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Qiong Ding[a]; Pei Liang[a]; Feng Song[a]; Aiming Xiang[a]
[a] Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, P.R. China

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Separation and Preconcentration of Silver Ion using Multiwalled Carbon Nanotubes as Solid Phase Extraction Sorbent

Qiong Ding, Pei Liang, Feng Song, and Aiming Xiang
Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, P.R. China

Abstract: A new method has been developed for the determination of silver ion based on separation and preconcentration with a microcolumn packed with multiwalled carbon nanotubes (MWNTs) prior to its determination by flame atomic absorption spectrometry (FAAS). The optimum experimental parameters for separation and preconcentration of silver, 'such as sample pH, sample flow rate and volume, elution conditions, and interfering ions, have been investigated. Silver ion can be quantitatively retained by MWNTs in the pH range $7 \sim 9$, and then eluted completely with 1.0 M HNO_3. The detection limit of this method for Ag was 0.60 ng mL^{-1}, and the relative standard deviation (RSD) was 3.8% at the 10 ng mL^{-1} Ag level. The method has been successfully applied for the determination of trace silver in geological and water samples.

Keywords: Multiwalled carbon nanotubes, preconcentration, silver, FAAS

INTRODUCTION

Low-level exposure to silver compounds is widespread owing to the use of soluble silver compounds to disinfect water for drinking and recreation

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Address correspondence to Pei Liang, Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China. Fax: +86-27-67867955; E-mail: liangpei@mail.ccnu.edu.cn

purposes. In many countries silver impregnated filters are used for water purification, and concentration of up to 50 $\sim$ 200 mg L^{-1} of silver (depending on country) are permitted to control antimicrobial activity with no risk to human health (1, 2). Silver also enters the environment through industrial wastes because it often exists as an impurity in Zn, Cu, As, and Sb ores (3). In natural waters, silver ion can be used as an indicator for geochemical prospecting, because stream silver rich areas are likely to be enriched in this element. On the other hand, the information about the interaction of silver with essential nutrients, especially selenium, copper, Vitamins E, and B12, have focused attention on its potential toxicity (4, 5). Although a trace amount of silver can be directly determined in different media by expensive analytical methods such as inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry, and electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry (FAAS) is not sufficient sensitivity for directly determination of silver traces. But it is an accepted method for an easy determination of silver, as the interferences of many elements are unimportant and there is only a small increase of the silver signal when the concentration of these elements (Fe, Ni, Mg, Pb, Ca, Cu, Na) is at high level (6). Prior to the determination of silver by FAAS, a preconcentration step is usually necessary in order to reach an appropriate level of sensitivity. Many preconcentration procedures for silver determination in various media have been developed, such as coprecipitation (7, 8), liquid–liquid extraction (9), cloud point extraction (10), solid-phase extraction (11, 12), etc. Recently, solid-phase extraction (SPE) technique has become increasingly popular in trace elements preconcentration due to its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode (13, 14). The main requirements with respect to substances to be used as solid-phase extraction sorbents are as follows: possibility of extracting a large number of elements over a wide pH range, fast and quantitative sorption and elution, high capacity, regenerability, and accessibility. Numerous substances have been proposed and applied as solid-phase extraction sorbents for the preconcentration of silver, such as chelating resin (15), modified silica (16, 17), activated carbon (18), alumina (19), polyurethane foam (20), etc.

Since its discovery in 1991, carbon nanotubes (CNTs) have attracted great attention because of their unique properties. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, and divided into multi-walled carbon nanotubes (MWNTs) (21) and single-walled carbon nanotubes (SWNTs) (22) according to the carbon atom layers in the wall of the nanotubes. The hexagonal arrays of carbon atoms in graphene sheets of CNTs surface have a strong interaction with other molecules or atoms, which make CNTs a promised adsorbent material substituted for activated carbon in many ways. Recently Long et al. reported that MWNTs

have better adsorption capacity for dioxin removal than that of activated carbon (23). Li et al. suggested that MWNTs show high efficiency for Pb^{2+}, Cd^{2+} and F^- removal from the aqueous solution after oxidation treatment with nitric acid (24–26). Cai et al. and Li et al. demonstrated that MWNTs could be used as effective adsorbents for the solid-phase extraction of some organic compounds (27–29).

The purpose of this work was to assess the analytical potential of MWNTs as a new adsorbent for the preconcentration of trace silver ion. A new method using a microcolumn packed with MWNTs as sorbent has been developed for the preconcentration of trace silver in geological and water samples prior to its determination by FAAS.

EXPERIMENTAL

Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge Genereal Instrument Co. Ltd, Beijing, P.R. China) was used for the determination of silver in the following conditions: wavelength: 328.1 nm, lamp current: 2.0 mA, slit width: 0.4 nm, burner height: 7.0 mm, acetylene flow: 1.5 L min^{-1}, air flow: 8.0 L min^{-1}. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was used in the separation/preconcentration process. A self-made PTFE microcolumn (20 mm × 3.0 mm i.d.), packed with MWNTs, was used in the manifold for separation/preconcentration. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connections.

Standard Solutions and Reagents

A stock standard solution (1000 μg mL^{-1}) of silver was obtained from the National Institute of Standards (Beijing, P.R. China) Working standard solutions were obtained by appropriate dilution of the stock standard solution. All the reagents used were of analytical grade or better. Doubly distilled water was used throughout the work.

MWNTs with the diameters range from 30 nm to 60 nm were kindly provided by the Nano Science & Technology Research Center, Central China Normal University. The method of preparation and characterization of MWNTs was reported previously (30). Before use, MWNTs were refluxed with concentrated nitric acid for 1 h, and then washed with doubly distilled water until neutral the pH was reached. The treated MWNTs was dried at 100°C and stored for further use.

Sample Preparation

Portions (0.5 g) of standard reference material (GBW07303, stream sediment reference material, P.R. China) were transferred into PTFE beakers, 6 mL of HF, 5 mL of concentrated HNO_3 and 3 mL of concentrated H_2SO_4 were added in turn, heated until the solution become transparent, continuously heated to near dryness and the residue dissolved in 0.1 mol L^{-1} HNO_3. After adjustment of pH to 7.0, the solution was made up with distilled water to 50 mL.

A lake water sample was collected from East Lake, Wuhan, P.R. China, and a tap water sample was freshly collected from a laboratory, after allowing the water to flow for 5 min. All the water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling.

Column Preparation

50 mg of MWNTs was introduced into a PTFE microcolumn (20 mm × 3.0 mm i.d) plugged with a small portion of glass wool at both ends. Before use, a 2.0 M HNO_3 solution and doubly distilled water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with a buffer solution.

General Procedure

Portions of an aqueous sample solution containing Ag^+ were prepared, and the pH value was adjusted to 7.0 with 0.1 M HNO_3 or ammonia. The solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. After loading, a further washing with a buffer solution served to remove the sample still present in the lines and in the column. The retained Ag^+ was eluted with 2.0 mL of 1.0 M HNO_3 solution. The analyte in the effluent was determined by FAAS at peak height mode. The column could be used repeatedly after regeneration with the 2.0 M HNO_3 solution and distilled water respectively.

RESULTS AND DISCUSSIONS

Effect of pH on Adsorption

The pH value plays an important role with respect to the adsorption of different ions on MWNTs. The oxidation of MWNTs with conc. nitric acid lead to the surface functionalization with oxygen-containing groups, and the isoelectric point (IEP) of MWNTs shifts to the lower pH values (26). When the pH of the solution is higher than the IEP of the oxidized MWNTs, the

negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. The decrease of pH leads to the neutralization of the surface charge, so the adsorption of cations onto MWNTs decreases quickly.

In order to evaluate the effect of pH, a series of sample solutions were adjusted to a pH range of $1 \sim 9$ with 0.1 M HNO_3 or ammonia and processed according to the recommended procedure. The adsorption percentage was calculated based on a difference between the amounts of Ag^+ in the starting sample and the solution outflowing from the column. The results of the effect of pH on the adsorption of Ag^+ are shown in Fig. 1. It can be seen that quantitative adsorption (>95%) for Ag^+ was obtained when the pH exceed 7.0. So a pH of 7.0 was selected as the compromise condition.

Elution of the Adsorbed Silver Ion

In order to elute the retained Ag^+ from the MWNTs microcolumn, nitric acid was assayed at different concentrations and volumes. It was found that a concentration of 1.0 M nitric acid (or higher) is required to obtain a quantitative elution if the eluent volume is set to 2.0 mL.

Effect of Flow Rate of Sample Solutions

In the column SPE system, the flow rate of the sample solution is one of the most important parameters, which not only affects the recovery of the

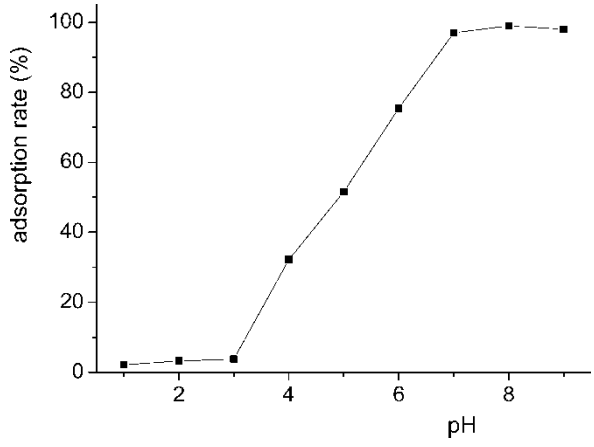

Figure 1. Effect of pH on the adsorption of Ag^+ on MWNTs Ag^+: 1.0 μg mL^{-1}; sample volume: 20 mL.

analyte, but also controls the time of analysis. Therefore, the effect of the flow rate of the sample solution was examined under the optimum conditions (1.0 μg mL^{-1} Ag^+, pH 7.0, 2.0 mL 1.0 M nitric acid as eluent, etc.). It was found that the flow rate in the range of 0.5 to 2.0 mL min^{-1} had no significant influence on the recovery of Ag^+. Thus, all subsequent experiments were performed at a flow rate of 2.0 mL min^{-1}, the highest flow rate of the manifold used in this experiment.

Effect of the Sample Volume

In order to explore the possibility of enriching low concentrations of analytes from large volumes, the effect of a sample volume on the retention of Ag^+ was also investigated. For this purpose, 25, 50, 100, 150, and 200 mL of sample solutions containing 1.0 μg of Ag^+ were passed through the microcolumn with optimum flow rate. It was found that quantitative recovery (>95%) of Ag^+ was obtained for the sample volume up to 100 mL. Above 100 mL the recovery for Ag^+ decreased slightly. In this experiment, 100 mL of a sample solution was adopted for the preconcentration of Ag^+ from water sample, and then eluted with 2.0 mL 1.0 M HNO_3, so an enrichment factor of 50 is achieved by this method.

Adsorption Capacity

To determine the adsorption capacity, 25 mL sample solutions having the different Ag concentrations (in the range from 5 to 50 μg mL^{-1}) was adjusted to pH 7.0 with 0.1 M HNO_3 or ammonia, and the proposed separation and preconcentration procedure described above was applied. The amount of Ag adsorbed at each concentration level was determined. The profile of the adsorption isotherm for silver was gained by plotting the concentration (μg mL^{-1}) versus the milligrams of Ag adsorbed per gram MWNTs, shown in Fig. 2. From the adsorption isotherm, the adsorption capacity of MWNTs for Ag was found to be 8.08 mg g^{-1}, it is higher than the commonly used sorbent for Ag, such as chelating resin (15) and silica gel (17). It indicates that MWNTs have great potential as promised adsorbent for the preconcentration of Ag.

Column Reuse

The stability and potential regeneration of the column were investigated. The column can be reused after being regenerated with 10 mL 2.0 M HNO_3 and 20 mL distilled water respectively, and stable up to 50 adsorption-elution cycles without obviously decreasing in the recovery for Ag^+.

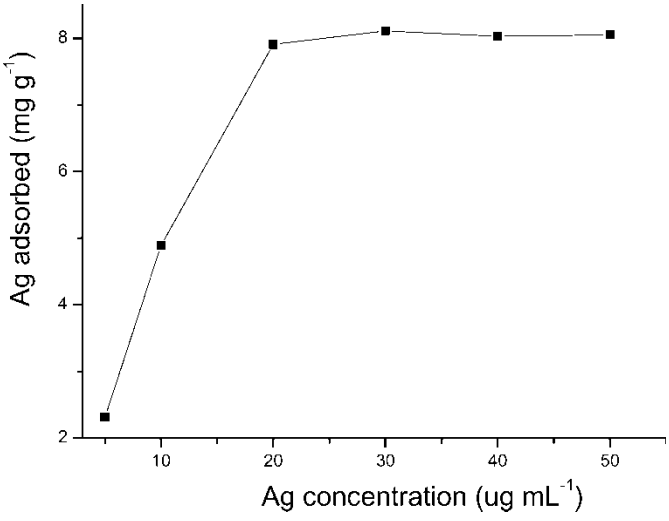

Figure 2. Adsorption isotherm of Ag^+ on MWNTs pH: 7.0; sample volume: 25 mL.

Effects of Coexisting Ions

The effects of common coexisting ions on the adsorption of Ag^+ on MWNTs were investigated. In these experiments, solutions of 0.1 μg mL^{-1} of Ag^+ containing the added interfering ions were treated according to the recommended procedure. The tolerance limits of coexisting ions, defined as the largest amount making the recovery of Ag^+ less than 90%, were given in Table 1. It can be seen that the major cations and anions in natural water has no obvious influence on the adsorption of Ag^+ under the selected conditions.

Analytical Performance of the Method

Under the optimum experimental conditions, the calibration curve for silver was linear up to 800 ng mL^{-1} with a correlation coefficient of 0.9993. The precision of the method, evaluated as the relative standard deviation (RSD), obtained after analyzing a series of eleven replicates for 1.0 μg Ag^+ in 100 mL of model solutions, was about 3.8%.

The limit of detection (LOD) of the proposed method was studied under the optimal experimental conditions. The detection limit based on three times the standard deviations of the blank (3σ) for Ag was found to be 0.60 ng mL^{-1}.

Analytical Application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of the content of Ag in a geological

Table 1. Tolerance limits of coexisting ions

Coexisting	Tolerance limit of ions (ion/Ag, w/w)
Na^+, K^+	5000
Ca^{2+}, Mg^{2+}	2000
Al^{3+}	500
Cu^{2+}, Pb^{2+}, Hg^{2+}	200
Cd^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}	100
Fe^{3+}	50
NO_3^-	2000
SO_4^{2-}, CO_3^{2-}, SiO_3^{2-}	1000
PO_4^{3-}	1000

Ag^+: 0.1 μg mL^{-1}.

standard reference material of stream sediment (GBW07605, P.R. China) The analytical value (0.60 ± 0.09 μg g^{-1}, n = 5) is in good agreement with the certified value (0.59 ± 0.07 μg g^{-1}).

The proposed method has been applied to the determination of Ag in tap water and lake water, and the recoveries of spikes of Ag were also studied. The analytical results and the recoveries were given in Table 2. The results indicated that the recoveries were reasonable for trace analysis.

CONCLUSIONS

It can be concluded from the results that MWNTs is an effective sorbent for trace amounts of silver ions that can be used for its preconcentration from its dilute aqueous solutions. The proposed solid phase extraction procedure

Table 2. Determination of Ag (ng mL^{-1}) in natural water samples (n = 5)

Samples	Added	Found	Recovery (%)
Tap water	0	ND	—
	10	9.92 ± 1.10	99.2
	20	19.80 ± 0.85	98
Lake water	0	ND	—
	10	9.64 ± 0.47	96.4
	20	19.12 ± 1.94	95.6

Sample volume: 100 mL.

based on MWNTs showed enough sensitivity for trace silver determinations in diverse kind of materials. The precision and accuracy were satisfactory. The method can be successfully applied to the separation, preconcentration, and determination of silver in real samples.

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