Selective Quantification of Trace Silver in Water Samples by Solidified Floating Organic Drop Micro-extraction Coupled with Electrothermal Atomic Absorption Spectrometry

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INTRODUCTION

Silver and silver-containing compounds are used widely in different fields such as for mining, silverware manufacturing, the electronic industry, and water disinfection (1-3). The increasing use of silver compounds can also contribute to an increase in environmental pollution. Owing to the toxicity of silver and silver-containing compounds to many aquatic organisms, even at low concentrations, it can lead to serious environmental problems (4,5). Bowen suggested that silver may pose a potential risk as a water pollutant due to a lack of recycling mined silver (6). Therefore, the development of analytical methods for the determination of traces of silver in waters is important.

Electrothermal atomic absorption spectrometry (ETAAS) is a reliable and practical technique for this purpose, and its use results in much lower instrumental and running costs in comparison to inductively coupled plasma mass spectrometry (ICP-MS) instrumentation (7). However, direct use of ETAAS for the determination of trace metal ions in environmental samples is limited not only due to the very low concentration available, but also by matrix interference (8). Hence, an initial sample pretreatment, such as preconcentration and/or separation of the analyte, is often necessary.

ABSTRACT

In this work, a novel solidified floating organic drop micro-extraction (SFODME) technique was developed and coupled with electrothermal atomic absorption spectrometry (ETAAS) for the determination of trace silver in water samples. Diethyldithiocarbamate (DDTC) was used as a chelating agent and 1-undecanol as the extraction solvent. The optimum experimental parameters for preconcentration of Ag(I), such as pH, chelating agent concentration, extraction solvent volume, extraction time and interfering ions, were investigated. Under the optimized conditions, the calibration curve was linear in the range of 0.2–50 $\mu\text{g L}^{-1}$ with a detection limit of 0.054 ng mL^{-1} (3 σ), an enrichment factor of 17, and the relative standard deviation of 2.1% ($n=7$, at 1.0 ng mL^{-1}). The proposed method was successfully applied to the determination of trace amounts of Ag(I) in water samples.

Several separation and preconcentration techniques, including solid phase extraction (1,9,10), cloud point extraction (11,12) and liquid-liquid extraction (13-16), have been applied for the extraction of trace amounts of silver ions from various environmental samples.

Solidified floating organic drop microextraction (SFODME) is a novel micro-extraction procedure for the separation and preconcentration of trace analytes of interest

from a bulk matrix (17). In this method, a small volume of 1-undecanol (extraction solvent), which has a lower density than water, low toxicity, and a low melting point (13–45 °C), was floated on the surface of the aqueous solution. The aqueous phase was stirred for a desired time. In this step, the analytes were extracted from the aqueous phase to the organic solvent. Then the sample was transferred to the ice bath. When the organic solvent was solidified, it was transferred into a small conical vial, and the melted organic solvent used for subsequent determination. The advantages of the SFODME method are simple operation, low cost, speed, high recovery, and is environmentally friendly (18). This method has been successfully applied for the preconcentration of organic compounds (19,20) and metal ions (21-24) in various types of samples.

In the present study, a novel solidified floating organic drop micro-extraction (SFODME) protocol, followed by ETAAS determination, was developed for the preconcentration of silver in water samples. In this method, diethyldithiocarbamate (DDTC) was selected as the chelating agent, which reacts with silver ions forming a very stable complex. 1-Undecanol, an environment-friendly organic compound, was selected as the extraction solvent. Various influencing parameters on the preconcentration of silver ions, such as pH, stirring time, concentration of chelating agent, and co-existing ions, were systematically studied.

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The method was applied to the determination of trace amounts of silver ions in real samples with satisfactory results.

EXPERIMENTAL

Instrumentation

A TAS-990 atomic absorption spectrometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, P.R. China), equipped with deuterium lamp background correction and a transversally heated graphite atomizer, was used as the detection unit. A silver hollow cathode lamp was employed as the radiation source at 328.1 nm with a slit width of 0.4 nm. Argon 99.99% was used as the protective and purge gas. The integrated absorbance mode was used throughout. The sample injection volume used was 10 μL for all experiments. The optimum operating parameters for ETAAS are given in Table I. The pH values were measured with a PHS-3C digital pH meter (Shanghai Dapu, Shanghai, P.R. China). A 85-2 heater/magnetic stirrer (Jintan Ronghua Instrument Manufacture Co. Ltd, P.R. China) with a 10 mm $\times$ 2 mm stirring bar was used for stirring the solutions.

Reagents and Standard Solutions

All reagents used in this study were at least of analytical grade. Doubly deionized water was used throughout this work. The standard stock solution of Ag(I) (1 mg mL^{-1}) was prepared by dissolving proper amounts of AgNO_3 in 1% nitric acid solution. Standard solutions of silver were prepared daily by appropriate dilution of the stock solutions. 1-Undecanol (Beijing Chemistry Reagent Company, P.R. China) was used as the extracting solvent. DDTc solution was prepared by dissolving appropriate amounts of DDTc (A.R, Shanghai Chemistry Reagent Company, Shanghai, P.R. China) in ethanol.

Pipettes and vessels required for the experiments were kept in 2.0 mol L^{-1} nitric acid solution overnight and subsequently washed thoroughly with doubly distilled deionized water before use.

Solidified Floating Organic Drop Micro-extraction Procedure

Aliquots of 5 mL of sample solution containing 1 ng mL^{-1} Ag were adjusted to pH 3.0 and placed in a 10-mL vial containing a stir bar. Then 20 μL of DDTc solution in 1-undecanol (0.05 mg mL^{-1}) was added. The magnetic stirrer was turned on and the solution mixed for 10 minutes. In this step, silver ions react with DDTc and are extracted into 1-undecanol. After the extraction time, the sample vial was transferred into an ice bath until the organic solvent solidified (5 minutes). The solidified solvent was transferred into a conical vial where it was melted immediately. Finally, it was diluted to 100 μL with ethanol. Then, 10 μL of the extraction solvent was removed using a 50- μL microsyringe and injected into the ETAAS for analysis.

Samples Preparation

The tap water samples were taken from our laboratory after allowing the water to flow for 10 minutes. The lake water samples were collected from Yuncheng University (Yuncheng, P.R. China). The water samples were filtered through a 0.45- μm membrane filter (to reduce the organic matter and the fine particles, which will cause

disturbing influences), acidified to pH 2 with diluted HNO_3 , and stored at 4 $^{\circ}\text{C}$ in the refrigerator. The samples were analyzed as soon as possible after sampling.

Portions (0.5000 g) of GBW 07303 Stream Sediments (Institute of Geophysical and Geochemical Exploration, Hebei, P.R. China) were transferred into PTFE beakers, 10 mL of concentrated HNO_3 was added, and the solution left standing overnight. Then, 3 mL of H_2O_2 was added to the samples and the solution heated to near dryness. The residue was dissolved in 0.1 mol L^{-1} HNO_3 solution, transferred into a 50-mL volumetric flask, and then diluted to the mark. A blank was also prepared in a similar way without the sample.

RESULTS AND DISCUSSION

Effect of Volume of Extraction Solvent

The effect of 1-undecanol volume on the extraction of the silver signal was studied in the range of 10–50 μL . As can be seen in Figure 1, when the volume of the extraction solvent was increased, the analytical signal of silver increases up to 20 μL . By further increasing the volume of 1-undecanol, it remained constant. Therefore, 20 μL of 1-undecanol was chosen as the optimum extraction solvent volume.

Effect of pH

The pH is one of the most significant factors affecting the formation of the Ag-DDTC complex. Thus, the

TABLE I
Temperature Program for the Determination of Silver by ETAAS

Step	Temperature ($^{\circ}\text{C}$)	Ramp (s)	Hold (s)	Argon Flow Rate (mL min^{-1})
Drying	120	15	10	250
Pyrolysis	500	5	15	250
Atomization	1900	0	3	0
Cleaning	2100	1	3	250

effects of sample pH on the extraction efficiency of silver ions were investigated in the pH range of 1.0–9.0, and the results are shown in Figure 2. As can be seen, the signal intensities of the silver ions increased with an increase in the pH starting at 1.0, and the highest signal was obtained at pH 3.0. The signal decreased with a further increase in pH from 4.0 to 9.0. Thus, pH 3.0 was used for the sample solution in the extraction process.

Effect of DDTC Concentration

The concentration of DDTC has a direct effect on the formation of the Ag-DDTC complex as well as its extraction. The influence of the DDTC concentration in the range of 0–0.2 mg mL⁻¹ on the recovery of silver is shown in Figure 3. The recovery increased with an increase in the DDTC concentration up to 0.05 mg mL⁻¹, and then remained constant. Therefore, the DDTC concentration of 0.05 mg mL⁻¹ was selected for further study.

Effect of Extraction Time

Extraction time is an important factor influencing the extraction efficiency and speed of the analysis. For this reason, a study was carried out by varying the extraction time from 5 minutes to 30 minutes at constant experimental conditions. The results displayed in Figure 4 show that after 10 minutes, the signal intensities of the analytes remained constant. Thus, an extraction time of 10 minutes was selected for subsequent experiments.

Fig. 1. Effect of extraction solvent volume on SFODME of Ag(I). Other experimental conditions: Ag, 1.0 ng mL⁻¹; sample volume, 5.0 mL; extraction time, 10 min; DDTC concentration, 0.05 mg mL⁻¹.

Fig. 2. pH of sample solution on SFODME of Ag(I). Other experimental conditions: Ag, 1.0 ng mL⁻¹; sample volume, 5.0 mL; extraction time, 10 min; DDTC concentration, 0.05 mg mL⁻¹.

Fig. 3. Effect of DDTC concentration on the SFODME of Ag(I). Other experimental conditions: Ag, 1.0 ng mL⁻¹; sample volume, 5.0 mL.

Fig. 4. Effect of the extraction time on the SFODME of Ag(I). Other experimental conditions: Ag, 1.0 ng mL⁻¹; sample volume, 5.0 mL.

Effect of Coexisting Ions

The potential interferences from co-existing ions on the preconcentration and determination of silver ions were carefully investigated. In these experiments, solutions of 1 ng mL^{-1} of Ag^+ containing the interfering ions were treated according to the optimized procedure. Table II shows the tolerance limits of the co-existing ions. The results show that large amounts of alkali and alkaline earth metal ions have no interference due to lower DDTC complex stability. The obtained results also indicate that the method proposed results in high selectivity for the determination of the analytes in various water samples.

TABLE II
Interference of Coexisting Ions for the Determination of Silver

Interfering Element	Conc. ($\mu\text{g mL}^{-1}$)	Recovery (%)
Na^+	1,000	103
K^+	1,000	101
Mg^{2+}	5.00	96.4
Ca^{2+}	5.00	98
Zn^{2+}	0.50	95.3
Cu^{2+}	0.20	97.1
Pb^{2+}	0.20	101

Analytical Characteristics and Potential Applications

Under the optimum conditions, the analytical performance of the proposed method was investigated. Linearity was observed over the $0.2\text{--}50 \text{ ng mL}^{-1}$ range with a correlation coefficient of 0.997. The regression equation of the calibration curve without preconcentration was $A=0.0594C + 0.0449$, and that of the micro-extraction procedure was $A=0.0035C + 0.0041$ (where A is the absorbance and C is the concentration of silver in ng mL^{-1}). The results are shown in Figures 5 and 6.

The limit of detection, based on three times the standard deviation of the blank signal for extracting 5 mL of water, was 0.054 ng mL^{-1} of silver. The relative standard deviations (RSD) was 2.1% for Ag^+ ($c=1 \text{ ng mL}^{-1}$, $n=7$, sample volume

$= 5 \text{ mL}$). The enrichment factor, defined as the slope ratio of two calibration curves with micro-extraction and without micro-extraction, was 17.

Analysis of Real Water Samples

In order to verify the accuracy of the proposed procedure, the method was applied to determine the Ag concentration in environmental certified reference material (CRM) GBW07303 Stream Sediments. The certified amount of Ag in this CRM is $0.60 \pm 0.06 \mu\text{g g}^{-1}$. The obtained values by using the proposed method was $0.57 \pm 0.03 \mu\text{g g}^{-1}$, which is in good agreement with the certified concentration. The method was applied to determine Ag in lake water and tap water samples, and the results are listed in Table III. As seen, the relative recoveries for the spiked samples are in an acceptable range.

TABLE III
Analytical Results (Mean $\pm$ S.D., $n=3$) of Silver in Water Samples

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Tap Water	0	1.40 ± 0.012	-
	1.5	2.84 ± 0.025	96.0
	3	4.39 ± 0.076	99.7
Lake Water	0	2.63 ± 0.10	-
	4	6.50 ± 0.14	96.8
	8	10.44 ± 0.24	97.6

Fig. 5. The regression equation without SFODME procedure.

Fig. 6. The regression equation with SFODME procedure.

CONCLUSION

A novel solidified floating organic drop micro-extraction (SFODME) method combined with ETAAS was developed to validate the separation and determination of trace silver in complicated samples. DDTc and 1-undecanol were selected as the chelating reagent and extraction solvent in the proposed method, respectively. Several variables affecting the micro-extraction efficiency were investigated and optimized. The proposed micro-extraction protocol effectively minimizes the interference from coexisting heavy metal ions. It has been demonstrated that the proposed method is simple, fast, and low cost, has low organic solvent consumption, is environmentally friendly and excellent for use in the determination of Ag in complicated samples.

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