

Determination of Ultratrace Silver Using Surfactant as Sensitizer by Catalytic Near Field Laser Thermal Lens Spectrometry

HAN, Quan[†](韩权) YAN, Hong-Tao*(阎宏涛) QIAN, Zhen-Jie(钱振杰)

Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

A new method for the determination of ultratrace silver(I) by near field laser thermal lens spectrometry has been developed. This method is based on the silver(I) catalyzed discoloring reaction of bromocresol green oxidized by sodium persulfate in the presence of α,α' -bipyridine as an activator and TritonX-100 as a sensitizer. The reaction mechanism was discussed. The linear range of the method is 0—1.6 ng·mL⁻¹ and the detection limit is 2×10^{-2} ng·mL⁻¹ for silver. The method has been applied to the determination of silver in lead powder and photographic paper with satisfactory results.

Keywords thermal lens spectrometry, kinetic analysis, determination of silver, α,α' -bipyridine activator, TritonX-100

Introduction

Thermal lens spectrometry (TLS) is an excellent method for trace analysis.¹⁻³ Methods classified as TLS are based upon a thermal change in the optical properties of a sample on the absorption of laser energy which leads to a temperature rise in the sample and consequently to the formation of an inhomogeneous spatial profile of the refractive index. The change in the divergence of a laser beam on the resulting optical element (thermal lens) is proportional to the amount of absorbing substance. It allows the detection of absorbance as low as 10^{-7} — 10^{-8} , concentration of *ca.* 10^{-11} mol·L⁻¹ and the analysis of 10^{-15} L³ volumes with *ca.* 10^{-2} absorbing molecules.^{1,2} TLS can be successfully used both in static and dynamic (flow injection or chromatographic) measurements.³

Kinetic analysis is one of the most important methods in modern analytical chemistry. However, there are few data on TLS applications in kinetic analysis methods so far.^{4,5} In this paper, a new method for the determination of ultratrace silver(I) by catalytic near field laser thermal lens spectrometry has been established. It is based on the oxidation of bromocresol green (BG) by sodium persulfate in the presence of α,α' -bipyridine as an activator and TritonX-100 as a sensitizer. The detection limit of the method is 2×10^{-2} ng·mL⁻¹. The method has been applied to the determination of silver in lead powder and photographic paper.

Experimental

Apparatus

A near field laser thermal lens spectrometer was

used as described previously.⁶ A He-Ne laser (TEM₀₀, $\lambda = 632.8$ nm) acted as both exciting and probing laser beam. After being modulated and focused, the laser beam was irradiated on the sample cell. The TLS signals produced in the determined solutions were detected and processed by a photoelectric device and M1052 lock-in amplifier.

A TU-1221 spectrophotometer (Beijing Puxi General Instruments Co., Ltd., P. R. China) was employed to measure the absorption spectrum. The pH of solution was measured using a PHS-3C pH meter (No. 3 Shanghai Analytical Instruments Factory, P. R. China).

Reagents

Analytical reagent grade chemicals and doubly distilled water were used in the experiment.

A standard stock solution of silver(I) (1.00 mg·mL⁻¹) was prepared by dissolving 0.0787 g of silver(I) nitrate in 50 mL of doubly distilled water. A 40 ng·mL⁻¹ working solution was prepared by appropriate dilution of the stock solution.

Bromocresol green (BG) solution (1.0×10^{-4} mol·L⁻¹) was prepared by dissolving 0.0175 g of BG in 250 mL of doubly distilled water.

Sodium persulfate solution (0.5 mol·L⁻¹), α,α' -bipyridine solution (1.0×10^{-2} mol·L⁻¹) and TritonX-100 solution (0.5%) were obtained by dissolving appropriate weights of the reagents in 250 mL of doubly distilled water, respectively.

Buffer solution (pH=6.0) was prepared by adding 0.1 mol·L⁻¹ sodium citrate solution to 0.2 mol·L⁻¹ potassium dihydrogen phosphate solution until a pH of 6.0 was obtained.

* E-mail: htyan@nwu.edu.cn; [†] work in Xi'an Arts and Science College now.

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Oxammonium hydrochloride solution ($0.5 \text{ mol}\cdot\text{L}^{-1}$) was prepared by dissolving 0.18 g of oxammonium hydrochloride in 50 mL of doubly distilled water.

Procedure

To a 25-mL volumetric flask, the sample or standard solution containing up to 40 ng of silver, 2.0 mL of $1.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ α,α' -bipyridine solution, 1.5 mL of $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ bromocresol green (BG) solution, 2.0 mL of pH 6.0 buffer solution, 1.0 mL of 0.5% tritonX-100 solution and 3.0 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ sodium persulfate solution were added respectively. The resulting solution was diluted to the mark with doubly distilled water. The flask was placed in a water bath ($35 \pm 0.2 \text{ }^\circ\text{C}$) immediately for reaction and after 7 min the reaction was stopped by adding 0.5 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ oxammonium hydrochloride solution. Then the thermal lens signal of the catalysed reaction (S_c) was measured. Meanwhile, the thermal lens signal of uncatalysed reaction (S_0) was obtained in the same procedure but containing no silver. The difference value (ΔS) between S_0 and S_c was calculated ($\Delta S = S_0 - S_c$).

Results and discussion

Absorption spectra

The absorption spectra of the catalysed reaction and the uncatalysed reaction are shown in Figure 1. Both the catalysed reaction (curves 2 and 4) and the uncatalysed reaction (curves 1 and 3) exhibited a maximum absorbance at 617 nm, which is near the output wavelength 632.8 nm of He-Ne laser. However, the strength of absorption peak is different. It shows that ultratrace silver(I) has strongly catalytic effect on the oxidation of bromocresol green to form a colorless compound by sodium persulfate and the rate of oxidation obviously increases in the presence of TritonX-100.

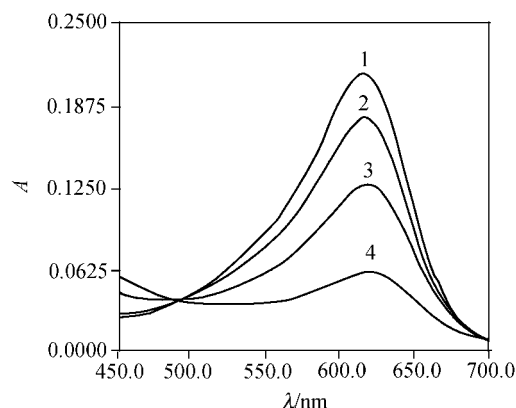


Figure 1 Absorption spectra. 1. BG + α,α' -bipyridine + $\text{S}_2\text{O}_8^{2-}$; 2. BG + α,α' -bipyridine + $\text{S}_2\text{O}_8^{2-}$ + Ag(I); 3. BG + α,α' -bipyridine + $\text{S}_2\text{O}_8^{2-}$ + TritonX-100; 4. BG + α,α' -bipyridine + $\text{S}_2\text{O}_8^{2-}$ + Ag(I) + TritonX-100

Influence of acidity

The influence of pH on the sensitivity was investi-

gated in the experiment. It was found that the maximum value of ΔS was obtained in pH=5.5—6.5 with sodium citrate-potassium dihydrogen phosphate buffer solution. Therefore, the reaction was carried out at pH=6.0.

Optimum concentration of reagent

The effect of the concentration of BG and sodium persulfate was tested in the experiment. BG is the indicator of the catalysed reaction monitored. The lower the concentration the weaker the S_c . However, the higher concentration produced larger blank signal. It was found that the optimum concentration of BG for the determination of silver(I) was $6.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$. Therefore, 1.5 mL of $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ BG solution was used. The experimental results also show that ΔS is maximal in the concentration range of 5.0×10^{-2} — $8.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ sodium persulfate. Therefore, $6.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ sodium persulfate was chosen in the experiment.

Activation of α,α' -bipyridine

The effect of some *n*-donor substances previously employed for activation of Ag(I)-catalysed oxidation reactions was examined, and their efficiency was found to decrease in the order of α,α' -bipyridine > 1,10-phenanthroline > ethylenediamine. Thus, α,α' -bipyridine was chosen as an activator, and it was found that the optimum concentration of α,α' -bipyridine was in the range of 6.8×10^{-4} — $1.4 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. Therefore, $8.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ α,α' -bipyridine was chosen.

Selection of surfactants

The effect of surfactants, such as cetyltrimethylammonium bromide (CTMAB), sodium dodecyl sulfate (SDS), TritonX-100, Tween80 and OP, was examined in the experiment. The result shows that non-ionic surfactants have sensitization effect in varying degrees, and TritonX-100 is more efficient than any others. Therefore, TritonX-100 was adopted. It was found that ΔS increased with the increasing concentration of TritonX-100 and reached the maximum when the concentration of TritonX-100 was $3.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. This concentration approached the CMC value ($3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) of TritonX-100, which shows that the effect of sensitization is the best when TritonX-100 forms micelles in the solution.

Effect of temperature

The influence of temperature was investigated in the range of 20—40 $^\circ\text{C}$. It was found that the catalysed reaction occurred very slowly at room temperature. ΔS increased with increasing temperature in the range of 25—35 $^\circ\text{C}$, and decreased when temperature was higher than 35 $^\circ\text{C}$ because of the acceleration of the uncatalysed reaction. Therefore, 35 $^\circ\text{C}$ was chosen in the experiment.

Oxammonium hydrochloride can stop the reactions efficiently. It was found that ΔS did not change within 1 h after adding 0.5 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ oxammonium hydrochloride solution to stop the reactions.

Reaction order and rate equation

For a given amount of catalyst silver(I), it was found that ΔS value depended linearly on the reaction time within 7 min, which indicates that the reaction rate is constant, and the catalytic reaction was of pseudo-zero-order in $S_2O_8^{2-}$ and BG. Therefore, the equation of reaction rate was as follows:

$$-dc_{BG}/dt = k_a c_{Ag^+} + k \quad (1)$$

where c_{BG} is the concentration of bromocresol green at time t , c_{Ag^+} and k_a represent the concentration of catalyst silver(I) and the reaction rate constant respectively, and k is a constant.

The thermal lens signal strength is given by:⁷

$$S_c = 2.303EA \quad (2)$$

where E and A represent a sensitivity enhancement coefficient relative to the thermal-physics characteristic of solvent and absorbance of sample ($A = \epsilon bc_{BG}$) respectively. Differentiate Eq. (2) to t :

$$-dc_{BG}/dt = (2.303\epsilon bE)^{-1} \cdot (-dS_c/dt) \quad (3)$$

Substitution of Eq. (3) into Eq. (1) gives

$$-dS_c/dt = 2.303\epsilon bE(k_a c_{Ag^+} + k) \quad (4)$$

Integral Eq. (4) from 0— t gives

$$\Delta S_{c, \text{begin}} - S_c = k'_a c_{Ag^+} t + k't \quad (5)$$

$S_{c, \text{begin}} - S_c$ in Eq. (5) is the total result of the catalytic reaction system. The change of thermal lens signal ΔS only caused by catalytic reaction is

$$\Delta S = (S_{c, \text{begin}} - S_c) - (S_{c, \text{begin}} - S_{c_0}) = k'_a c_{Ag^+} t \quad (6)$$

When the fixed time method is applied,

$$\Delta S = Kc_{Ag^+} \quad (7)$$

Eq. (7) is the quantitative relationship for the determination of silver by TLS.

Calibration graph and detection limit

Under the above experimental procedure, a good linearity was obtained over the concentration range 0—1.6 $\text{ng} \cdot \text{mL}^{-1}$ of silver and the regression equation was $\Delta S = 0.4708 c_{Ag^+} (\text{ng} \cdot \text{mL}^{-1}) + 0.0665$ with a correlation coefficient, $\gamma = 0.9982$. The limit of detection calculated three times from the standard deviation of blank was $2 \times 10^{-2} \text{ng} \cdot \text{mL}^{-1}$.

In TLS, the sensitivity can be improved considerably

by using organic or aqueous organic media because the thermal lens signal depends on the thermal-physics properties of the medium.^{1,8} It was shown that after adding oxammonium hydrochloride solution to stop the reactions, mixing the solutions of catalysed reaction and uncatalysed reaction with ethanol (1+1) respectively, and then measuring their thermal lens signals and calculating ΔS ($\Delta S = S_c - S_0$) provided a 5-fold increase in the slope of the calibration graphs.

Interference of foreign species

A number of cations and anions were examined in the experiment. The tolerance limit was taken as the amount that causes an error less than $\pm 5\%$ in the determination of silver. For the determination of 24 ng of silver in 25 mL of sample by the method, it was found that 10^4 -fold amounts of NH_4^+ , NO_3^- or Pb^{2+} , 2.5×10^3 -fold amounts of $\text{C}_2\text{O}_4^{2-}$, 10^3 -fold amounts of Na^+ or EDTA, 5×10^2 -fold amounts of K^+ , Ba^{2+} , F^- , Cl^- or SO_4^{2-} , 10^2 -fold amounts of Sr^{2+} , Ni^{2+} , Co^{2+} , Bi^{3+} or tartrate, 50-fold amounts of Al^{3+} , Mn^{2+} , Cu^{2+} or Hg^{2+} , 10-fold amounts of Fe^{3+} did not interfere the measurement. In the presence of 0.1 mL of $1.4 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ EDTA, 200-fold amounts of Fe^{3+} did not interfere the determination.

Determination of silver in lead powder

Weigh accurately 0.2000 g of lead powder and dissolve it in 3 mL of nitric acid and 20 mg of tartaric acid⁹ by heating on an electric hot plate. Dilute the solution with doubly distilled water to 250 mL in a calibrated flask. Take suitable aliquots of the sample solution, add 0.1 mL of $1.4 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ EDTA solution, and continue the determination according to the procedure. The results for the determination of silver in lead powder are shown in Table 1.

Determination of silver in photographic paper

A piece of photographic paper ($1 \times 1 \text{cm}^2$) was put in a conical flask. Add 5 mL of $0.2 \text{mol} \cdot \text{L}^{-1}$ nitric acid and heat on a boiling water bath for 20 min. Dilute the solution with doubly distilled water to 100 mL. Take suitable aliquots of the sample solution, add 0.1 mL of $1.4 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ EDTA solution, and continue the determination according to the procedure. Table 2 shows the result for the determination of silver in photographic paper.

Mechanism of catalytic reaction

Under the experimental condition, Ag(I) can be oxidized by $S_2O_8^{2-}$ to form Ag(II), and Ag(II) can oxidize bromocresol green (BG) to form discoloring products. The process of the catalytic reaction may be represented as follows:

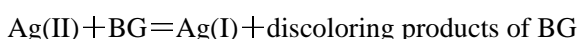
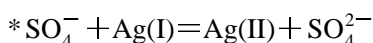
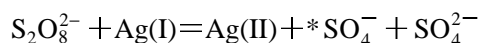


Table 1 Determination results of silver in lead powder

Sample ^a	Standard value/(g•T ⁻¹)	Found (n=6)/(g•T ⁻¹)	RSD (n=6)/%	Relative error/%
Lead powder 01Z-111	998	980	3.4	1.8

^a Provided by Analysis and Inspection Center, Northwest Nonferrous Geological Research Institute, Xi'an, China

Table 2 Determination results of silver in photographic paper

Sample	Present method (n=6)/(μg Ag•cm ⁻²)	RSD (n=6)/%	AAS ^a method (n=6)/(μg Ag•cm ⁻²)
Photographic paper sample No. 3	11.0	3.2	10.8

^a Atomic absorption spectrometry.

The over-all reaction rate is dependent on the rate of the step $\text{Ag}^{\text{I}} \rightarrow \text{Ag}^{\text{II}}$, and an acceleration of this step causes an increase in the over-all reaction rate. α, α' -Bipyridine is an organic ligand that can enhance the stability of $\text{Ag}(\text{II})$ and accelerate the formation of Ag^{II} , and for the system, α, α' -bipyridine was found to be a good activator for this reaction.

Mechanism of Sensitization of TritonX-100

When BG was mixed with TritonX-100, the color of the solution changed from deep blue to blue-green and the absorption peak shifted toward longer wavelength with increasing TritonX-100 concentration under the experimental condition. It indicates that the $\text{p}K_{\text{a}_1}$ value of BG increases in the presence of TritonX-100. Because there is interaction of the hydrogen bond between the hydroxyl ($-\text{OH}$) in BG and ether oxygen bond ($-\text{O}-$) in Triton-100, the dissociation of H^+ of the hydroxyl ($-\text{OH}$) is more difficult in BG. Furthermore, there is also a hydrophobic interaction between BG molecules and the alkyl group in TritonX-100 due to that BG is sparingly soluble in water. The two kinds of interaction lead to BG to be gathered in micelle and the redistribution of the electronic cloud of BG molecule. The molecule of BG gathering in micelle is easier to be oxidized by catalytic active substance $\text{Ag}(\text{II})$. It

was also found that the potential of $\text{Ag}(\text{II})$ changes lower in the presence of TritonX-100 in the experiment. As a result, $\text{Ag}(\text{I})$ is easier to be oxidized by $\text{S}_2\text{O}_8^{2-}$ to form $\text{Ag}(\text{II})$. Therefore, the catalytic reaction rate is accelerated.

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