Carbon Nanotube-Coated Capillary Micro-extraction Combined with Graphite Furnace Atomic Absorption Spectrometry for the Determination of Cd, Hg, and Pb in Food Packaging Materials

Liying Zhang and Zhefeng Fan

Department of Chemistry, Shanxi Normal University, Linfen 041004, P.R. China

INTRODUCTION

The rapid development of food packaging materials used for packaging all kinds of foods, beverages, oils, and fats is of major health concern. Food bags contain metals which inevitably transfer to the food and thus enter the body. It is known that excess ingestion of metals can cause food-borne poisoning and metal pollution of food is one of the main types of pollution. Even at low concentrations, cadmium (Cd), lead (Pb), and mercury (Hg) are toxic substances for humans and animals. Hence, the determination of these elements in food packaging materials is important.

Because the amount of cadmium, mercury, and lead leaching from food packaging materials into the food is very small (on the order of a few ng mL⁻¹), powerful techniques are required and only a few available today show sufficient sensitivity. In order to achieve accurate, reliable, and sensitive results, a separation and pre-concentration step is often necessary prior to analysis. Current separation and pre-concentration techniques include liquid-liquid extraction (1), co-precipitation (2), solid phase extraction (3-6), solid-phase micro-extraction (7-9), and cloud point extraction (10-14).

Capillary micro-extraction (CME), developed from solid-phase micro-extraction (SPME), as a new

ABSTRACT

A simple and sensitive method was developed using carbon nanotube-coated capillary micro-extraction for the separation/pre-concentration of Cd, Hg, and Pb in food packaging materials prior to determination with a graphite furnace atomic absorption spectrometer. Carbon nanotube (CNT) sheets were immobilized onto the capillary wall using aminopropyltriethoxysilane as a coupling agent. Scanning electron microscopy (SEM) images provided visible evidence of the carbon nanotubes on the capillary wall.

The optimized experimental conditions, including matrix modifier agent, pH, sample volume, eluent concentration, volume, and coexisting ions were investigated. The limits of detection (3s) were as low as 0.41 ng mL⁻¹ for Cd, 0.24 ng mL⁻¹ for Hg, and 0.52 ng mL⁻¹ for Pb. The relative standard deviations (R.S.D.s) were 3.8%, 2.6%, and 2.1% (c=10 ng mL⁻¹, n = 7) for Cd, Hg, and Pb, respectively. The proposed method was successfully applied to the determination of Cd, Hg, and Pb in food packaging materials with satisfactory results.

direction in the solvent-less sample preparation for the pre-concentration of trace analytes, is a novel miniature extraction technique utilizing a capillary column as the extraction device. It uses a sportive coating on the inner surface of the capillary as the extraction medium in which the analyte in the aqueous sample is directly extracted and

pre-concentrated. CME techniques have been successfully applied to the determination of a variety of compounds in biological, environmental, and food samples. This technique offers several advantages such as simplicity and easy automation. It is a time-efficient, inexpensive, solvent-free sample pretreatment technique that easily couples with different separation and detection techniques (15-19). Mester and Pawliszyn first developed a method for the speciation of trimethyllead and triethyllead by CME on-line, coupled with LC-MS. Hu and co-authors (20-23) developed many CME systems for the trace element determination and speciation.

In capillary micro-extraction, selection of the appropriate extraction materials is most important. They are available in four major categories: inorganic coating materials, organic coating materials, organic-inorganic hybrid materials, and polymer materials.

Carbon nanotubes (CNTs) are a novel and interesting material first discovered in 1991. The CNTs have a hollow layered structure, a large specific surface area and aspect ratio, high chemical and thermal stability, where the end cap, cavity, and wall are easily modified, and thus an ideal adsorbent material. They have been successfully used to remove many kinds of pollutants due to their unique characteristic and strong adsorption capability (24). CNTs are promising to be a better capillary coating materials.

In this work, we developed a novel CNT-coated capillary for use in the determination of trace

*Corresponding author.
E-mail: zhefengfan@163.com
Fax: (86) 357-2051070

amounts of Cd, Hg, and Pb in food packaging materials by graphite furnace atomic absorption spectrometry (GFAAS).

EXPERIMENTAL

Instrumentation

A Model TAS-990 atomic absorption spectrometer (Puxi Instrument Factory, Beijing, P.R. China), equipped with deuterium lamp background correction and a transversally heated graphite atomizer, was used as the detection system. Cd, Hg and Pb hollow cathode lamps were employed as the radiation source at 228.80 nm, 253.7 nm, and 283.35 nm, respectively, with a slit width of 0.4 nm. Argon (99.99 %) was used as the protective and purge gas. The graphite furnace temperature program for the determination of Cd, Hg, and Pb is listed in Table I. A HL-2S peristaltic pump (Shanghai Qipu Instrument, P.R. China) was used to adjust the flow rate of the sample. All pH measurements were carried out using a PHS-3C digital pH meter equipped with a combination glass-calomel electrode (Shanghai Tianda, Shanghai, P.R. China). A scanning electron microscopy image of the CNT-coated capillary was taken with a JEOL-7500F electron micrograph (Japanese Electronics Instrument, Japan). Doubly deionized water was

obtained with a Milli-Q™ Plus purification system.

Reagents and Materials

The stock standard solutions of 1.0 mg mL⁻¹ of Cd, Hg, and Pb were prepared by dissolving spectral pure-grade Cd(NO₃)₂, HgCl₂, and Pb(NO₃)₂ (The First Reagent Factory, Shanghai, P.R. China) in doubly distilled water, respectively. A 50 mg mL⁻¹ amount of ammonium dihydrogen phosphate was used. The fused silica capillary was obtained from Hebei Yongnian Optical Fiber Factory, P.R. China. CNTs (Beijing Nachen Science Instrument Company, Beijing, P.R. China) were used to prepare the coating. Dimethylformamide (DMF) was obtained from Tianjin Guangfu Instrument Factory (Tianjin, P.R. China). Tetraethoxysilane (TEOS) (J&K Chemical LTD, <http://www.jkchemical.com>) and aminopropyltriethoxysilane were of analytical reagent grade (purchased from the Organic Silicon Material Company of Wuhan University, P.R. China). The pH was adjusted with 0.1 mol L⁻¹ NH₃·H₂O and 0.1 mol L⁻¹ HNO₃. All the other reagents used were of analytical reagent grade. All glassware was kept in 10% nitric acid for at least 48 hours and washed three times with doubly distilled water before use. Doubly distilled water was used throughout.

Preparation of CNT-coated Capillary

The schematic for the preparation of the CNT-coated capillary (Yongnian Optical Fiber Factory, Hebei, P.R. China, <http://www.rui-feng.com>) is shown in Figure 1. The fused silica capillary (100 cm, 0.25 mm, i.d.) was first activated with 0.1 mol L⁻¹ NaOH and then with 0.1 mol L⁻¹ HCl. After rinsing with doubly distilled water, it was dried for 8 hours under N₂ flow.

The aminopropyltriethoxysilane solution was prepared according to the method described in reference (20). Briefly, 2.0 mL TEOS was dissolved in a 5.0-mL mixture of ethanol/HCl (0.01 mol L⁻¹) (4/1, v/v) while stirring and also after the TEOS had completely hydrolyzed at room temperature for 30 minutes. After drop-wise addition of 0.5 mL aminopropyltriethoxysilane (dissolved in 1.0 mL ethanol), this mixture was stirred for another 30 minutes, leading to the formation of aminopropyltriethoxysilane-silica solution. The solution was stored to age for one day at room temperature before use. The aminopropyltriethoxy-silane-silica solution was allowed to fill the fused silica capillary and was sealed at both ends for six hours at 120 °C. Then it was driven out slowly under helium pressure (20 psi) and the capillary further purged with DMF for two hours.

A 50-mg amount of CNT was added to a 250-mL mixture of H₂SO₄/HNO₃ (3:1, v/v) and ultrasound at 40 °C for 24 hours, poured into 800 mL of water, and left standing for three days. After washing and drying, the sediment was brought to pH=7 by adding 5.0 mL of SOCl₂, and was kept at 75 °C for 24 hours.

The solution containing the CNTs was allowed to fill the capillary tube and sealed at both ends for 96 hours at 95 °C. Afterwards,

TABLE I
GFAAS Temperature Program for Determination of Cd, Hg, and Pb
(matrix modifier used: ammonium dihydrogen phosphate)

Step	Temperature (°C)			Ramp Time (s)			Hold Time (s)			Ar Flow (mL·min ⁻¹)		
	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb
Solvent evaporation	80	80	100	10			10			250		
Drying	100	100	100	10			10			250		
Pyrolysis	800	600	850	10			15			250		
Atomization	1700	1900	1800	0			3			0		
Cleaning	2300	2200	2400	1			2			250		

the capillary was further purged with DMF for one hour and then with methyl alcohol for 0.5 hours.

Sample Preparation

The packaging materials were cut into small pieces after cleaning, then soaked for two hours at 60 °C with 4% acetic acid for a 2 mL/cm² area. Then 15 mL of the soaking solution was transferred to a 25-mL volumetric flask, and made up to volume with 1% nitric acid.

Analytical Procedure

Sample solutions were prepared, and the pH value was adjusted to the desired value with 0.1 mol L⁻¹ NH₃•H₂O and 0.1 mol L⁻¹ HNO₃. The solution was passed through

the column by using a peristaltic pump at the desired flow rate. Afterwards, the metal ions retained on the column were eluted, and 0.1 mL of the matrix modifier was added. The analytes in the effluents were determined by graphite furnace atomic absorption spectrometer (GFAAS).

RESULTS AND DISCUSSION

Characterization of CNT Coating

The SEM image (Figure 2) reflects good coating of the CNTs in the capillary. It can be seen that as a nanometer-sized material, the coating surface has high chemical activity and adsorption capacity.

Effect of pH

The pH value plays an important role in the absorption of various ions on the CNT-coated capillary. The retention of Cd, Hg, and Pb on the CNT-coated capillary was investigated within the pH range of 1.0 to 8.0. The results in Figure 3 show that a quantitative absorption for Cd, Hg, and Pb was obtained in the pH range of 4.0 to 6.0. A pH of 5.0 was selected for the pre-concentration of Cd, Hg, and Pb in the further experiments.

Effect of Sample Flow Rate

The sample flow rate could have an influence on the retention of Cd, Hg, and Pb on CNT-coated capillaries. To study the effect of sample flow rate, 5.0 mL (containing 10 ng mL⁻¹ of the studied metal ion solution) was passed through the capillary at flow rates varying from 0.2 to 1.0 mL min⁻¹. It was found that quantitative recoveries were obtained for the studied metal ions with a sample flow rate below 0.8 mL min⁻¹. Allowing for the decrease in the adsorption kinetics at a high flow rate, a flow rate of 0.7 mL min⁻¹ was employed in this work.

Effect of Sample Volume

To study the effect of sample volume, various sample volumes from 1 to 50 mL, containing 30 ng of the studied metal ions, were

Fig. 1. Schematic of CNTs bonded to an open tube capillary column.

A = H₂SO₄/HNO₃ (3:1 v/v); B = SOCl₂, 75 °C, 24 h; C = DMF, WD-50, TEOS, 120 °C, 6 h; D = 95 °C, 96 h.

Fig. 2. Scanning electron micrographs of CNT-coated capillary. A = uncoated capillary; B = coated capillary.)

Fig. 3. Effect of sample pH on the absorbance of Cd, Hg, and Pb on CNT-coated capillary.

Cd, 10 ng mL⁻¹; Hg, 10 ng mL⁻¹; Pb, 10 ng mL⁻¹.

passed through the capillary, and the adsorbed metal ions were eluted with 0.1 mL 0.1 mol L⁻¹ nitric acid elution. It was found that quantitative recoveries were obtained for the studied metal ions with sample volumes below 35 mL. However, using larger amounts of the sample solution is time-consuming in this procedure. So, 5.0 mL samples were used for real sample analysis.

Eluent Volume and Flow Rate

The effects of eluent volume and flow rate from the CNT-coated capillary were investigated by using HNO₃ and HCl at different concentrations (0.1 to 1.0 mol L⁻¹), with the flow rates varying from 0.1 to 1.0 mL min⁻¹. It was found that quantitative recoveries were obtained for the studied metal ions with HNO₃. Quantitative recoveries for the metal ions were obtained with 0.1 mL of 0.1 mol L⁻¹ HNO₃ for Cd, Hg, and Pb at a flow rate of 0.4 mL min⁻¹.

Regeneration of CNT-coated Capillary

Regeneration is another important factor in evaluating the adsorption material. The CNT-coated capillary was easily regenerated by using 1 mL of 0.1 mol L⁻¹ HNO₃ at a flow rate of 0.4 mL min⁻¹. Under this circumstance, the capillary could be used for more than 80 times without decreasing the adsorption efficiency.

Effects of Coexisting Ions

Interference by other coexisting ions, such as K⁺, Na⁺, Mg²⁺, Ca²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Al³⁺, was studied by using solutions of 10 ng mL⁻¹ of Cd, Hg and Pb. The tolerance limits of the coexisting ions, defined as the largest amount that would result in the recovery of the studied element of less than 95%, were 10 mg mL⁻¹ for K⁺, Na⁺; 5 mg mL⁻¹ for Mg²⁺; 3 mg mL⁻¹ for Ca²⁺; 500 µg mL⁻¹ for Mn²⁺; 300 µg mL⁻¹

for Fe²⁺; 80 µg mL⁻¹ for Fe³⁺, and 50 µg mL⁻¹ for Al³⁺. From the experimental results obtained, it can be concluded that the CNT coating material had an excellent selectivity towards Cd, Hg, and Pb under the optimized conditions; the developed method was not affected by potential interferences.

Analytical Performance

The performance of the pre-concentration system using the CNT-coated capillary is shown in Table II which demonstrates that this method is more sensitive. The limit of detection (LOD), calculated according to three times the standard deviation of the blank, was 0.41 ng mL⁻¹ for Cd, 0.24 ng mL⁻¹ for Hg and 0.52 ng mL⁻¹ for Pb, with an enrichment factor of 15.2, 15.4 and 12.7, respectively (the standard before the enrichment of the curve slope divided by the slope of the standard curve after enrichment). The relative standard deviations (RSD) were as follows: Cd = 3.8%, Hg = 2.6%, and Pb = 2.1% (c=10 ng mL⁻¹, n = 7).

Sample Analysis

To further verify the accuracy of the developed method, we analyzed three kinds of packaging

materials. To calculate the recovery efficiency of this method, the sample solution was spiked with 0.5 ng mL⁻¹ Cd, Hg, and Pb. The results in Table III show that very good recoveries were obtained ranging from 96–106%.

CONCLUSION

To our knowledge, this article is the first in publishing the use of carbon nanotubes (CNTs) as the capillary wall coating material for metal ion separation, for use as a more accurate and effective analysis method for the determination of trace and even trace heavy metal ions. In this study, the CNTs have been successfully employed for the capillary micro-extraction (CME) of trace Cd, Hg, and Pb from food packaging materials. Also, a high recovery from 96% to 106% was obtained. It is obvious that this method is more sensitive, inexpensive and simple, and very suitable for the determination of heavy metals in food packaging materials.

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TABLE II
Performance Data for Cd, Hg, and Pb Speciation by GFAAS

Parameters	Cd	Hg	Pb
Working range (ng mL ⁻¹)	0.41–100	0.24–90	0.52–110
Calibration curve (ng mL ⁻¹)	A= 0.0072C + 0.0235	A= 0.0686C + 0.0321	A= -3.9997C + 0.0058
Correlation coefficient	0.9984	0.9976	0.9969
Enrichment factor	15.2	15.4	12.7
Precision (%)	3.81	2.62	2.13
Detection limit (3s) (ng mL ⁻¹)	0.41	0.24	0.52

TABLE III
Analytical Results (mean $\pm$ s, n=3) for Cd, Hg, and Pb in Food Packaging Materials

Sample	Element	Found (ng mL ⁻¹)	Added (ng mL ⁻¹)	Total (ng mL ⁻¹)	Recovery (%)	RSD (%)
Dixie cup	Cd	0.39	0.5	0.90 $\pm$ 0.12	102	2.06
	Hg	0.25	0.5	0.74 $\pm$ 0.07	98	1.95
	Pb	0.28	0.5	0.80 $\pm$ 0.15	104	2.26
Plastic wrap	Cd	0.31	0.5	0.79 $\pm$ 0.18	96	1.78
	Hg	0.36	0.5	0.85 $\pm$ 0.16	98	2.58
	Pb	0.43	0.5	0.97 $\pm$ 0.13	108	3.05
Plastic packages	Cd	0.28	0.5	0.77 $\pm$ 0.12	98	2.86
	Hg	0.49	0.5	1.02 $\pm$ 0.09	106	2.47
	Pb	0.65	0.5	1.17 $\pm$ 0.14	104	3.02

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