# Catalytic Spectrophotometric Determination of Ultratrace Amounts of Silver with Solubilizing Effect of Nonionic Surfactant

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The synthesis and analytical properties of 4,4'-bis(antipyrinyl-4-diazoamino) biphenyl (BAPDAB) were described for the first time. A catalytic kinetic method for the determination of silver was proposed. In the presence of Triton X-100 as a solubilizing agent and 2,2'-dipyridyl as an activator, silver has a very strong catalytic effect on oxidative decoloration of BAPDAB by persulfate in acetic acid medium. The reaction was followed spectrophotometrically by measuring the decrease of absorbance of BAPDAB at 478 nm and 50 ℃. The calibration graphs are of good linearity in the range of $8.0 \times 10^{-10}$—$1.0 \times 10^{-6}$ mol/L by a fixed time method. The limit of detection is down to $5.0 \times 10^{-10}$ mol/L. The catalytic reaction is pseudo-first-order with respect to silver, which in real samples was determined with satisfactory results.

**Keywords**    catalytic spectrophotometric determination, silver, nonionic surfactant

## Introduction

Triazene reagents are interesting because of their strong complexation abilities with transition metals.[1-6] However, little decoloration of them catalyzed by silver ion has been studied in analytical chemistry. Many analysists have reported the use of catalytic reactions for the determination of silver. The silver catalytic oxidation of organic reagents by persulfate in the presence of an activator has been widely utilized in spectrophotometry[7-11] and electrochemistry.[12,13] But these methods suffer a small linear dynamic range, many interfering species and a poor limit of detection ( > 1 ng/mL). In this paper,

we report the synthesis of 4,4'-bis(antipyrinyl-4-diazoamino)biphenyl (BAPDAB) and the determination of ultratrace amounts of silver by a catalyzed oxidation of BAPDAB with persulfate using 2,2'-dipyridyl as an activator and Triton X-100 as a solubilizing agent and describe the optimized analytical conditions.

## Experimental

### Apparatus

The product was characterized with elemental analysis (Carlo-Erba 1106 element analyzer), IR (Alpha centauri FI-IR spectrophotometer). Absorption spectra were recorded on a Model UV-300 Hitachi spectrophotometer with a 1 cm quartz cell. A Model 501 super thermostatic bath (Shanghai, China) with an accuracy ± 0.01 ℃ was used to keep the reaction temperature constant at 50 ℃. A stopwatch was used for recording the reaction time. The pH measurements were carried out with a pHS-4C digital meter (Chengdu, China).

### Synthesis of 4,4'-bis(antipyrinyl-4-diazoamino)-biphenyl

4-Aminoantipyrine (8.2 g) was added to a solution containing 100 mL of water, 25 mL of concentrated aq. HCl. After the solution was cooled by ice water to the range of 0—5 ℃, 1.6 g of $NaNO_2$ in 10 mL of water was

slowly added dropwise with constant stirring. After additional 30 min of stirring, 3.7 g of benzidine in 30 mL of ethanol was added dropwise while the temperature was maintained at 5 ℃. The mixture was stirred for two hours and kept overnight, and then diluted with water. The mixture was adjusted with 15% $Na_2CO_3$ to pH = 7— 8, and the reddish black product filtered off. The product was washed with ethanol-water mixture solvent for 5 times and finally dried in vacuum over anhydrous $CaCl_2$. Yield is 79.6%. Elemental analysis of the product gave the molecular formula $C_{34}H_{32}N_{10}O_2$. Calcd.: C, 66.20; H, 5.84; N, 22.73. Found: C, 66.15; H, 5.92; N, 22.63. The infrared spectrum (KBr pellet) showed 3387.5($v_{N-H}$), 1403 ($v_{N=N}$), 1627 ($v_{C=O}$), 1315 ($v_{C-N}$) cm$^{-1}$ peaks respectively.

BAPDAB is insoluble in water, slightly soluble in ethanol and very soluble in $N,N$-dimethylformamide and dimethylsulphoxide.

*Reagents*

A 4,4'-bis(antipyrinyl-4-diazo amino)biphenyl stock solution of $1 \times 10^{-2}$ mol/L in ethanol was prepared by dissolving the proper amount of BAPDAB in analytical grade $N,N'$-dimethylformamide and diluted to the mark with ethanol in a 250 mL volumetric flask.

Stock solution of silver ($1 \times 10^{-2}$ mol/L) was prepared by dissolving a weighted amount of $AgNO_3$ (99.99%) in water in 100 mL volumetric flask. Stock solutions of potassium persulfate, 2, 2'-dipyridyl and Triton X-100 were prepared by dissolving the proper amount of their corresponding compounds, respectively, in water and diluting the resulting solution to obtain required concentration. A sodium acetate-acetic acid buffer with pH = 3.50 was used.

All other reagents were of analytical grade and distilled deionized water was used throughout.

*Recommended procedure*

The reaction was followed spectrophotometrically by monitoring the change in absorbance of the reaction mixture at 478 nm by a fixed time method for the first 0.5— 10 min from the beginning of the reaction.

An aliquot sample solution containing an appropriate amount of Ag$^+$ was transferred into a 1 cm, 4 mL quartz cell. Then 0.7 mL of buffer solution (NaOAc-

HOAc, pH = 3.5), 0.9 mL of $2 \times 10^{-2}$ mol/L 2, 2'-dipyridyl and 0.3 mL of $7.43 \times 10^{-2}$ mol/L Triton X-100 and 0.4 mL of $4.04 \times 10^{-4}$ mol/L BAPDAB were added to the cell, successively. The solution was diluted to 2.5 mL with water. The cell was inserted into the cell compartment of the spectrophotometer, where its temperature was kept constant at 50℃. After 5 min, 1.1 mL of $1.96 \times 10^{-2}$ mol/L $K_2S_2O_8$ was added into the cell and the solution was stirred to mix well. The decrease in absorbance was measured within 0.5—10 min ($\Delta A_c$). Time was recorded as soon as the last drop of the persulfate solution was added.

The measurement in the absence of silver(I) was carried out to obtain the values for the uncatalyzed reaction ($\Delta A_{unc}$). The net reaction rate was calculated from the difference of the absorbance at a fixed time ($\Delta A_c - \Delta A_{unc}$). All of the solutions were preheated to the working temperature of $50 \pm 0.01$ ℃ in a thermostat bath.

*Analysis of a real sample*

A suitable amount of pond water sample (1000 mL) was treated with concentrated nitric acid and sulfuric acid and then heated to dryness. Then aliquots of concentrated nitric acid were added and heated again. The residue was cooled to room temperature and dissolved by distilled deionized water. The solution was diluted to the desired volume. Then a suitable aliquot of the solution was analyzed by the proposed method.
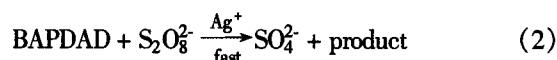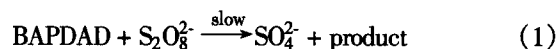
A known amount (about 1.5 g) of the developed panchromatic film was treated with 3 mol/L sodium hydroxide until the gelatinous film separated from the rigid support, which was discarded after being washed. Then the proper amount of concentrated nitric acid was added and the solution was heated until silver dissolved completely. The solution was filtered and the filtrate was diluted to the desired volume with distilled deionized water. The suitable aliquot of the solution was analyzed by the proposed method.

## Results and discussion

*Mechanism of reaction and rate equation*

BAPDAB can be very slowly oxidized by persulfate at room temperature. In the presence of ultratrace amounts of Ag$^+$ as a catalyst and 2,2'-dipyridyl as an

activator, the reaction becomes very fast. This reaction between BAPDAB and persulfate oxidation occurs according to the equation:

$$BAPDAD + S_2O_8^{2-} \xrightarrow{slow} SO_4^{2-} + product \qquad (1)$$

$$BAPDAD + S_2O_8^{2-} \xrightarrow[fast]{Ag^+} SO_4^{2-} + product \qquad (2)$$

Due to the presence of $Ag^+$, $Ag^{2+}$ ions are formed, which makes the reaction much faster. Fig. 1 shows the absorption spectra of BAPDAB-$Ag^+$-$S_2O_8^{2-}$ system at different time. As shown in this figure the change in absorbance with time at 478 nm can be used for monitoring the oxidation process.
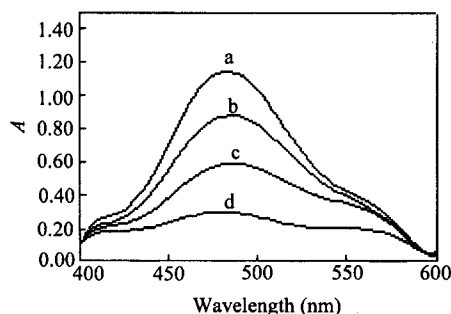


**Fig. 1** Variation of absorption of BAPDAB-$S_2O_8^{2-}$-$Ag^+$ system with wavelength at different time. Conditions: pH = 3.5; [$K_2S_2O_8$] = 0.06 mol/L; [2,2'-dipyridyl] = 0.005 mol/L; [Triton X-100] = 6.2 × 10$^{-4}$ mol/L; [BAPDAB] = 4.9 × 10$^{-5}$ mol/L; $T$ = 50 °C. (a) 0, (b) 2, (c) 5 and (d) 8.5 min from initiation of the reaction.

Under the given conditions, the catalyzed and uncatalyzed reactions occur simultaneously. The overall rate equation is:

$$\begin{aligned} r &= -d[BAPDAB]/dt \\ &= k_c[BAPDAB]^a[S_2O_8^{2-}]^b[Ag^+]^c \\ &\quad + k_{unc}[BAPDAB]^{a'}[S_2O_8^{2-}]^{b'} \end{aligned} \qquad (3)$$
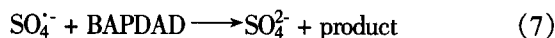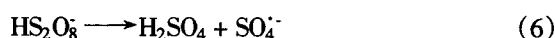
where $k_c$ and $k_{unc}$ are the rate constants for the catalyzed and uncatalyzed reactions, respectively. From Eq. (3), it can be also seen that the reaction rate of the system is determined by the concentrations of $S_2O_8^{2-}$, BAPDAB and $Ag^+$. It can be presumed that the reaction be pseudo

first-order with respect to [$Ag^+$] due to much greater concentrations of $S_2O_8^{2-}$ and BAPDAB than [$Ag^+$]. By integration of Eq. (3) and by incorporating Beer's law, the final expression can be obtained as:

$$\Delta A_c - \Delta A_{unc} = \Delta A = k'[Ag^+]t \qquad (4)$$

where $t$ is the reaction time and $k'$ is the overall rate constant. From Eq. (4), the reaction is first-order with respect to [$Ag^+$].
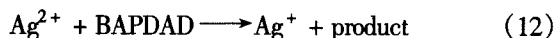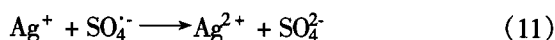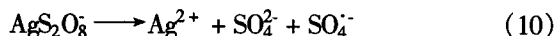
The following reactions explain the mechanism in the absence of $Ag^+$:

$$S_2O_8^{2-} + H^+ \Leftrightarrow HS_2O_8^- \qquad (5)$$

$$HS_2O_8^- \longrightarrow H_2SO_4 + SO_4^{-} \qquad (6)$$

$$SO_4^{-} + BAPDAD \longrightarrow SO_4^{2-} + product \qquad (7)$$

Earlier investigators[14-17] suggested direct oxidation of $Ag^+$ to $Ag^{2+}$ by an electron transfer mechanism:

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{2-} + SO_4^{-} \qquad (8)$$
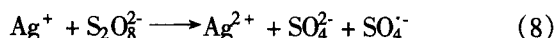
In the presence of ultratrace amounts of silver as a catalyst and 2,2'-dipyridyl as an activator, the following reactions and the given earlier reactions explain the mechanism:

$$Ag^+ + S_2O_8^{2-} \Leftrightarrow AgS_2O_8^- \qquad (9)$$

$$AgS_2O_8^- \longrightarrow Ag^{2+} + SO_4^{2-} + SO_4^{-} \qquad (10)$$

$$Ag^+ + SO_4^{-} \longrightarrow Ag^{2+} + SO_4^{2-} \qquad (11)$$

$$Ag^{2+} + BAPDAD \longrightarrow Ag^+ + product \qquad (12)$$

In the reaction process, 2,2'-dipyridyl as an activator can stabilize $Ag^+$ and decrease the electric potential of $Ag^{2+}/Ag^+$.[18]

A mechanism supposed can be that water, coordinated to $Ag^+$ in $AgS_2O_8^-$(aq.), is oxidized by the loss of an electron to $S_2O_8^{2-}$ through the orbital of $Ag^+$. Formation of a similar complex was suggested by Miller[19,20] in his studies on the $Ag^+$-$S_2O_8^{2-}$ system.

*Effect of variables on the reaction rate*

The effects of pH, reagent concentration, time of the reaction and temperature on the reaction were studied, respectively. A fixed time of 10 min from initiation of the reaction was chosen for further experiments, giving a good comparison between sensitivity and short analysis time.

The effects of pH on the catalyzed and uncatalyzed reaction are shown in Fig.2. It can be seen that the net reaction rate increases up to pH 3.5. A greater pH value than 3.5 would cause the sensitivity to decrease. In this experiment, pH value must be strictly controlled at 3.5 using buffer solution. Otherwise, the experimental error may be great and the accuracy of results may be questionable. For this reason the sodium acetate plus acetic acid buffer solution with pH = 3.5 was selected for further study.
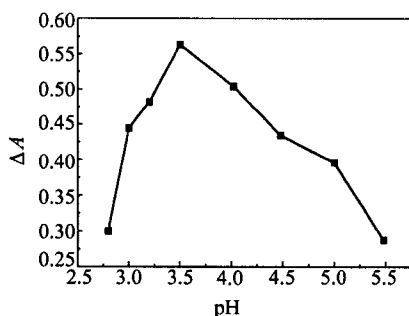


**Fig. 2**  Effect of pH on the relative reaction rate $r = \Delta A = \Delta A_c - \Delta A_{unc}$. Conditions: $[K_2S_2O_8] = 0.04$ mol/L; $[2,2'$-dipyridyl] $= 0.004$ mol/L; [Triton X-100] $= 3.87 \times 10^{-4}$ mol/L; [BAPDAB] $= 4.9 \times 10^{-5}$ mol/L; $T = 50$ ℃.

Fig. 3 shows the influence of persulfate concentration on the rate of reaction. The results indicate that the net reaction rate increased with increase of persulfate concentration up to 0.06 mol/L. Higher concentration of the reagent caused a decrease in sensitivity. This effect is due to the fact that at higher concentration of persulfate, the oxidation of BAPDAB for the uncatalyzed reaction is too fast to accurately detect the catalytic effect of $Ag^+$. Thus a persulfate concentration of 0.06 mol/L was used for further study.

The experimental results reveal that the concentration of $2,2'$-dipyridyl has a significant effect on the rate of reaction as shown in Fig. 4. In the concentration

range of 0.004—0.006 mol/L, the net reaction rate is high and stable. Higher concentration of the reagent causes a decrease in sensitivity. Therefore 0.005 mol/L $2,2'$-dipyridyl concentration was selected as the optimized one.
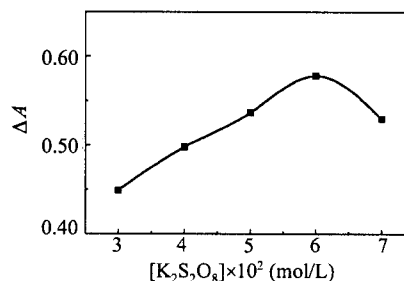


**Fig. 3**  Effect of persulfate concentration on the reaction rate. Conditions: pH = 3.5; $[2,2'$-dipyridyl] $= 0.004$ mol/L; [Triton X-100] $= 3.87 \times 10^{-4}$ mol/L; [BAPDAB] $= 4.9 \times 10^{-5}$ mol/L; $T = 50$ ℃.
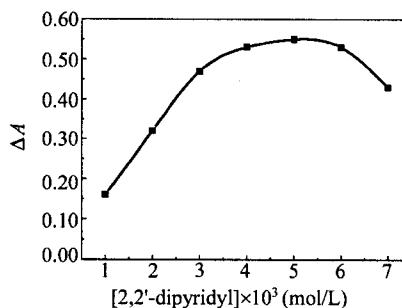


**Fig. 4**  Effect of $2,2'$-dipyridyl concentration on the reaction rate. Conditions: pH = 3.5; $[K_2S_2O_8] = 0.06$ mol/L; [Triton X-100] $= 3.87 \times 10^{-4}$ mol/L; [BAPDAB] $= 4.9 \times 10^{-5}$ mol/L; $T = 50$ ℃.

Because BAPDAB is insoluble in water, appropriate surfactant must be introduced in the system. In the present paper, many kinds of surfactants, *i. e*. Triton X-100, Tween-80 and cetyltrimethyl ammonium bromide (CTMAB) were tested. It is found that when Triton X-100 is introduced in the system, the solubility effect is pronounced.

The effect of Triton X-100 concentration on the rate of reaction was investigated too. Fig. 5 shows that when Triton X-100 concentration is less than $6.2 \times 10^{-4}$ mol/L, the net reaction rate increases with Triton X-100 concentration increasing, while the concentration of the reagent is more than $6.2 \times 10^{-4}$ mol/L, the sensitivity decreases. Thus $6.2 \times 10^{-4}$ mol/L Triton X-100 concentration was selected.

Fig. 6 shows the effect of BAPDAB concentration on the rate of reaction. According to Fig. 6, when the concentration of BAPDAB is less than $5.4 \times 10^{-5}$ mol/L, the net reaction rate increases with increasing BAPDAB concentration. Therefore, $4.9 \times 10^{-5}$ mol/L BAPDAB concentration was employed. Higher concentration of BAPDAB is not favorable to its molar absorptivity coefficient.
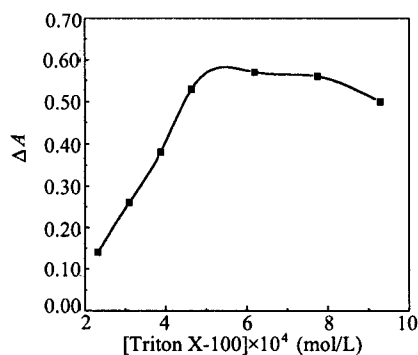


**Fig. 5**   Effect of Triton X-100 concentration on the reaction rate. Conditions: pH = 3.5; $[K_2S_2O_8] = 0.06$ mol/L; $[2,2'$-dipyridyl$] = 0.005$ mol/L; $[BAPDAB] = 4.9 \times 10^{-5}$ mol/L; $T = 50$ ℃.
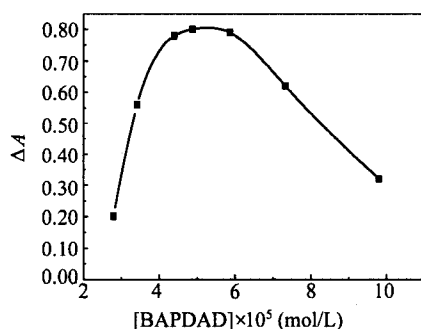


**Fig. 6**   Effect of BAPDAB concentration on the reaction rate. Conditions: pH = 3.5; $[K_2S_2O_8] = 0.06$ mol/L; $[2,2'$-dipyridyl$] = 0.005$ mol/L; $[Triton X-100] = 6.2 \times 10^{-4}$ mol/L; $T = 50$ ℃.

The influence of temperature on the reaction rate was studied in the range of 25—60 ℃ in the presence of optimized pH and reagent concentration (Fig. 7). Both reaction rates increase with temperature increasing but the effect is more remarkable for the catalyzed reaction up to 50 ℃. At temperatures higher than 50 ℃, decrease in $\Delta A$ was observed. From this finding, it is important to keep experimental temperature constant at 50 ℃. Thus 50 ℃ was chosen for this study.

*Calibration graph*

The calibration graph was obtained under the optimized working conditions and with 478 nm as the determination wavelength by the fixed-time method. Measurements were made for 10 min from initiation of the reaction. Under the optimized conditions described above, $Ag^+$ can be determined in the concentration range of $1.0 \times 10^{-6}$—$7.0 \times 10^{-8}$ mol/L; $\Delta A = 0.450 + 364597.268C$ ($R = 0.9992$, $n = 10$ and $RSD = 0.002$) and for the range of $7.0 \times 10^{-8}$—$8.0 \times 10^{-10}$ mol/L $Ag^+$, $\Delta A = 0.447 + 3500000C$ ($R = 0.9995$, $n = 15$ and $RSD = 0.013$) where $C$ is the silver concentration in mol/L and $\Delta A$ is the change in absorbance at the fixed time. The relative standard deviation for 10 replicate determinations of 8, 15, 40, 200, 600 ng/mL $Ag^+$ is 2.3%, 1.8%, 1.9%, 2.1% and 1.7% respectively. The experimental limit of detection is down to $5.0 \times 10^{-10}$ mol/L.
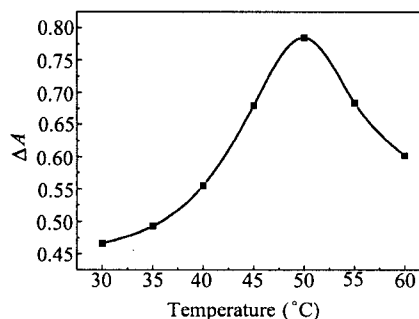


**Fig. 7**   Effect of temperature on the reaction rate. Conditions: pH = 3.5; $[K_2S_2O_8] = 0.06$ mol/L; $[2,2'$-dipyridyl$] = 0.005$ mol/L; $[BAPDAB] = 4.9 \times 10^{-5}$ mol/L; $[Triton X-100] = 6.2 \times 10^{-4}$ mol/L; $T = 50$ ℃.

*Interference study*

The influence of more than 40 species was examined on the determination of 0.1 $\mu$g/mL $Ag^+$. The results are summarized in Table 1. The tolerance limit was defined where the concentration of foreign ions caused less than 3% relative error. Most of the cations and anions had no interfering effect. The tolerance limit of $Br^-$, $I^-$, $S_2O_3^{2-}$ and $CN^-$ can be increased to 100 ng/mL by pre-treatment of concentrated nitric acid.

*Application to a real sample*

Silver was determined in pond water and developed panchromatic film (Table 2), and the results were in

agreement with those by atomic absorption spectrometry    (AAS) method.

**Table 1**    Effect of various ions on the determination of 0.100 $\mu g/mL$ of silver in the optimized conditions

| Species | Tolerance limit ($\mu g/mL$) |
|---|---|
| $NH_4^+$, $K^+$, $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, $CO_3^{2-}$, $IO_3^-$, $ClO_3^-$, $Ba^{2+}$, $Ce^{4+}$, $Mo^{6+}$, $Sr^{2+}$, $Se^{4+}$, $W^{6+}$, $Os^{8+}$, $Cd^{2+}$, $Ca^{2+}$, $Ni^{2+}$, $Zn^{2+}$ | 1000 |
| $S^{2-}$, $Cl^-$, $F^-$, $Fe^{2+}$, $Cr^{6+}$, $Mg^{2+}$, $Cr^{3+}$, $S_2O_3^{2-\,a}$ | 600 |
| $Sn^{2+}$, $Br^{-a}$, $I^{-a}$, $CN^{-a}$, $Cu^{2+}$ | 100 |

$^a$ After removal of interfereces by the proposed method.

**Table 2**    Determination of silver in real samples

| Sample | Silver found | | |
|---|---|---|---|
| | Proposed method | RSD (%, $n = 10$) | Standard method$^a$ |
| pond water | 0.0238 $\mu g/mL$ | 1.6 | 0.024 $\mu g/mL$ |
| photographic film | 0.0051% | 1.1 | 0.0052% |

$^a$ Obtained by AAS method.

## Conclusion

A kinetic-spectrophotometric method is proposed for the determination of ultratrace amounts of silver. The method is simple, highly sensitive, inexpensive and rapid.

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