Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 154 (2016) 157–163

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Development of new portable miniaturize solid phase microextraction of silver-APDC complex using micropipette tip in-syringe system couple with electrothermal atomic absorption spectrometry

Naeemullah [a,*], Tasneem Gul Kazi [a], Hassan Imran Afridi [a], Faheem Shah [b], Sadaf Sadia Arain [a], Salma Aslam Arain [a], Abdul Haleem Panhwar [a], Mariam Shahzadi Arain [a], Muhammad Kashif Samoon [c]

[a] *National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan*
[b] *Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad 22060, Pakistan*
[c] *Center for Pure and Applied Geology, University of Sindh, Jamshoro 76080, Pakistan*

ARTICLE INFO

*Article history:*
Received 24 June 2015
Received in revised form 7 October 2015
Accepted 22 October 2015
Available online 24 October 2015

*Keywords:*
Silver(I)
Micropipette tip
Activated carbon cloth
Solid phase microextraction
Syringe
Electrothermal atomic absorption spectrometry

ABSTRACT

An innovative and simple miniaturized solid phase microextraction (M-SPME) method, was developed for preconcentration and determination of silver(I) in the fresh and waste water samples. For M-SPME, a micropipette tip packed with activated carbon cloth (ACC) as sorbent, in a syringe system. The size, morphology and elemental composition of ACC before and after adsorption of analyte have been characterized by scanning electron microscopy and energy dispersive spectroscopy. The sample solution treated with a complexing reagent, ammonium pyrrolidine dithiocarbamate (APDC), was drawn into the syringe filled with ACC and dispensed manually for 2 to 10 aspirating/dispensing cycle. Then the Ag- complex sorbed on the ACC in micropipette was quantitatively eluted by drawing and dispensing of different concentrations of acids for 2 to 5 aspirating/dispensing cycles. The extracted Ag ions with modifier were injected directly into the electrothermal atomic absorption spectrometry for analysis. The influence of different variables on the extraction efficiency, including the concentration of ligand, pH, sample volume, eluent type, concentration and volume was investigated. Validity and accuracy of the developed method was checked by the standard addition method. Reliability of the proposed methodology was checked by the relative standard deviation (%RSD), which was found to be <5%. Under the optimized experimental variables, the limits of detection (LOD) and enhancement factors (EF), were obtained to be 0.86 ng $L^{-1}$ and 120, respectively. The proposed method was successfully applied for the determination of trace levels of silver ions in fresh and waste water samples.

## 1. Introduction

Silver(I) has both important and harmful impacts on many biological processes and an increasing level in different environmental samples have been observed, which might be due to their importance in modern industries, medicines and nanoproducts [1–3]. It is well documented that silver(I) creates toxicity to many biological systems, even at low concentrations [4,5]. Silver(I) can enter into the environment via industrial waters and might pose a potential risk as a water pollutant [6]. The most common technique for the determination of silver ions is flame and furnace atomic absorption spectrometry [7]. The direct determinations of silver(I) in environmental samples by different atomic spectrometric techniques are usually quite difficult, due to its very low concentration and matrix interferences [8–12]. Thus, prior to assess its low concentration in complex matrix, separation and preconcentration techniques are compulsory to eliminate or minimize matrix effects for enhancing the sensitivity of detection techniques. Several methods have been reported for the separation and preconcentration of silver(I), such as coprecipitation [13], liquid–liquid extraction [14], solid-phase extraction [15–17] and cloud point extraction [18]. The solid-phase extraction has been widely used because of its simplicity, low cost, and ability to combine with different detection techniques in both online and off-line modes [19,20]. The conventional SPE method is laborious and time-consuming [21]. Recently, new efforts have been placed on miniaturizing the SPE extraction procedure by reducing the extrant to aqueous phase ratio [22]. The solid phase microextraction (SPME) provides very efficient enrichment method, due to use of very small sample volume and reduces the consumption of organic solvents, which makes it more environmentally friendly. The SPME is also simplifying the overall sample preparation procedure by minimizing the number of required steps [23]. However, the mechanical strength and the life time of the sorbent materials commonly used in SPME are short, in addition to handling problem, which limits their application [24–26]. The activated carbons are mainly microporous and also contain meso- and macro-pores, which are facilitating the adsorbate especially liquid

---

[*] Corresponding author.
*E-mail address:* naeemullah433@yahoo.com (Naeemullah).

http://dx.doi.org/10.1016/j.saa.2015.10.031
1386-1425/

molecules to the interior area of carbon particle [27–29]. The ACC adsorbents have many advantages such as, higher specific surface area, mechanical strength and possibility of regeneration as compared to other material. These advantages have led to the frequent use of ACC as an adsorbent for removal of organic and inorganic compounds [30–38].

In the present study a simple and fast, inexpensive preconcentration method was developed by using a micropipette tip-syringe system packed with an adsorbent (ACC), for the enrichment of silver(I) in fresh and waste water samples. The APDC was used as complexing reagent. The ACC was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), before and after adsorption of silver(I)–complex. The silver–APDC complex retained on ACC in syringe system was eluted with acid at different concentrations and volumes. The extracted Ag was determined by electrothermal atomic absorption spectroscopy (ETAAS). The effects of various experimental parameters on the enrichment efficiency of the developed M-SPME procedure were investigated and optimized. The optimized M-SPME procedure was applied to analyze the real samples.

## 2. Experimental

### 2.1. Chemical reagents and glassware

Ultrapure water obtained from the ELGA lab water system (Bucks, UK), was used throughout the work. Stock standard solution of silver(I) at a concentration of 1000 μg $L^{-1}$ was obtained from the Fluka Kamica (Bush, Switzerland). Working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. Concentrated nitric acid and hydrochloric acid were analytical reagent grade from Merck (Darmstadt, Germany) and were checked for possible trace silver(I) contamination by preparing blanks for proposed procedure. The ammonium pyrrolidinedithiocarbamate (APDC), were obtained from (Fluka) and prepared by dissolving appropriate amount of it in 10 mL of ethanol (Merck), then diluting to 100 mL with 0.01 mol $L^{-1}$ acetic acid and kept in refrigerator at 4 °C for one week. The 0.1 mol $L^{-1}$ of acetate and phosphate buffer were used to control the pH of the solutions. The pH of the samples was adjusted to the desired pH by the addition of (0.1 mol/L of HCl/NaOH) solution in the buffers. The glass and plastic wares were soaked in 10% nitric acid overnight and rinsed many times with deionized water to avoid contamination. Pipette tip and syringe from Huaxin Chemical Reagent (Baoding,China). The ACC used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225.

### 2.2. Instrumentation

A pH meter (Ecoscan Ion 6, Malaysia) was employed for pH adjustments. Global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations. The analysis of silver(1) was carried out by means of a double beam Perkin-Elmer AA Analyst 700 atomic absorption spectrometer (Norwalk, CT, USA), equipped with a graphite furnace HGA-400, pyrocoated graphite tube with integrated platform, an autosampler AS-800 and a deuterium lamp as background correction system. The single element hollow cathode lamp of silver (Perkin) was used as radiation sources at analytical wavelength 328.1 nm. The $Pd + Mg(NO_3)_2$) was used as modifier. Sample/standard solution with modifier was mixed in the ratio of (1:1) directly in the autosampler cups, and 20 μL was injected into the graphite furnace. The graphite furnace heating program was set for different steps: drying temperature °C (120/15/20)/ramp/hold(s), ashing temperature (°C)/ramp/hold(s) (500/5/15), atomization temperature(°C))/ramp/hold(s) (1900/0/3) and cleaning temperature(°C)/ramp/hold(s) (2100/1/2). Argon gas (200 mL/min) was used as the purge gas except during the atomization step. The integrated absorbance signals computed by the AA spectrometer were employed throughout. The surface morphology of ACC with and without sorbed silver(I) complex was carried out by scanning electron microscopy (SEM) (FEI Company, Hillsboro, USA). For the elemental analysis of silver(I) contents on ACC, energy dispersive X-ray (EDX) was performed using a XFlash® 4010 (Bruker).

### 2.3. Design of M-SPME in-syringe system

The proposed M-SPME in-syringe system setup was quite simple, a micropipette tip (100 uL polypropylene) was washed with distilled, ultra pure water and ethanol sequentially, then dried at room temperature. About 1.0 to 4.0 mg of ACC was packed into the micropipette tip and connected with syringe system. Prior to extraction, the ACC in the micropipette tip was conditioned by aspirating and dispensing repeatedly with acidic ethanol followed by distilled water to remove the co-adsorbed matrix materials from the extraction system. 2 mL of each standard (50 ng $L^{-1}$) and real sample were taken into vials (10 mL in capacity). Then 100 uL of borate buffer and 100 μL of APDC solutions ($1.0 \times 10^{-3}$ to $5.0 \times 10^{-3}$ mol $L^{-1}$) were added to the contents of tubes, pH was adjust at the range of 2–8, by the addition of 0.1 mol $L^{-1}$ of HCl/NaOH [39]. The aliquot of each sample/standard was aspirated into the conditioned micropipette tip syringe system and dispensed back into the same sample tube. These two steps are referred as one aspirating/dispensing cycle. The adsorption of the silver(I) onto the ACC was performed by 2–10 aspirating/dispensing cycles in a specific interval of time from 0.40–3.20 min. Finally, analyte retained on ACC were eluted with 50 μL of 2.5 mol $L^{-1}$ of $HNO_3$ into a vial using 2 to 5 aspirating/dispensing cycles in time of 0.2 to 1.0 min. The eluate aspirated back into the micropipette syringe system and inserted manually into the cup of autosampler cups for analysis.

## 3. Results and discussion

### 3.1. Characteristic and morphology of activated carbon cloth

The morphology of ACC was evaluated by SEM at different magnification power. It was observed in Fig. 1a, that the external surface of the ACC samples is smooth, which remarkably increases the surface area and demonstrates the porous nature of the activated carbon, which provides an enormous adsorption capacity for preconcentration of metal ions. SEM images of the metal complex (Ag–APDC) adsorbed on the surface of ACC samples is shown in Fig. 1b. It is evident that the surface of ACC becomes rough and irregular than without impregnation of Ag–APDC. The surface morphology of the Ag–APDC-adsorbed ACC also exhibits groove, which indicates that the surface is engraved because of the incorporation of metal complex by adsorption. The energy disperse X-ray spectrum of without loading Ag–APDC on ACC is shown in Fig. 2a, suggests that no foreign metals are present as an impurity on the adsorbent. Silver(I) peak was clearly observed on activated carbon cloth after pretreated with Ag–APDC as shown in Fig.2b.

### 3.2. Pyrolysis and atomization curves of silver(I) by ETAAS

The purpose of the pyrolysis step prior to the atomization is to remove the matrix as much as possible to reduce the magnitude of the background signal, which is very important in ETAAS measurements. In order to avoid silver(I) losing during the pyrolysis step, the optimal pyrolysis temperature should be selected. The experiment was designed to achieve complete vaporization and atomization of silver(I) in the graphite furnace. Fig. 3 shows the influence of pyrolysis temperature in the range of 200–1000 °C, on the relative response (%). The maximum absorbance was achieved in the range of 350–500 °C. Therefore, 450 °C was selected as the optimized pyrolysis temperature for the determination of silver(I). The effect of the atomization temperature, in the range of 1000–1900 °C, on the analytical signal of silver(I) was also studied and the results are shown in Fig.3. It was observed that, the maximum signal was obtained at 1700 °C and remained unchanged with the further increasing of temperature. The optimal pyrolysis and atomization