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Resonance Light Scattering Spectra of Silver Thiocyanate System and its Application in Analysis

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Abstract: A novel determination method of Ag^+ was established. In acetic acid-sodium acetate buffer (pH 5.0) medium, Ag^+ reacts with SCN^- to form AgSCN in the presence of TritonX-100, which results in an increase of resonance light scattering (RLS) and giving a new RLS spectrum. The maximum RLS peak was at 585 nm. The enhancement of resonance light scattering at 585 nm was proportional to the concentration of Ag^+ ranging from 0.0045-4.00 μg mL^{-1} (r=0.9991), and the detection limit was 1.37 ng mL^{-1} with the recovery of 97.70%~104.80%.

Keywords: Resonance light scattering, silver, silver thiocyanate.

Silver is an important noble metal, widely applied in chemical engineering, metallurgy and medicine. The determination of trace silver in environmental water samples has been one of routine items in the detection of water quality, so it is important to establish a sensitive and convenient analysis method.

Spectrophotography[1], atomic absorption spectrometry[2], chemiluminescence[3] and fluorospectrophotometry are the general determination methods of silver. Since the new resonance scattering spectroscopic method was used for biomacromolecular research by Pasternack[4] in 1993, many domestic and overseas investigations[5-7] had indicated that the technique had a good foreground. In this paper, the resonance light scattering spectrum of AgSCN system was studied. The enhancement of RLS of AgSCN system was proportional to the concentration of Ag^+ in suitable concentration range, and this method had been successfully applied to the determination of Ag^+ in water sample of enviromnment.

Experimental

970-CRT spectrofluorometer (Sanke Co. Ltd, Shanghai) was used for recording the RLS spectra and measuring the intensity at the given wavelength. PB-20 (Sartorius Co. Ltd) acidimeter was employed for pH adjustment. JYZ-200 automatic tensionmeter was used for determining the surface tension of TritonX-100 solution.

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The concentrations of potassium thiocyanate (KSCN) and TritonX-100 were 0.01 $molL^{-1}$ and 1.0% respectively. The Ag (I) standard solution (1.00 $mgmL^{-1}$) was prepared by dissolving 0.1575 g silver nitrate in 100 mL doubly distilled water and pre-served in the refrigerator at 4℃, which was diluted to 100 μg mL^{-1} working solution before use. pH 5.0 acetic acid-sodium acetate buffer was used to adjust the acidity of tested solution. All other reagents used were of analytical grade and doubly distilled water was used throughout the experiment.

To a 10 mL color comparison tube, Ag (I) working solution, 0.45 mL TritonX-100 solution, 2.0 mL buffer solution and 0.20 mL KSCN solution was added successively. Then the mixture was diluted to the scale with doubly distilled water and kept static for 15 min. Finally, the RLS spectra were recorded by synchronous scanning at $\lambda_{ex}=\lambda_{em}$ =200~800 nm and the scattering intensity was meaured at the given wavelength (585 nm) against the reagent blank.

Results and Discussion

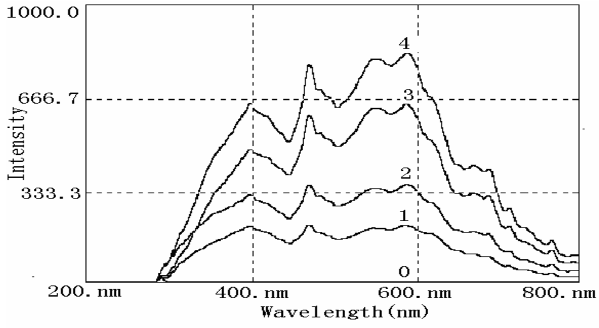
Spectral characteristics

As indicated in **Figure 1**, KSCN solution itself has a very weak scattering at 470 nm. As Ag^+ was added to KSCN solution, the RLS of system increased gradually and a new peak appeared at 585 nm. The change of RLS spectra suggested that Ag^+ reacted with SCN^- to form AgSCN in the presence of TritonX-100.

The optimal conditions for the determination

The effect of solution acidity showed that the scattering intensity was maximum and constant, when the acidity was in the pH range 3.0-8.0. Therefore, 2.00 mL pH 5.0 acetic acid-sodium acetate buffer solution was selected for studies.

Figure 1 The RLS spectra



Concentration of Ag^+ (from 0 to 4): 0.0, 1.0, 2.0, 3.0, 4.0 μg mL^{-1}, KSCN (1.0×10^{-3} mol L^{-1}), pH 5.0

The scattering intensity was also affected greatly by the volume of KSCN solution. When the volume of KSCN solution was 0.10-0.40 mL, ΔI_{RLS} reached maximum and remained constant, if it was less than 0.10 mL or more than 0.4 mL led to the decrease of ΔI_{RLS}, because of incomplete reaction or the formation of soluble complex $[Ag(SCN)_2]^-$. Accordingly, the experiment was carried out with 0.2 mL KSCN solution in the final volume of 10 mL.

In order to enhance the sensibility and stability of tested system, TritonX-100, Tween-80, PVA-124 and SDBS were selected for investigating the effect of medium on ΔI_{RLS}. The results showed that the stability of system was increased in all surfactant medium, but their sensibility are as follows: TritonX-100 > SDBS > Tween-80 >PVA-124. At the same time, the critical micelle concentration (*cmc*) of TritonX-100 was measured by determining its surface tension and $cmc=2.0 \times 10^{-4}$ mol L^{-1} (0.12 mL 1.0% TritonX-100). The sensibility and stability enhanced only when the volume of TritonX-100 was more than 0.12 mL, because the molecule began to form micelles. When the volume of TritonX-100 was 0.40-0.50 mL, the amount of scattering particles was nearly equal to the amount of micelles, that is to say, all scattering particles had come into the active center of the micelles and ΔI_{RLS} reached maximum. Therefore, 0.45 mL TritonX-100 solution was the optimum volume.

The complex reaction was completed after 15 min under the optimum conditions and the RLS intensity kept stable at least for 1.5 h at room temperature.

Calibration curve, detection limit and precision

The calibration curve for the determination of Ag(I) was constructed under the optimum experimental conditions. Excellent linearity was obtained in the range of 0.0045-4.00 μg mL^{-1}. The linear regression calibration equation was $\Delta I_{\mathrm{RLS}}=-2.51 +214.06C$ (μg mL^{-1}) (r=0.9991) and the detection limit was 1.37 ng mL^{-1}. The precision and recovery are shown in **Table 1**.

Effect of foreign ions

The effect of number of cation and anions was examined in the experiment. The tolerance limitation was taken as the amount that causes an error of ±5% in RLS signal. When 2.0 μg mL^{-1} Ag^+ sample was determined by this method, it was found that 10^3-fold amounts of Ca^{2+}, Cu^{2+}, NH_4^+, HCO_3^-, SO_4^{2-}, HPO_4^{2-}, 8×10^2-fold amounts of Al^{3+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, 5×10^2-fold amounts of Mg^{2+} and Mn^{2+}, 2×10^2-fold amounts of Co^{2+} and NO_2^-, 50-fold amounts of Pb^{2+}, 20-fold amounts of Fe^{3+} and Fe^{2+}, 2-fold amounts of Br^- and I^-, 1-fold amounts of Cl^- did not interfere with the determination.

Sample Analysis

The proposed method was used to the determination of Ag (I) in synthetic samples and environmental water samples, and the results are shown in **Table 1** and **Table 2**.

Table 1 Results for the determination of Ag^+ in synthetic water samples

No.	Concentration of Ag^+ (μg mL^{-1})	Coexisting substances (μg)	Found (μg mL^{-1})	RSD(n=6) (%)	Relative error (%)
1	0.500	Mg^{2+}100, Al^{3+}200, Zn^{2+}200, Cd^{2+}200, NH_4^+500, SO_4^{2-}500	0.483	1.68	-3.40
2	1.000	Mg^{2+}100, Al^{3+}200, Zn^{2+}200, Cu^{2+}200, NH_4^+500, SO_4^{2-}500	1.006	1.27	0.60
3	2.000	Al^{3+}500, Zn^{2+}500, Ni^{2+}500, Mn^{2+}500, NH_4^+500, SO_4^{2-}500, HCO_3^-500	1.951	2.39	-2.43

Table 2 Results of the determination of Ag^+ in environmental water samples (n=5)

Water samples	Original (μg mL^{-1})	Added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Industrial waste water	0.322	0.500	0.524	104.80
Developing agent	1.438	2.000	1.954	97.70

References

1. P. Nagaraja, M. S. Hemantha Kumar, H. S. Yathirajan. *Anal. Sci.*, **2002**, *18*(7), 815.
2. C. T. Camagong, T. Honjo. *Anal. Bioanal. Chem.*, **2002**, *373*(8), 856.
3. X. Y. Zhang, H. L. Liu, S. Q. Li. *Chin. J. Anal. Chem.*, **2001**, *29*(1), 116.
4. R. F. Pasternack, C. Bustamante, P. J. Collings, *et al.*, *J. Am. Chem. Soc.*, **1993**, *115*, 5393.
5. C. Z. Huang, Y. F. Li, X. D. Liu. *Anal. Chim. Acta*, **1998**, *375*, 89.
6. L. P. Wang, Z. L. Jiang. *Analysis and Testing Technology and Instruments*, **2000**, *6*(1), 21.
7. X. L. Xiao, Y. S. Wang, G. R. Li, C. Y. Lü. *Spectroscopy and Spectral Analysis*, **2004**, *24*(2), 190.

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