catalytic reaction.

Influence of variables

In order to optimize the reaction to get the best sensitivity, the variables affect the sensitivity such as pH, SPADNS concentration, peroxodisulfate concentration, 1,10-phenanthroline concentrations and temperature on the rate of catalyzed reaction [with Ag^+] and uncatalyzed reaction [without Ag^+] was studied.

The influence of pH on the sensitivity was studied in the range 2.5-6.5. Fig. 2 shows that the net reaction rate increases with pH up to 3.5 and decreases at higher pH values. This phenomenon is due to the fact that, in pH < 3.5 reagent of PADNS is protonated and thus the rate of reaction decreases. On the other hand at higher pH values (pH > 3.5), the ability of peroxodisulfate to oxide SPADNS increases with decreasing the catalytic role of Ag^+. Therefore, a pH of 3.5 was selected as the optimum pH value.

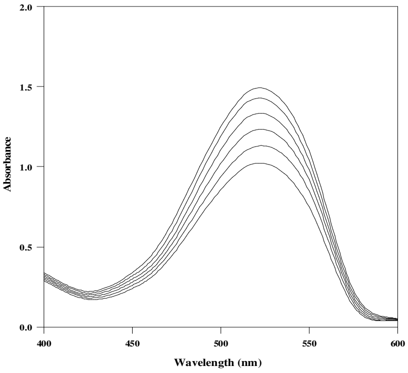

Fig. 1. Decreasing of absorbance of SPADNS reagent in the SPADNS-$S_2O_8^{2-}$-Ag(I) system with time interval 1.0 min, conditions: pH 3.5, 7.36 × 10^{-5} M SPADNS, 0.040 M $S_2O_8^{2-}$, 2.96 × 10^{-4} M 1,10-phenanthroline and 0.040 μg/mL Ag(I) at 35°C

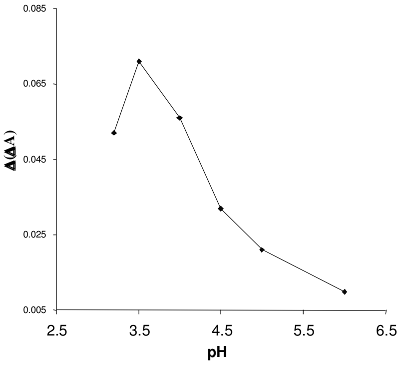

Fig. 2. Influence of pH on the rate reaction, conditions: 0.040 μg/mL Ag(I), 7.36 × 10^{-5} M SPADNS, 0.040 $S_2O_2^{2-}$ M and 1.48 × 10^{-4} M 1,10-phenanthroline at 30°C

The effect of the peroxodisulfate concentration on the rate of reaction was studied in the range of 0.010-0.050 M (Fig. 3). The results show that the net reaction rate increases with increasing peroxodisulfate concentration up to 0.040 M peroxodisulfate and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with peroxodisulfate concentration (> 0.040 M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reaction (ΔA_s-ΔA_b) diminishes at higher peroxodisulfate concentrations. Therefore, a peroxodisulfate concentration of 0.04 M was selected for further study.

Fig. 4 shows the effect of the SPADNS concentration on the sensitivity for the range of 2.9 × 10^{-5}-1.03 × 10^{-4} M. This sensitivity (net reaction rate) increases with increasing SPADNS concentration up to 7.36 × 10^{-5} M and decreases at higher concentration. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of 7.36 × 10^{-5} M of SPADNS was selected as the optimum concentration.

The effect of 1,10-phenanthroline concentration on the sensitivity was studied in the range of 8.9 × 10^{-5}-4.44 × 10^{-4} M. Fig. 5 shows that, the net reaction rate increases with increasing 1,10-phenanthroline concentration up to 2.96 × 10^{-4} M and decreases at higher concentration. This means that the rate of uncatalyzed reaction increases with 1,10-phenanthroline concentration (> 2.96 × 10^{-4} M) to a greater extent than the catalyzed reaction

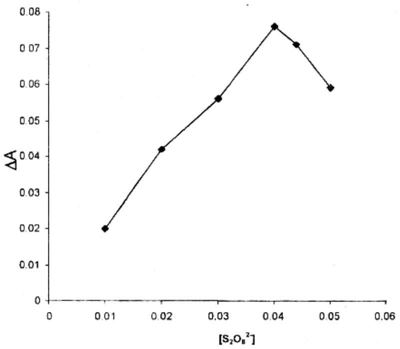

Fig. 3. Effect of peroxodisulfate concentration on the rate reaction, conditions: 0.040 µg/mL Ag(I), pH 3.5, 7.36×10^{-5} M SPADNS and 1.48×10^{-4} M 1,10-phenanthroline at 30°C

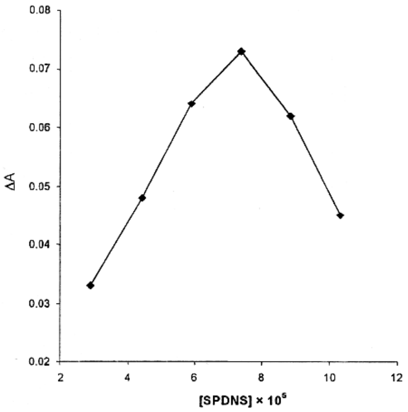

Fig. 4. Effect of SPADNS concentration on the reaction rate, conditions: 0.040 µg/mL Ag(I), pH 3.5, 0.040 M peroxodisulfate and 1.48×10^{-4} M 1,10-phenanthroline at 30°C

and the difference between the rates of catalyzed and uncatalyzed reaction ($\Delta A = \Delta A_s - \Delta A_b$) diminishes at higher 1,10-phenanthroline concentration. Therefore an 1,10-phenanthroline concentration of 2.96×10^{-4} M was used for further study.

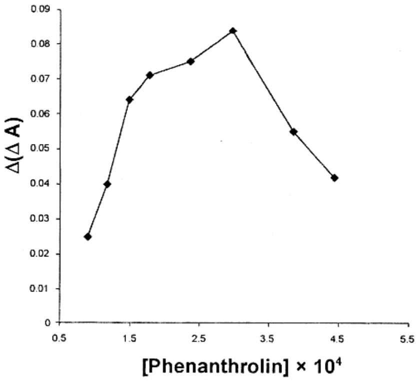

Fig. 5. Effect of 1,10-phenanthroline concentration on the reaction rate, conditions: 0.040 µg/mL Ag(I), pH 3.5, 0.040 M peroxodisulfate and 7.36×10^{-5} M SPADNS at 30°C

The effect of ionic strength on the reaction rates for both the catalyzed and uncatalyzed reactions was investigated, the salt concentration being varied from 0 to 0.008 M using 0.01 M $NaNO_3$ solution. The results indicated that, with increase in $NaNO_3$ concentration, the rates of both catalyzed and uncatalyzed reactions increase. Thus, a standard addition method was used for determination of silver in real samples.

The effect of temperature on the sensitivity was studied in the range 15-45°C with the optimum pH and other reagent concentrations. The results showed that, as the temperature increases up to 35°C, 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, 35°C was selected for further study.

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 interval of 0.5-5.5 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration ranges 0.002-0.10 μg/mL Ag(I). The equation of the calibration graph is $\Delta A = 0.0941 + 0.7788C_{Ag(I)}$ (n = 6, r = 0.9998), where ΔA is change in absorbance for the sample reaction for 0.5-5.5 min from initiation of the reaction (catalytic reaction) and C is Ag(I) concentration in μg/mL. The limit of detection from $Y_{LOD} = Y_b + 3S_b$ is 0.26 ng/mL, where, Y_{LOD} is signal for limit of detection, Y_b is average blank signal (n = 10) and S_b is standard deviation of blank signal (n = 10, uncatalyzed reaction)[12]. The relative standard deviation for ten replicate determinations of 0.040 and 0.10 μg/mL Ag(I) was 1.9 and 2.3 %, respectively.

Interference study: In order to assess the application of the proposed method to real samples, the efffect of various ions on the determination of 0.040 μg/mL Ag(I) was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 3 %. The results are summarized in Table-1. Many ions did not interfere, even when they were present in 100 fold excess over Ag(I). The interference of anions (Cl^-, Br^-, I^- and SCN^-) can be removed by addition of 1.0 mL concentrated nitric acid into 10 mL of the sample solution and heating to dryness[8]. In order to eliminate interferences of Cu^{2+}, Co^{2+} and Ni^{2+}, a two-step extraction with 5 mL chloroform was performed after addition of 1 mL saturated dimethylglyoxime into the solution[13]. Iron may be removed by preextraction as its acetylacetonate complex into chloroform[14].

Real sample analysis: In order to application of proposed method in analysis real samples, it was applied to the determination of Ag(I) in photographic solution and lake and river water. For determination of Ag(I) in photographic solution an accurate weighted quantity of this sample (2.03 g) was first treated with 25 mL of 3 M NaOH and 65 mL of concentrated nitric acid was added and the solution was heated and filtered. Then the resulting solution was evaporater nearly to dryness on a sand bath. The residue was dissolved in double distilled water and was diluted to 250 mL volumetric flask. After suitable dilution of resulting solution, it was analyzed by standard addition method and Ag(I) was determined by both AAS and the proposed method. Various water samples was also analyzed by both method (Table-2). The recoveries varied between 95 and 104 % with a relative standard deviation of the mean value of < 2.7 %, showing good reproducibility and accuracy.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 0.040 μg/mL Ag(I)

Tolerance limit ($w_{ion}/w_{Ag(I)}$)	Species
1000	Rb^+, Li^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Rh^{3+}, Os^{8+}, PO_4^{3-}, Citrate, $C_2O_4^{2-}$, SO_3^{2-}, NO_3^-, HCO_3^-
800	Se^{4+}, Se^{6+}, Te^{4+}
500	Mn^{2+}, Bi^{3+}, Al^{3+}, ClO_4^-, SO_4^{2-}, ClO_3^-
250	Zn^{2+}, Pb^{2+}
50	Ni^{2+}, Co^{2+}, Fe^{3+}
20	Hg^{2+}, Cu^{2+}
Interfere	I^- Br^-, Cl^-, SCN^-

TABLE-2
DETERMINATION OF Ag(I) IN REAL SAMPLES USING PROPOSED METHOD AND AAS

Sample	Ag(I) added (ng/mL)	Ag(I) found (ng/mL)	Recovery (%)	AAS (ng/mL)	RSD (%) (n = 5)
Photographic solution	-	431.0	-	450.0	1.8
	200	625.0	97.0	628.0	2.4
Lake water	20	19.0	95.0	19.2	2.2
	60	58.4	97.3	59.1	2.0
River water	50	51.6	103.2	51.1	2.6
	90	92.8	103.1	91.2	2.5

Conclusion

The kinetic-spectrophotometric method developed for the determination of Ag(I) is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures. With this method, it is possible to determine Ag(I) at levels as low as 0.26 ng/mL without the need for any preconcentration step.

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