



## Modified Peanut Shell Micro-Column Solid Phase Extraction for the Determination of Silver in Environmental Water Samples by Flame Atomic Absorption Spectrometry

J. YANG\*, Y.M. ZHANG, F.P. CHEN and H.X. ZHANG

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou City, P.R. China

\*Corresponding author: Fax: +86 371 67756718; Tel: +86 371 67756733; E-mail: chemyj2011@126.com

(Received: 6 April 2011;

Accepted: 12 November 2011)

AJC-10642

Peanut shell was chemically modified with phosphoric acid and sodium diethyldithiocarbamate (DDTC), the obtained powder was used as solid phase extraction adsorbent for the determination of trace amounts of silver in environmental water samples by flame absorption spectrometry (FAAS). The effect of pH, sample flow rate and volume, elution conditions and co-existing ions on the recovery of the analyte was investigated. The results showed that silver could be adsorbed at pH 5 and eluted by 5 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>. Under the optimized conditions, the adsorption capacity of modified peanut shell was found to be 14 mg g<sup>-1</sup> for silver. The detection limit of the proposed method was 1.1 ng mL<sup>-1</sup> for silver with an enrichment factor of 16.3. The proposed method has been successfully applied to the determination of trace silver in Yellow river, Liusha river and Jialu river water. The recovery of silver for spiked samples was between 96 and 112 %.

**Key Words:** Modified peanut shell, Solid phase extraction, Silver, Environmental samples, Flame absorption spectrometry.

### INTRODUCTION

Silver is an essential environmental element and it is toxic for biological systems. Unfortunately, the silver contamination of environment became an environmental problem with the widespread use of silver compounds and silver-containing procedures in industry, medicine, jewellery, cloud seeding and in the disinfection of water. In many countries, silver impregnated filters are used for water disinfection and silver concentrations up to 200 µg L<sup>-1</sup> are permitted to maintain antimicrobial activities for human health<sup>1</sup>. It is possible for silver entered into environment from industry wastes because silver often presented as the impurity of different metal ores<sup>2</sup>. Also, information about the interaction between silver and essential nutrients, especially vitamin E and B<sub>12</sub>, selenium and copper, has focused attention on its potential toxicity<sup>3,4</sup>. Consequently, it is very important to develop sensitive and simple analytical methods for the monitoring silver in environmental.

Compared with other element detecting techniques, flame atomic absorption spectrometry (FAAS) has the characteristics of good precision and simplicity with lower cost and is one of the most popular used element detector. However, direct determination of metals at trace level by FAAS is often difficult, not only because of its insufficient sensitivity, but also because of matrix effects. To solve this problem, separation-preconcentration procedures are often involved prior to analysis by FAAS.

Preconcentration is a very important issue for improvement of sensitivity and separation is an efficient technique to reduce the interference of sample matrix<sup>5</sup>. Various separation-preconcentration procedures have been used for this purpose, including liquid-liquid extraction<sup>6,7</sup>, solid phase extraction<sup>8,9</sup>, ion exchange techniques<sup>10</sup>, coprecipitation<sup>11</sup> and cloud point extraction<sup>12,13</sup>.

Recently, solid phase extraction (SPE) technique has become increasingly popular for the enrichment of metal ions prior to their determination because of the following advantages over traditional liquid-liquid extraction, (i) high preconcentration factor; (ii) simple operation; (iii) rapid phase separation; (iv) can be combined with different detection techniques and (v) time saving and cost saving<sup>5</sup>.

It is well known that the adsorption medium plays a key role in improving the selectivity of solid phase extraction and much more attention has been paid to the investigation of new adsorption materials for solid phase extraction in recent years<sup>14</sup>. Many adsorption materials, such as chelating resins, silica gel, carbon sorbents, inorganic based sorbents, biological adsorption material and nanomaterials have been used in solid phase extraction<sup>5,14,15</sup>. Recently, it has been showed<sup>16-18</sup> that materials obtained from modified agriculture wastes, such as peanut shell, saw dusts, exhibit a large adsorption capacity towards heavy metal ions such as Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>5+</sup> and Pb<sup>2+</sup>. Modified peanut shell and soybean hull have been used as adsorbent of solid phase extraction for the preconcentration of trace Pb<sup>2+</sup>, Cd<sup>2+</sup>

and  $\text{Cu}^{2+}$  in food samples with larger adsorption capacity in previous work<sup>19,20</sup>, which showed that material obtained from agriculture wastes was an potential adsorbent for solid phase extraction. In this paper, the adsorbent was prepared with a different preparation procedure and packed in a homemade micro-column. The solid phase extraction preconcentration procedure was combined with FAAS for the determination of trace silver in food samples.

## EXPERIMENTAL

TAS-986 atomic absorption spectrometry (Beijing purkinje general instrument Co. Ltd., Beijing, China.) with silver hollow cathode lamps (KY-1) was used for the determination. The instrumental parameters used were those recommended by the manufacture. The pH values were controlled with a PHS-3C pH-meter (Shanghai precision & scientific instrument Co. Ltd., Shanghai, China). A HL-2S constant flow pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) and a self-made poly-tetrafluoroethylene (PTFE) micro-column (30 mm × 4.0 mm, i.d.) packed with modified peanut shell were used in the solid phase extraction process.

**Standard solutions and reagents:** All reagents used were analytical-reagent grade. The stock standard solutions (1.000 g L<sup>-1</sup>) of silver was prepared by dissolving appropriate amounts of silver nitrate (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) in deionized water. HCl (0.1 mol L<sup>-1</sup>), acetate-acetic acid buffer and NaOH (0.1 mol L<sup>-1</sup>) were used for pH adjustment. Different stock solutions of potentially interfering ions (1.000 g L<sup>-1</sup>) were prepared according to the conventional method. Working solutions were prepared daily by appropriate dilutions of stock solutions. The laboratory glassware was kept in a 5% (v/v) nitric acid solution overnight. Afterwards, it was rinsed thoroughly with deionized water and dried.

**Preparation of the adsorbent:** The cleaned and sieved (0.074 mm) 5 g peanut shell powder was added to 50 mL 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> for 1 h with the stirring of a magnetic stirrer. Then the supernatant was removed after standing and the powder left was dried at 50 °C. Subsequently, the powder was heated at 180 °C for 1.5 h. After that, the powder was washed with deionized water for several times in order to eliminate the redundant H<sub>3</sub>PO<sub>4</sub>. The resulting powder was dried at 50 °C. Then the dried powder was added to 50 mL sodium diethyldithiocarbamate (DDTC) solution (0.1 mol L<sup>-1</sup>) for 24 h with stirring. After cleaned by deionized water for three times, the resulting powder was dried at 50 °C for future use.

**Preparation of micro-column:** A total of 70 mg of modified peanut shell powder was filled into a PTFE micro-column (30 mm × 4.0 mm, i.d.) plugged with a small portion of absorbent cotton at both ends. Before use, deionized water was passed through the column in order to clean it.

**Procedure of column experiments:** In the column experiments, a 100.0 mL sample or standard solution containing silver was adjusted to pH 5.0 and was passed through the column by a peristaltic pump with 2.0 mL min<sup>-1</sup> of sample flow rate. Afterwards, silver retained on the column was eluted with 5.0 mL 0.5 mol L<sup>-1</sup> of HNO<sub>3</sub> with 0.5 mL min<sup>-1</sup> elution flow rate. Finally, the analyte in the effluents was determined by FAAS.

**Sample preparation:** Yellow river water, Liusha river water and Jialu river water (all rivers are in Henan province, China) was collected and several drops of HNO<sub>3</sub> (0.5 mol L<sup>-1</sup>) were added. Then the water was passed through 0.45 μm filtration membrane, the obtained water was used for determination.

## RESULTS AND DISCUSSION

**Effect of pH:** pH value plays a key role in the solid phase extraction procedure. An appropriate pH value can not only improve the adsorption efficiency, but also suppress the interference of the matrix. The adsorption behaviour of silver on modified peanut shell was studied according to the procedure of column experiments. Fig. 1 showed the effect of pH on the adsorption (R %) of silver on modified peanut shell. It can be seen that silver was adsorbed quantitatively (R larger than 90%) on modified peanut shell within a pH range of 4.0-5.5. The precipitate was observed at pH larger than 7, for further experiments, pH 5 was chosen for preconcentration of silver.

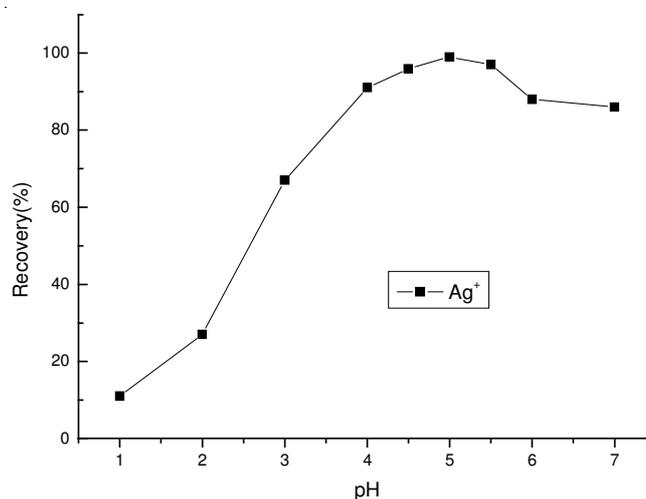


Fig. 1. Effect of pH on the adsorption (R %) of silver on modified peanut shell. The concentration of target analyte:  $\text{Ag}^+$  0.5 μg mL<sup>-1</sup>, sample flow rate: 2.0 mL min<sup>-1</sup>, sample volume: 50 mL, eluent flow rate: 0.5 mL min<sup>-1</sup>

**Optimization of elution conditions:** It is obvious from Fig. 1 that the adsorptions of silver decrease sharply with the decrease of pH value. For this reason, various concentrations (0.5-2.0 mol L<sup>-1</sup>) of HNO<sub>3</sub> were studied for the elution of retained analytes at 0.5 mL min<sup>-1</sup> of elution flow rate from the column with 50 mL standard solution containing 0.5 μg mL<sup>-1</sup> of silver. The results showed that quantitative recoveries (> 90%) could be obtained when the HNO<sub>3</sub> concentration was higher than 0.5 mol L<sup>-1</sup>.

The elution volume and elution flow rate could affect the elution efficiency remarkably. The effect of elution volume on the quantitatively elution of analytes was investigated by choosing 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> as elution solution. 6.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> was used to elute the analyte on the modified peanut shell, the eluent was collected at 0.5 mL intervals. Fig. 2 showed the recovery of analytes in each portion determined by FAAS. As can be seen, no analytical signal of silver was detected in the portion when elution volume larger than 5 mL.

That means quantitatively elution could be obtained when elution volume higher than 5 mL for silver. It was also found that quantitatively elution could be obtained with elution flow rate no more than 0.5 mL min<sup>-1</sup>. Thus, the elution conditions used in the following experiments were as follow: the elution solution was 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>, the elution volume was 5 mL and the elution flow rate was 0.5 mL min<sup>-1</sup>.

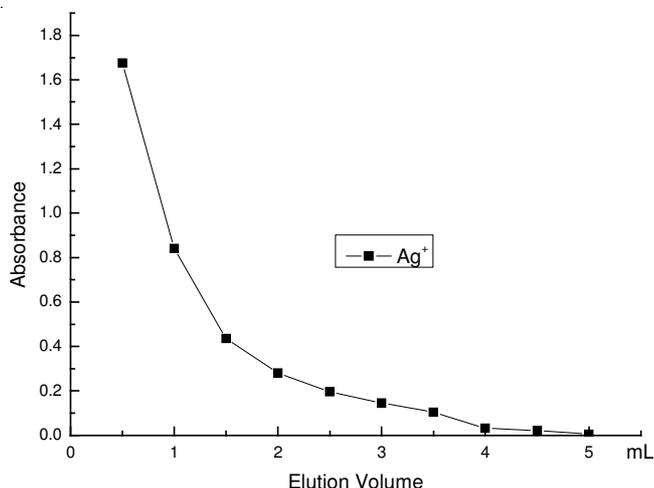


Fig. 2. Effect of eluent volume on the recovery of silver. The concentration of target analyte: Ag<sup>+</sup> 0.5 µg mL<sup>-1</sup>, sample flow rate: 2.0 mL min<sup>-1</sup>, sample volume: 50 mL, eluent flow rate: 0.5 mL min<sup>-1</sup>

**Effect of sample flow rate and sample volume:** The sample flow rate should be optimized to ensure quantitatively retention along with minimization of the time required for sample processing. It was found that the flow rate in the range of 0.2-2.0 mL min<sup>-1</sup> had no significant effect on the recoveries of silver according to the procedure of column experiments. For further experiments, 2 mL min<sup>-1</sup> was chosen as the sample flow rate.

In order to obtain a high or achievable preconcentration factor of very dilute analyte solutions from large volumes, it is imperative to investigate the effect of sample volume on the retention of analytes on the modified peanut shell. It was found that quantitative recovery for silver was obtained when sample volumes were less than 100 mL. So a theoretical enrichment factor of 20 can be achieved by this method.

**Effect of concomitant:** The effect of some co-existing ions on the preconcentration and determination of silver was investigated. In this experiment, the mixture solutions of 50 ng mL<sup>-1</sup> silver containing the added interfering ions were treated according to the procedure of column experiments. The content of silver in the effluent was determined in order to calculate the recovery of silver. The tolerances of the co-existing ions, defined as the maximum concentration that would achieve > 90 % recovery of the target analyte (Table-1). It can be seen that the presence of major cations had no obvious influence on the silver adsorption under the selected conditions.

**Column regenerability and adsorption capacity:** The regenerability and stability of the column was investigated by passing 100 mL of standard silver solution (50.0 ng mL<sup>-1</sup>) and then passing 5.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and 10 mL of deionized water through the column packed with 70 mg of modi-

TABLE-1  
TOLERANCE LIMITS OF CO-EXISTING IONS

Substance	Maximum tolerable amount	Recovery (%)
K <sup>+</sup> , Na <sup>+</sup>	0.6 mg mL <sup>-1</sup>	95.7
Ca <sup>2+</sup>	0.3 mg mL <sup>-1</sup>	93.4
Mg <sup>2+</sup>	0.3 mg mL <sup>-1</sup>	98.3
Fe <sup>3+</sup>	2.0 µg mL <sup>-1</sup>	101.2
Pb <sup>2+</sup>	0.5 µg mL <sup>-1</sup>	93.0
Cd <sup>2+</sup>	2.0 µg mL <sup>-1</sup>	102.3
Zn <sup>2+</sup>	1.0 µg mL <sup>-1</sup>	96.3
Cu <sup>2+</sup>	0.2 µg mL <sup>-1</sup>	94.6
Ni <sup>2+</sup>	2.0 µg mL <sup>-1</sup>	99.2

fied peanut shell. It was observed that the column could be reused up to 30 runs with the recoveries of the target ion larger than 90 %.

The adsorption capacity of modified peanut shell was studied in order to evaluate the amount of adsorbent required to quantitatively concentrate the analytes from a given solution. The method used was adapted from the recommended by Maquieira *et al.*<sup>21</sup>. The adsorption capacities of silver was 14 mg g<sup>-1</sup>.

**Analytical performance:** Under the optimized conditions, the analytical performance of the proposed method was evaluated. Based on the definition of IUPAC, the detection limits (3σ) of this method was 1.1 ng mL<sup>-1</sup> for silver, the relative standard deviation (RSD) were 2.9 % (c = 50 ng mL<sup>-1</sup>, n = 7). The calibration graph for the preconcentration procedure was A = 0.00252C + 0.00851 (R = 0.998) for 5-100 ng mL<sup>-1</sup> and the calibration graph without preconcentration was A = 0.000155C - 0.03048 (R = 0.997). The enrichment factor (EF, calculated as the ratio of the slopes of the calibration graphs with preconcentration and direct aspiration, respectively) was 16.3.

For comparative purposes, the performance characteristics of the proposed method and other selected off-line SPE/FAAS systems reported in the literature are given in Table-2. The proposed procedure shows larger adsorption capacity and comparable detection limit over other SPE off-line methods. Moreover, the adsorbent used in this work was easily prepared from agriculture wastes.

**Sample analysis:** The proposed method was applied to the determination of trace silver in river water (Yellow river, Liusha river and Jialu river). The analytical results and the recoveries for the spiked samples were given in Table-3. It could be seen that the recovery for the spiked samples is between 96 and 112 %.

## Conclusion

A simple, rapid and reliable method was developed for the preconcentration and FAAS determination of trace silver in environmental water samples by using sodium diethyldithiocarbamate modified peanut shell as micro-column packing material. The adsorption behaviour of silver on modified peanut shell had been systematically studied. It was found that modified peanut shell showed a high adsorption capacity for silver and the analyte retained on it could be easily desorbed. Hence, modified peanut shell showed great potential as an adsorbent for the preconcentration of trace metal ions in samples with complicated matrix.

TABLE-2  
COMPARATIVE DATA FROM SOME RECENT STUDIES ON OFF-LINE SPE/FAAS SYSTEM

Analyte	Absorbent	Adsorption capacity	Detection limit	Enrichment factor	Sample flow rate	Eluent/volume
Ag <sup>+</sup> Ni <sup>2+</sup>	Bacillus sphaericus-loaded chromosorb 106	Ag <sup>+</sup> 7.20 mg g <sup>-1</sup> Ni <sup>2+</sup> 6.55 mg g <sup>-1</sup>	Ag <sup>+</sup> 1.05 ng mL <sup>-1</sup> Ni <sup>2+</sup> 1.42 ng mL <sup>-1</sup>	25	250 mL 5.0 mL min <sup>-1</sup>	10 mL HCl (1.0M) <sup>22</sup>
Ag <sup>+</sup>	Bonded 2-mercaptobenzothiazole-silica gel	0.34 mg g <sup>-1</sup>	–	300	300 mL 10 mL min <sup>-1</sup>	1 mL sodium thiosulfate 0.005 M <sup>23</sup>
Ag <sup>+</sup>	Amberlite XAD-16 resin	4.66 mg g <sup>-1</sup>	47 ng mL <sup>-1</sup>	10	100 mL 2.5 mL min <sup>-1</sup>	10 mL KCN (1.0 M) <sup>24</sup>
Ag <sup>+</sup>	DDTC Modified peanut shell	14.0 mg g <sup>-1</sup>	1.1 ng mL <sup>-1</sup>	20	100mL 2.0 mL min <sup>-1</sup>	5.0 mL HNO <sub>3</sub> (0.5 M)

TABLE-3  
ANALYTICAL RESULTS FOR Cu<sup>2+</sup> IN RIVER WATER SAMPLES (MEAN ± SD, n = 3)

Sample	Added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	Recovery (%)
Yellow river water	0	–	–
	10	11.2 ± 0.4	112
	20	20.4 ± 0.7	102
Liusha river water	0	–	–
	10	10.6 ± 0.4	106
	20	19.8 ± 0.8	99
Jialu river water	0	–	–
	10	9.6 ± 0.3	96
	20	21.0 ± 0.6	105

#### ACKNOWLEDGEMENTS

Natural Science Fundamental Research Fund of Science and Technology Department of Henan Province (112300410080), Natural Science Fundamental Research Fund of Education Department of Henan Province (2009B150008) and Natural Science Foundation of Henan University of Technology (2006 BS005, 09XJC003) are gratefully acknowledged.

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