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Alizarin violet modified carbon paste electrode for the determination of trace silver(I) by adsorptive voltammetry

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Abstract

A sensitive and selective procedure for the determination of trace silver(I) at alizarin violet modified carbon paste electrode has been developed. Silver(I) was accumulated on the electrode surface via complex formation with modifier in 0.1 mol/L acetate buffer (pH 5.2). After electrochemical reduction of silver(I) had been carried out, the reoxidation wave of silver(0) appeared at 0.05 V (versus SCE) on scanning the potential in the positive direction in 0.1 mol/L $H_2SO_4 + 2.0 \times 10^{-4}$ mol/L KBr. For a preconcentration time of 3 min, the detection limit is 1.0×10^{-10} mol/L and the linear range is from 3.0×10^{-10} to 1.2×10^{-7} mol/L. Many coexisting metal ions have little or no effect on the determination of silver(I). The proposed method was applied to the determination of silver in waste water and zinc alloy samples with satisfactory results.

Keywords: Adsorptive voltammetry; Modified carbon paste electrode; Silver; Alizarin violet

1. Introduction

The development and application of chemically modified carbon paste electrodes (CMCPEs) have received considerable attention in recent years due to their many advantages, such as easy manufacture, non-poison, *low* price, wider operational potential window, renewable surface, stability in various solvents and longer *life time* [1,2]. The incorporation of specially chosen modifiers in the electrodes for collection of the analytes prior to voltammetric analysis gives rise to high selectivity and sensitivity. Coupled with a medium exchange step, additional discrimination against background interferents can be achieved.

The content of silver in various real samples is generally very low, so analytical methods with great sensitivity are required for its reliable measurement. Because of the extremely positive reduction potential of silver(I), it cannot be determined directly by polarography [3]. A limited number of studies on the use of CMCPEs for voltammetric determination of silver(I) have been reported. The modifiers used include 2,2′-dithiopyridine [4], 2-mercaptoimidazole [5], 1,4,8,11-tetrathiacyclotetraadodecane [6], imine-thioether polymer [7], keratin [8], zeolites [9], *N*-benzoyl-*N*′,*N*′-diisobutylthiourea [10], 2,3-dicyano1,4-naphthoquinone [11] and thiosulfate-donor podand [12]. However, most of these procedures give higher detection limits (10^{-7} to 10^{-8} mol/L) [4,6,8–12] and have difficulties achieving the sensitivity required for the determination of low levels of silver in some real samples. The method employing a CPE modified with Imine-thioether polymer (a chelating resin) has appeared to be the most sensitive and the detection limit is 3×10^{-10} mol/L for a preconcentration time of 5 min [7]. But the synthesis of the chelating resin is time-consuming.

Alizarin violet (AV) is an important chromogenic reagent in spectrophotometric analysis. We have recently reported the adsorptive voltammetry of tin(IV) at a alizarin violet modified carbon paste electrode (AV-CPE) [13]. Based on the aforementioned experiences, we concluded that AV can accumulated Ag(I) by the formation of complex. In this paper, a highly sensitive and selective voltammetric procedure for the determination of silver was described, based on the

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accumulation of Ag(I) on the surface of AV-CPE followed by anodic stripping after reducing the accumulated Ag(I) to Ag(0). The proposed method provides a very low detection limit (1.0×10^{-10} mol/L for a preconcentration time of 3 min) and good selectivity. The satisfactory results have been obtained for the determination of silver in zinc alloy and waste water samples by this method.

2. Experimental

2.1. Apparatus

Electrochemical experiments were performed with a JP-303 polarographic analyzer (Chengdu Instrument Factory, China), with a three electrode system consisting of a AV-CPE as the working electrode, *a saturated calomel reference electrode* (with 1.0 mol/L KNO_3 salt bridge) and a platinum wire counter electrode. pH values were measured with a pHS-3C model pH meter (Shanghai Leici Instrument Factory, China).

2.2. Reagents and solutions

A 1.00×10^{-3} mol/L silver(I) stock solution was prepared by dissolving the required amount of silver nitrate in 0.10 mol/L nitric acid. Working solutions were prepared by diluting the stock solution with water. Alizarin violet (Mark, Japan), spectrally pure carbon powder and chromatographically pure methyl-benzene-silicon oil (SCR, Shanghai Chemicals Co., China) were used to prepare the modified electrode. All other chemicals were of guaranteed reagent or analytical reagent grade. Doubly distilled water was used throughout.

2.3. Fabrication of the AV-CPE

Unmodified carbon paste was prepared by thoroughly mixing 1.0 g carbon powder with 0.3 g silicon oil in a mortar. Modified carbon pastes were prepared in a similar way except that the carbon powder was first mixed with the desired weight of alizarin violet. A portion of the paste was packed into a glass-tube ($\Phi = 4$ mm), in which a copper wire was inserted to establish electrical contact. The electrode surface was polished on a piece of tracing paper until it had a shiny appearance. Subsequently the electrode was subjected to cyclic scans between −500 to 500 mV for several times in 1.0 mol/L HCl until reproducible behavior was observed.

2.4. Procedure

Each measurement cycle consisted of three steps, as described below:

2.4.1. Accumulation step

The modified electrode was immersed in a magnetically stirred 0.1 mol/L acetate buffer (pH 5.2) containing Ag (I) for 3 min at 0.0 V. After this time period, the electrode was removed, rinsed with water and dried with absorbent paper.

2.4.2. Reduction step

The electrode was then transferred into 0.10 mol/L H_2SO_4 solution containing 2.0×10^{-4} mol/L KBr. A potential of −0.20 V was applied for 30s in still solution.

2.4.3. Stripping step

Immediately after the reduction time expired, the second order derivative linear scan voltammogram was recorded by applying a positive-going potential scan from −0.20 to +0.30 V at 200 mV/s. At the end of the scan, the potential was held at +0.30 V for 60 s to facilitate complete removal of the accumulated analyte.

All experiments were performed at ambient temperature and it was not necessary to remove oxygen from the solution.

3. Results and discussion

3.1. Electrochemical response of Ag(I) at AV-CPE

The ability of the AV-CPE to accumulate Ag(I) was studied. Fig. 1a and b show the cyclic voltammograms obtained in 0.10 mol/L H_2SO_4 +2.0×10^{-4} mol/L KBr for a unmodified electrode after accumulation in acetate buffer (pH 5.2) containing 4.0×10^{-8} mol/L Ag(I) and for the AV-CPE after accumulation in a blank acetate buffer, respectively. Obviously, in both cases, no distinct redox peak was observed except for the residual current. However, when the AV-CPE was dipped into the accumulation medium containing 4.0×10^{-8} mol/L

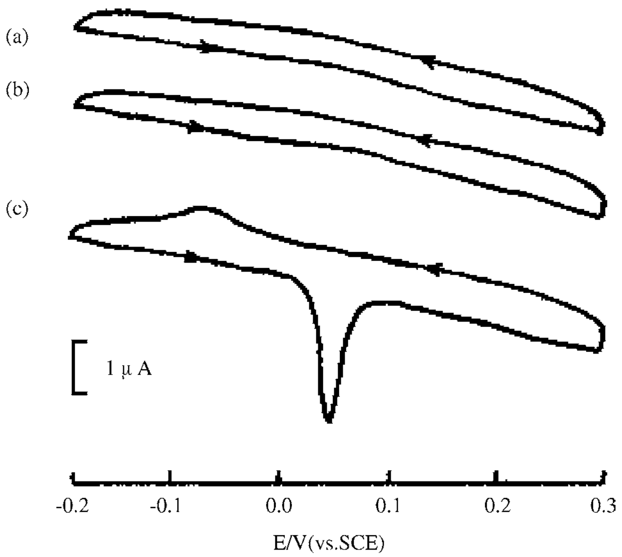

Fig. 1. Cyclic voltammograms in 0.1 mol/L H_2SO_4 + 2.0×10^{-4} mol/L KBr after accumulation in 0.1 mol/L acetate buffer (pH 5.2) for 3 min (a) unmodified CPE, 4.0×10^{-8} mol/L Ag(I) in accumulation medium; (b) AV-CPE, no Ag(I) in accumulation medium; (c) AV-CPE, 4.0×10^{-8} mol/L Ag(I) in accumulation medium. All at scan rate of 100 mV/s.

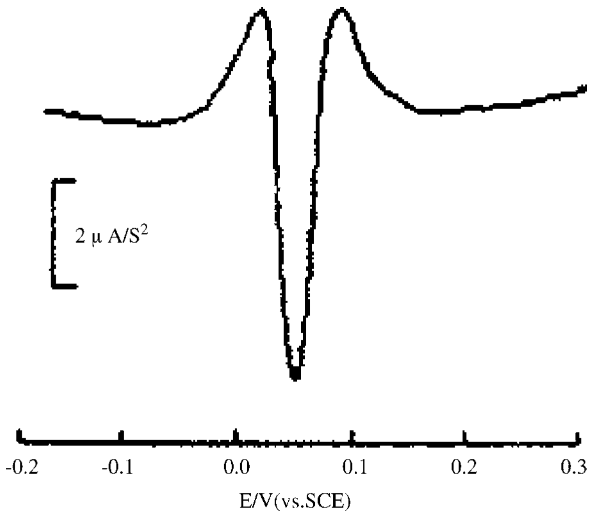

Fig. 2. Second order derivative voltammetric curve at the AV-CPE. Accumulation medium: 0.1 mol/L acetate buffer (pH 5.2) containing 4.0×10^{-9} mol/L Ag(I). Accumulation potential: 0.0 V, accumulation time: 3 min, stripping medium: 0.1 mol/L $H_2SO_4 + 2.0 \times 10^{-4}$ mol/L KBr, reduction potential: −0.2 V, reduction time: 30 s, scan rare: 200 mV/s.

Ag(I) for 3 min followed by cycling in the stripping medium, a well-defined anodic stripping peak with peak potential of +0.05 V appeared (Fig. 1c). This peak was due to the reoxidation of Ag(0) produced by the reduction of accumulated Ag(I) at −0.20 V. On the reverse scan, a smaller cathodic peak was obtained at ca. −0.08 V due to the reduction of Ag(I). Thus, these results provided conclusive evidences for the preconcentration of Ag(I) at the AV-CPE.

Second order derivative linear scan voltammetry is a sensitive electroanalytical technique, in which the second order derivative of the current with respect to time is measured as a function of electrode potential [14]. Fig. 2 shows a typical second order derivative linear scan voltammetric curve at AV-CPE in 0.10 mol/L $H_2SO_4 + 2.0 \times 10^{-4}$ mol/L KBr after accumulation for 3 min at 0.0 V in 0.10 mol/L acetate buffer (pH 5.2) containing 4.0×10^{-9} mol/L Ag(I). Preliminary experiments comparing second order derivative linear scan voltammetry with differential pulse voltammetry showed that the peak shape and sensitivity were improved by using the second order derivative linear scan mode which was therefore used for analytical purposes.

3.2. Effect of AV loading

The accumulation of Ag(I) at the AV-CPE was based on the complex formation reaction between the metal ion and the modifier. Therefore the concentration of AV in the carbon paste had significant influence on the voltammetric response of the modified electrode. The peak current increased with increasing the ratio of AV to carbon powder up to 3.0%, after which the peak current remained essentially constant until 5.0%. The increase in peak current is due to the increase in accumulation sites. The peak current decreased at AV loadings above 5.0%. This was presumably attributed to the reduction of conductive area at the electrode surface. The ratio of AV to carbon powder in the mixture was set at 4.0%.

3.3. Choice of accumulation medium

We examined biphthate, Na_2HPO_4-KH_2PO_4, NaOAc-HOAc and B-R buffers as accumulation media. Best results were obtained in acetate buffer. The optimal concentration of the buffer was 0.10 mol/L.

The dependence of the peak current on pH of the buffer is shown in Fig. 3. The optimum pH range is 4.7–5.8. This is readily explained because at lower pH, the complexation is less effective, whereas at higher pH, the hydrolysis of silver(I) interferes with the complexation. Therefore, pH 5.2 was chosen for the analysis.

3.4. Effect of accumulation potential, E_a and accumulation time, t_a

The influence of accumulation potential on the anodic stripping peak current was studies by varying the accumulation potential from −0.60 to +0.30 V, as shown in Fig. 4. In the range of −0.40 to +0.15 V, the peak current is nearly independent of accumulation potential. When the accumulation was carried out at an open circuit, a much smaller peak current was obtained. Thus the 0.0 V accumulation potential was used in all experiments.

Fig. 5 shows the plots of anodic peak current versus the accumulation time for two different concentrations of Ag(I). At first, the peak current increased with accumulation time, indicating that before adsorptive equilibrium is reached, the longer the accumulation time, the more Ag(I) was adsorbed and thus the peak current became larger. However, after a specific accumulation period, the peak current tended to level off,

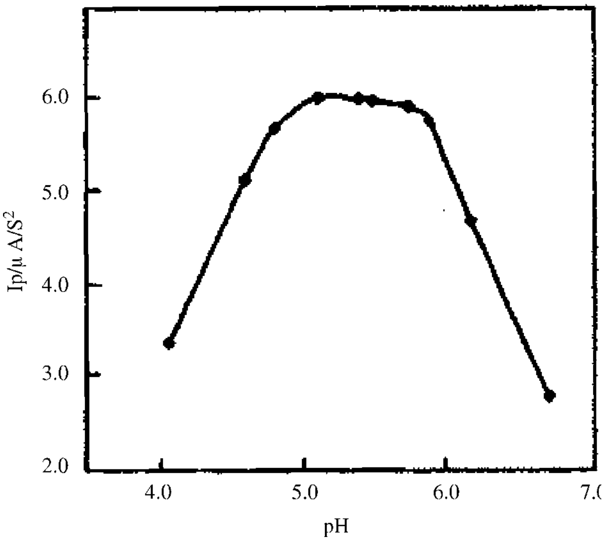

Fig. 3. Effect of pH of acetate buffer on the peak current. Other conditions as in Fig. 2.

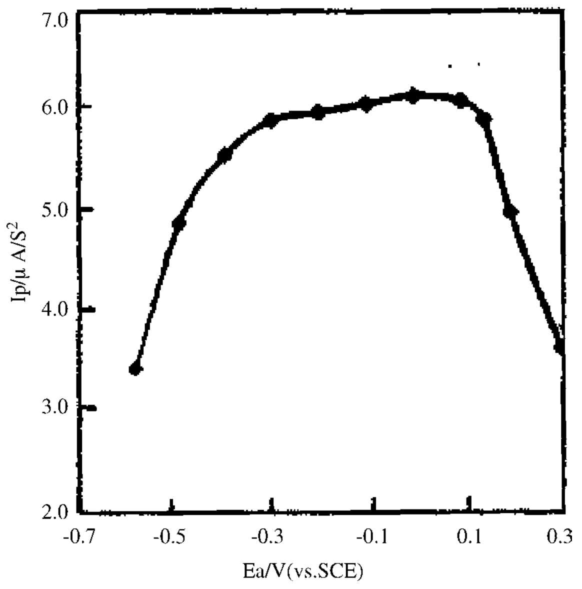

Fig. 4. Effect of accumulation potential on the peak current. Other conditions as in Fig. 2.

illustrating that adsorptive equilibrium was achieved. An accumulation time of 180 s was chosen for further experiments.

3.5. Choice of stripping medium

We examined 0.10 mol/L HCl, 0.10 mol/L HNO_3, 0.10 mol/L H_3PO_4, 0.10 mol/L H_2SO_4, 0.10 mol/L H_2SO_4 + 2.0 ×10^{-4} mol/L KBr, 0.10 mol/L HNO_3 + 2.0 × 10^{-4} mol/L KBr, 0.10 mol/L acetate buffer (pH 5.2) and 0.10 mol/L formate buffer (pH 3.7) for their suitabilities as stripping media. Of these, 0.10 mol/L H_2SO_4 + 2.0 × 10^{-4} mol/L KBr gave the highest sensitivity and the best peak shape. The influences of different concentrations of H_2SO_4 and KBr on the peak current were also investigated, ranging from 0.03 to o.20 mol/L and from 1.0 × 10^{-5} to 1.0 × 10^{-3} mol/L, respectively. The results indicated that 0.10 mol/L H_2SO_4 + 2.0 × 10^{-4} mol/L KBr was the best choice and this was therefore used as the stripping medium.

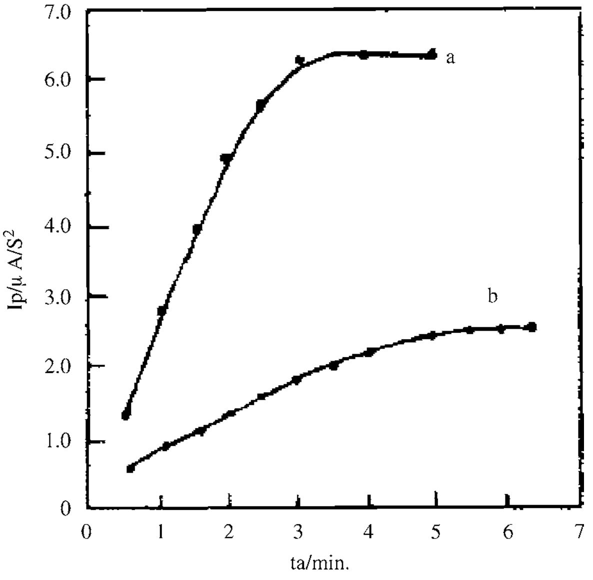

Fig. 5. Dependence of the peak current on accumulation time at different silver(I) concentrations: (a) 4.0 × 10^{-9} mol/L, (b) 8.0 × 10^{-10} mol/L. Other conditions as in Fig. 2.

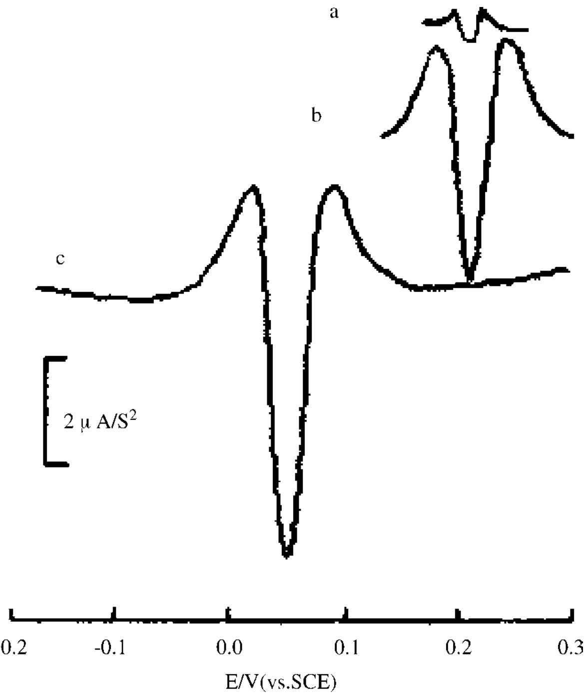

Fig. 6. Anodic stripping voltammograms obtained in 0.1 mol/L H_2SO_4 (a), 0.1 mol/L H_2SO_4 + 2.0 × 10^{-4} mol/L KCl (b) and 0.1 mol/L H_2SO_4 + 2.0 × 10^{-4} mol/L KBr (c). Other conditions as in Fig. 2.

It has been reported that chloride can improve the sensitivity of the anodic stripping peak current of silver due to the formation of AgCl during the anodic potential scan [7]. We studied the influences of chloride and bromide on the peak current respectively. In 0.10 mol/L H_2SO_4 stripping solution, a smaller current response was obtained at +0.22 V (Fig. 6a). When a certain amount of Cl^- ion was added to the solution, the peak current increased about six times compared to that obtained without chloride and the peak potential remained unchanged (Fig. 6b). If the stripping step was carried out in 0.10 mol/L H_2SO_4 + 2.0 × 10^{-4} mol/L KBr, the sensitivity of the stripping current was enhanced ca. 10 times compared to that obtained in 0.10 mol/L H_2SO_4 and the peak potential shifted to +0.05 V (Fig. 6c). These experimental results show that the electrode reaction processes in the presence of Br^- ion are somewhat different from that involving Cl^- ion. A possible mechanism is that Ag^+ produced during the anodic potential scan reacts with Br^-, forming at first AgBr precipitate, and then $[AgBr_2]^-$ complex. The electrode reaction is therefore accelerated. Thus the peak current increases and the peak potential shifts towards the negative direction.

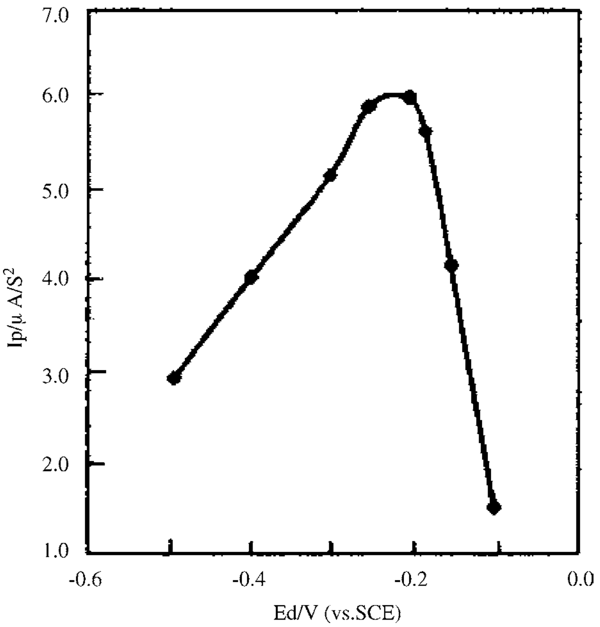

Fig. 7. Plot of anodic stripping peak current vs. reduction potential. Other conditions as in Fig. 2.

3.6. *Effect of reduction potential, E_d and reduction time, t_d*

It can be seen from Fig. 7 that the anodic stripping peak current of silver increased as the reduction potential became more negative, and reached the highest point from −0.20 to −0.25 V. At the less negative potentials, the reduction of Ag(I) is incomplete. At potentials more negative than −0.25 V, the peak current decreased again probably owing to hydrogen evolution. A reduction potential of −0.20 V was employed for all subsequent measurements.

The peak current also depended on the reduction time. It increased linearly from 0 to 20 s, and then remained constant up to 60 s. A reduction time of 30 s was chosen.

3.7. *Linear range, detection limit and reproducibility*

Under the conditions selected, a linear relationship between the second order derivative peak current and the concentration of Ag(I) was obtained over the rang 3.0×10^{-10}–1.2×10^{-7} mol/L with a correlation coefficient of 0.998. The detection limit was estimated to be 1.0×10^{-10} mol/L (S/N = 3) for 180s accumulation time. For ten successive determinations of 4.0×10^{-9} and 8.0×10^{-10} mol/L Ag(I), the relative standard deviations were 4.0 and 4.7%, respectively.

3.8. *Interference studies*

Many co-existing metal ions were examined as possible interferents in the determination of 4.0×10^{-9} mol/L Ag(I). The results showed that a 1000-fold excess of Al(III), Fe(III), Cr(III), Mg(II), Ca(II), Ba(II), Cd(II), Zn(II), Co(II) and As(III), a 500-fold excess of In(III), Se(IV), Ge(IV), Pb(II) and Ni(II), a 200-fold excess of Sn(IV) and Hg(II), a 50-fold excess of Cu(II) and Sb(III), a 20-fold excess of Bi(III) and a 10-fold excess of Au(III) do not interfere in the determination of Ag(I) with an error of ≤5.0%. Cu(II), Bi(III) and Au(III) gave rise to stripping peaks close to that of Ag when their concentrations were higher than those mentioned above. If a reduction potential of −0.15 V was applied in the reduction step, a 200-fold excess of Cu(II) and a 50-fold excess of Bi(III) did not show any significant effect on the Ag peak. In this case, the Ag response was depressed by ca.30% due to the incomplete reduction of the Ag(I)–AV complex, but the proportionality between analytical signal and analyte concentration was preserved and Ag(I) could be determined using the standard addition method.

Table 1
Determination results of silver in samples ($n = 5$)

Sample	Found by this method	R.S.D. (%)	Certified (μg/g)	Found by GF-AAS
Zinc alloy				
001	0.28 μg/g	4.3	0.30	
002	0.63 μg/g	4.1	0.60	
003	1.42 μg/g	3.7	1.43	
Waste water				
1	1.9 μg/l	4.9		2.2 μg/l
2	2.7 μg/l	4.7		2.9 μg/l
3	4.5 μg/l	4.1		4.2 μg/l

3.9. *Analytical applications*

The proposed method was applied to the determination of silver in zinc alloy and waste water samples. The samples were treated with nitric acid. The resulting solution was evaporated to dryness. The residue was dissolved in 1×10^{-3} mol/L nitric acid and content of silver was determined by the standard addition method according to the procedure described above. The measured values are in agreement with the certified values or those obtained by graphite furnace atomic absorption spectrometry (GF-AAS), as shown in Table 1.

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