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Determination of Utratrace Silver Using Surfactant As Sensitizer by Catalytic Near Field Laser Thermal Lens Spectrometry

Quan HAN, Hong Tao YAN*, Zhen Jie QIAN

Department of Chemistry, Northwest University, Xi'an 710069

Abstract: A new method for the determination of utratrace silver(I) by near field thermal lens spectrometry has been developed. This method is based on the silver(I) catalyzed discoloring reaction of bromocresol green oxidized by sodium persulphate in the presence of α, α′-bipy as activator and Triton X-100 as sensitizer. The linear range of this method is 0～1.6 ng·mL^{-1} of silver. The detection limit is 2×10^{-2} ng·mL^{-1}. The method has been applied to the determination of silver in lead power and photographic paper with satisfactory results.

Keywords: Thermal lens spectrometry, kinetic method of analysis, silver determination, α,α′-bipy activator, Triton X-100 sensitizer.

Thermal lens spectrometry (TLS) is an excellent tool for trace analysis[1]. TLS allows the detection of absorbances of $10^{-7}\sim10^{-8}$, concentration of ≈ 10^{-11} mol·L^{-1} and the analysis of 10^{-15} L volumes with ≈10^{-2} absorbing molecules[2]. Kinetic analysis is playing an increasingly important part in modern analytical chemistry. Therefore, TLS shows much promise in combination with kinetic analysis. However, there are few data on TLS applications in kinetic analysis method so far[3~4]. A new method for the determination of trace silver(I) by near field laser thermal lens spectrometry has been established in this paper. It is based on the oxidation of bromocresol green (BG) by sodium persulfate in the presence of α, α′-bipy as an activator and Triton X-100 as sensitizer. The detection limit is 2×10^{-2} ng·mL^{-1}.

Experimental

Near field laser thermal lens spectrometer was used as described previously[5].

To a 25-mL standard flask, add the sample or standard solution containing up to 40 ng of silver, 2.0 ml of 1.0×10^{-2} mol·L^{-1} α, α′-bipy solution, 1.5 mL of 1.0×10^{-4} mol·L^{-1} bromocresol green (BG) solution, 2.0 ml of pH6.0 buffer solution, 1.0 mL of 0.5% Triton X-100 solution and 3.0 mL of 0.5 mol·L^{-1} sodium persulfate solution respectively, and dilute to the mark with doubly distilled water. Heat for 7 min in a water bath at 35± 0.2°C. Then, add 0.5 mL of 0.5 mol·L^{-1} oxammonium hydrochloride solution immediately to stop the reaction. Prepare the blank (uncatalysed reaction) in the same

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*E-mail: htyan@nwu.edu.cn

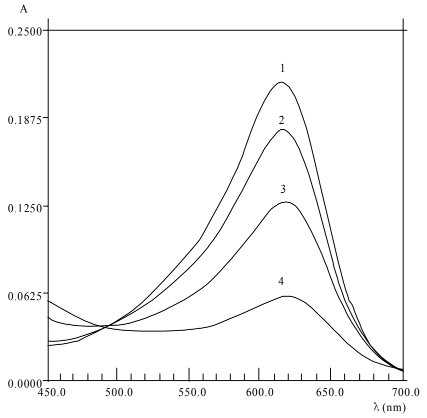
procedure but containing no silver. Measure the thermal lens signal of the catalysed reaction (S_c) and uncatalysed reaction (S_0) on a near field laser thermal lens spectrometer. Calculate the value of ΔS ($\Delta S = S_0 - S_c$).

Results and Discussion

Optimization of experimental conditions

The absorption spectra of the catalysed reaction and the uncatalysed reaction are shown in **Figure 1.** Both the catalysed reaction (curve 2,4) and the uncatalysed reaction (curve 1,3) exhibited an absorbance maximum at 617 nm, which is near the output wavelength 632.8 nm of He-Ne laser. Trace silver(I) has catalytic effect on the oxidation of bromocresol green by sodium persulfate, and the catalytic effect obviously increases in the presence of Triton X-100.

Figure 1 Absorption spectra



1. GB+α, α′-bipy+ $S_2O_8^{2-}$;
2. GB+ α, α′-bipy+ $S_2O_8^{2-}$ +Ag(I);
3. GB+α, α′-bipy+ $S_2O_8^{2-}$ + Triton X-100;
4. GB+ α, α′-bipy+ $S_2O_8^{2-}$ +Ag(I)+Triton X-100

Maximum value of ΔS was obtained for pH 5.5～6.5 with sodium citrate-potassium dihydrogen phosphate buffer solution. Subsequent determinations were therefore carried out at pH 6.0.

It was found that the optimum concentration of BG for thermal lens measurements was 6.0×10^{-6} mol·L^{-1}. Therefore, 1.5 L of 1.0×10^{-4} mol·L^{-1} BG solution was used.

The effect of sodium persulfate concentration was investigated. It was shown that ΔS is maximal in the concentration range of 5.0×10^{-2}～8.0×10^{-2} mol·L^{-1} sodium persulfate. In the experiment, 6.0×10^{-2} mol·L^{-1} of sodium persulfate was chosen.

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′-bipy > 1,10-phenanthroline > ethylenediamine. Thus, α, α′-bipy was chosen, and it was found that the optimum concentration of α, α′-bipy was in the range of 6.8×10^{-4}～1.4×10^{-3} $mol\cdot L^{-1}$. In the experiment, 8.0×10^{-4} $mol\cdot L^{-1}$ of α, α′-bipy was chosen.

The effect of surfactants including cationic, such as cetyltrimethylammonium bromide (CTMAB), anionic, sodium dodecyl sulfate (SDS), and non-ioninc, such as Triton X-100, Tween 80 and OP, was examined. The result shows that non-ionic surfactant has sensitization effect in varying degrees, and Triton X-100 was found to be more efficient. Thus Triton X-100 was chosen, and it was found that ΔS increased with increasing concentration of Triton X-100 and reached maximum when the concentration of Trion X-100 was 3.3×10^{-4} $mol\cdot L^{-1}$. This concentration approached the CMC value (3.0×10^{-4} $mol\cdot L^{-1}$) of Triton X-100, which showed that the effect of sensitization was the best when Triton X-100 formed micelles in the solution.

The catalysed reaction occured very slowly at room temperature. ΔS increases with temperature increasing in the range of 25～35°C, and decreases when temperature is higher than 35°C because of the accelerating of the uncatalysed reaction. Therefore, 35°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 $mol\cdot L^{-1}$ oxammonium hydrochloride solution to stop the reactions.

A good linearity is obtained over the concentration range of 0～1.6 $ng\cdot mL^{-1}$ of silver and the regression equation is $\Delta S=0.4708\ C_{Ag+}(ng\cdot mL^{-1})+0.0665$ with a correlation coefficient, $\gamma=0.9982$. The limit of detection (taken as three times the standard deviation of blank) is about 2×10^{-2} $ng\cdot mL^{-1}$.

A number of cations and anions were examined in the experiment. The tolerance limit was taken as the amount that causes an error of ±5% in the thermal lens signal. For the determination of 24 ng of silver in 25 mL sample by this method, it was found that 10^4-fold amounts of NH_4^+ and NO_3^-, Pb^{2+}, 2.5×10^3-fold amounts of $C_2O_4^{2-}$, 10^3-fold amounts of Na^+ and EDTA, 5×10^2-fold amounts of K^+, Ba^{2+}, F^-, Cl^- and SO_4^{2-}, 10^2-fold amounts of Sr^{2+}, Ni^{2+}, Co^{2+}, Bi^{3+} and tartrate, 50-fold amounts of Al^{3+}, Mn^{2+}, Cu^{2+} and Hg^{2+}, 10-fold amounts of Fe^{3+} do not interfere with the determination. In the presence of 0.1 mL 1.4×10^{-4} $mol\cdot L^{-1}$ EDTA, 200-fold amounts of Fe^{3+} do not interfere the determination.

Application

Weigh accurately 0.2000 g of lead powder and dissolve it in 3 mL of nitric acid and 20 mg tartaric acid 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 1.4×10^{-4} $mol\cdot L^{-1}$ EDTA solution, and continue the determination according to the procedure. **Table 1** shows the results for the determination of silver in lead powder.

Table 1 Determination results of silver in lead power

Sample*	Standard value ($g{\cdot}T^{-1}$)	Found ($g{\cdot}T^{-1}$)	RSD (%)	Relative error (%)
Lead powder 01Z-111	998	980	3.4	1.8

*Provided by Analysis and Inspection Center, Northwest Nonferrous Geological Research Institute.

Put a piece of photographic paper (1×1 cm^2) in a conical flask. Add 5 mL of 0.2 $mol{\cdot}L^{-1}$ 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 1.4×10^{-4} $mol{\cdot}L^{-1}$ EDTA solution, and continue the determination according to the procedure. **Table 2** shows the result for the determination of silver in photographic paper.

Table 2 Determination results of silver in photographic paper

Sample	Present method ($\mu gAg{\cdot}cm^{-2}$)	RSD(n=6) (%)	ASS method ($\mu gAg{\cdot}cm^{-2}$)
Photographic paper sample No.3	11.0	3.2	10.8

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