



## Application of multiwalled carbon nanotubes treated by potassium permanganate for determination of trace cadmium prior to flame atomic absorption spectrometry

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### Abstract

In this study we investigated the enrichment ability of oxidized multiwalled carbon nanotubes (MWCNTs) and established a new method for the determination of trace cadmium in environment with flame atomic absorption spectrometry. The MWCNTs were oxidized by potassium permanganate under appropriate conditions before use as preconcentration packing. Parameters influencing the recoveries of target analytes were optimized. Under optimal conditions, the target analyte exhibited a good linearity ( $R^2=0.9992$ ) over the concentration range 0.5–50 ng/ml. The detection limit and precision of the proposed method were 0.15 ng/ml and 2.06%, respectively. The proposed method was applied to the determination of cadmium in real-world environmental samples and the recoveries were in the range of 91.3%–108.0%. All these experimental results indicated that this new procedure could be applied to the determination of trace cadmium in environmental waters.

**Key words:** multiwalled carbon nanotubes (MWCNTs); solid-phase extraction; flame atomic absorption spectrometry

### Introduction

Cadmium, a heavy metal, is toxic to plants, animals and human beings. Research had shown that cadmium exhibited placental toxicity by restraining the proliferation of trophoblast cells which also affects the establishment of a viable pregnancy (Powlin *et al.*, 1997). Long-term expose of cadmium also induces renal damage (Min *et al.*, 1996). So cadmium is considered as one of the priority pollutants for monitoring in most countries and international organizations.

Nowadays, various technologies and methods have been developed for the analysis of heavy metal ions at trace levels, including stripping potentiometry, stripping voltammetry, flame atomic spectrometry, hydride generation atomic absorption spectrometry, electrothermal atomic absorption spectrometry (ETAAS) and X-ray fluorescence (Viksna and Lindgren, 1997; Hu *et al.*, 2003; Flores *et al.*, 2001, 2003; Acar, 2005; Pinzani *et al.*, 2002). Recently, many advanced apparatus of high sensitivity, such as inductively coupled plasma mass spectrometry

(ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), have been introduced and applied in analytical chemistry. Coupled with the preconcentration techniques, the detection limits for ICP-MS and ICP-AES are at the very low ng/L and ng/ml, respectively, which may be useful for the determination of trace metals in real samples (Hu *et al.*, 2006; Xia *et al.*, 2006; Zougagh *et al.*, 2002; Cui *et al.*, 2006). However, the cost of operation is very high, which makes them difficult to be used for routine analysis, and restricts their application in many fields. Compared with these new methods, flame atomic absorption spectrometry (AAS) is the most widely used method for the determination of metal ions due to its simple operation, low expense and high selectivity. Recently, AAS technology has been significantly improved. Compared with the conventional technique, the use of the L'vov platform in graphite furnace atomic absorption spectrometry enhances the sensitivity. Ma *et al.* (1999) compared the analytical performance of tungsten-coated non-pyrolytic graphite, pyrolytic graphite and pyrolytic L'vov platform graphite (PPG) tubes for the determination of gallium and found that the tungsten-coated PPG provided the best with the detection limit of 6 pg. The use of a microemulsion also enhanced the sensitivity and decreased the background signals (Cassella *et al.*, 2004). In addition, good recoveries, low background levels and rapid analysis could be obtained with the use of

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permanent modifiers in ETAAS for the detection of heavy metals in real samples (Giacomelli *et al.*, 2004). Although these methods can markedly increase the sensitivity, they can not meet the requirement for direct determinations, because of the interference of the complicated matrix in the real samples, pre-separation and preconcentration are important procedures for the high sensitivity and accuracy.

Conventional techniques for the separation and preconcentration of trace substances include liquid-liquid extraction, in which a large volume of organic solvent is used. Although room-temperature ionic liquids have been considered as a new green solvent and successfully applied to the extraction of metal ions from aqueous solutions (Wei *et al.*, 2003), this technique has been gradually replaced by some new methods, which have a low consumption of organic solvent and high enrichment factor, such as solid phase extraction (SPE), cloud point extraction, liquid membrane transport extraction and continuous ultrasound-assisted extraction (Ersöz *et al.*, 2004; Liang *et al.*, 2005; Sakamoto *et al.*, 2005; Yebra-Biurrun *et al.*, 2005). SPE is simple, rapid, efficient, easy to operate and popular for the enrichment of metal ions from water samples. In SPE, the packing materials are the crucial factor to obtain high recoveries. C18, activated carbon, modified silica, ion-imprinted compounds and biological substances were very popular materials (Ersöz *et al.*, 2004; Qi and Danielson, 2005; Gil *et al.*, 2006; Maltez and Carasek, 2005; Krishna *et al.*, 2005).

Carbon nanotubes (CNTs), a new and excellent material, were introduced in the 1990's. Compared with other common materials, this new material has many special advantages. It can also be used as an electrochemical biosensor for the determination of organophosphate pesticides, and used to modify electrodes for the absorptive stripping voltammetric detection and enzyme-based electrical detection of DNA hybridization (Deo *et al.*, 2005; Wang *et al.*, 2004a, b). However, one of the advantages is its adsorption ability. Many publications have indicated that multi-walled carbon nanotubes (MWCNTs) possessed excellent adsorptivity for organic pollutants such as bisphenol A, 4-*n*-nonylphenol, 4-*tert*-octylphenol and phthalate esters (Cai *et al.*, 2003a, 2003b). Wang *et al.* (2006b) had applied MWCNTs to the clean-up and preconcentration of benzodiazepine residues including diazepam, estazolam, alprazolam and triazolam in pork and established a new method for the simultaneous determination of these four compounds by GC-MS. Multi-walled carbon nanotubes had been also used as adsorbent for solid phase extraction of ten sulfonamides. This preconcentration method combined with high performance liquid chromatography had achieved the simultaneous determination of ten sulfonamides in eggs and pork (Fang *et al.*, 2006). Wang had applied MWCNTs to solid phase microextraction by fibers which were coated with MWCNTs. And the comparison of adsorbent effect to polybrominated diphenyl ethers was taken in MWCNTs coating fibers, active carbon coating fibers and PDMS-DB coating fibers. The results indicated that MWCNTs coating fibers giving much higher enrichment factors than active carbon and

PDMS-DB coating fibers (Wang *et al.*, 2006a). In addition, these materials could also used as adsorbent to Cr<sup>6+</sup> after forming chelate with ammonium pyrrolidine dithiocarbamate (Tuzen and Soylak, 2007).

Li *et al.* (2003) found that, compared with the as-grown CNTs, the adsorption capability for cadmium increased after it was oxidized by nitric acid, potassium permanganate and hydrogen peroxide. They also indicated that CNTs oxidized by potassium permanganate possessed higher adsorption capability than the other two. The reason is that hydroxyl, carboxyl or carbonyl were introduced to the surface of MWCNT at its defect sites (Zhang *et al.*, 2003; Li *et al.*, 2003), then metal ions would be adsorbed onto the surface of MWCNTs when solution containing metal ions flowed through these materials. Metal ions may be adsorbed by chemisorption process when they are present as free ions. On the other hand, physisorption would occur when the metal ions were chelated with chelators before flowing through the SPE cartridge. Up to now, there are no reports on the enrichment power of MWCNTs oxidized by potassium permanganate. In this article, the absorptive performance of MWCNTs oxidized by potassium permanganate was studied and the influence of some parameters was optimized using cadmium as the model element.

## 1 Experimental

### 1.1 Apparatus

A Z-5000 Polarized Zeeman atomic absorption spectrophotometer (Hitachi, Ltd., Japan) fitted with cadmium hollow cathode lamp was used. This apparatus was equipped with Zeeman effect background correction. The main instrument parameters are listed in Table 1. Packed cartridges of modified MWCNTs used in these experiments were prepared by modifying an Agilent ZORBAX SPE C18 (EC) cartridge (0.2 g, 3 ml, and polypropylene). Approximately 200 mg of MWCNTs were packed into the cartridges after the C18 packing was removed. The polypropylene upper frit and lower frit were retained at each end of the cartridge to hold the adsorbent packing in place. A model SHZ-3 (III) vacuum pump (Yuhua Instrument Co., Ltd., Zhengzhou, China) was used during the preconcentration process. Ultrapure water was prepared in the lab using a "Ultra-Clear" (SG Wasseraufbereitungsanlagen, Barsbüttel, Germany) water treatment device.

**Table 1 Instrument parameters for flame atomic absorption spectrometry (F-AAS)**

Parameter	
Lamp current (mA)	9
Wavelength (nm)	228.8
Slit (nm)	1.3
Burner head	Standard type
Burner height (mm)	5.0
Flame	Air-acetylene
Oxidant gas pressure (kPa)	160
Fuel gas flow rate (L/min)	2.0

## 1.2 Standard solutions and reagents

A stock standard solution (160  $\mu\text{g/ml}$ ) was obtained by dissolving ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) in ultrapure water. Working standard solutions were obtained by appropriate dilution of the stock standard solution. Diluted nitric acid and ammonia were used to adjust pH of the working solutions.

MWCNTs with an average external diameter of 30–60 nm were kindly provided by Tsing-Nafine Nano-Powder Commercialization Engineering Center, Chemical Engineering Department of Tsinghua University (Beijing, China). Before use, the MWCNTs were oxidized in a solution of potassium permanganate at  $80^\circ\text{C}$  for 2.5 h. The oxidized MWCNTs were washed with deionized water to remove remnant oxidant. Finally, the oxidized adsorbent was dried at  $100^\circ\text{C}$  for 2 h and transferred to the micro-column containing a frit at the bottom and in combination with a vacuum pump.

## 1.3 General procedure

Before use, the MWCNTs minicolumn was washed with 50 ml of 1 mol/L  $\text{HNO}_3$  and 50 ml ultrapure water to remove contaminants. The SPE procedure for  $\text{Cd}^{2+}$  ions was as follows: MWCNTs were pre-wetted with 10 ml of 1 mol/L  $\text{HNO}_3$  and 10 ml ultrapure water, then, the working solution containing  $\text{Cd}^{2+}$  ions of 16 ng/ml was passed through the minicolumn. After the target analyte was quantitatively adsorbed onto the MWCNTs, 5 ml of 0.5 mol/L  $\text{HNO}_3$  was used as eluent. Finally, the concentration

of the  $\text{Cd}^{2+}$  in the eluent was directly determined by F-AAS.

## 1.4 Water samples

Four water samples were collected, the snow samples were taken from Henan Normal University when the first snow came in 2006, two industrial samples of wastewater were collected from a preliminary sedimentation tank for the treatment of wastewater and final drainage exit after disposal in Huangyu Electrical Appliance Industry Company, Wenzhou, China, and the last wastewater was collected from waterspout in a sewage treatment plant at Luotufeng in Xinxiang. All of the water samples were immediately filtered through a  $0.45\text{-}\mu\text{m}$  membrane after collection and stored in brown reagent bottles at  $4^\circ\text{C}$ .

## 2 Results and discussion

### 2.1 Condition optimization

#### 2.1.1 Sample pH

Literature indicated that adsorption of cadmium by oxidized CNTs was strongly pH-dependent and some functional groups may be introduced to its surface after oxidation compared with as-grown CNTs (Li *et al.*, 2003). The pH values of the working solutions were adjusted between 2–10 and the other conditions were kept invariable. The final experimental results are given in Fig.1a. It is obvious that when the pH values of the working solution

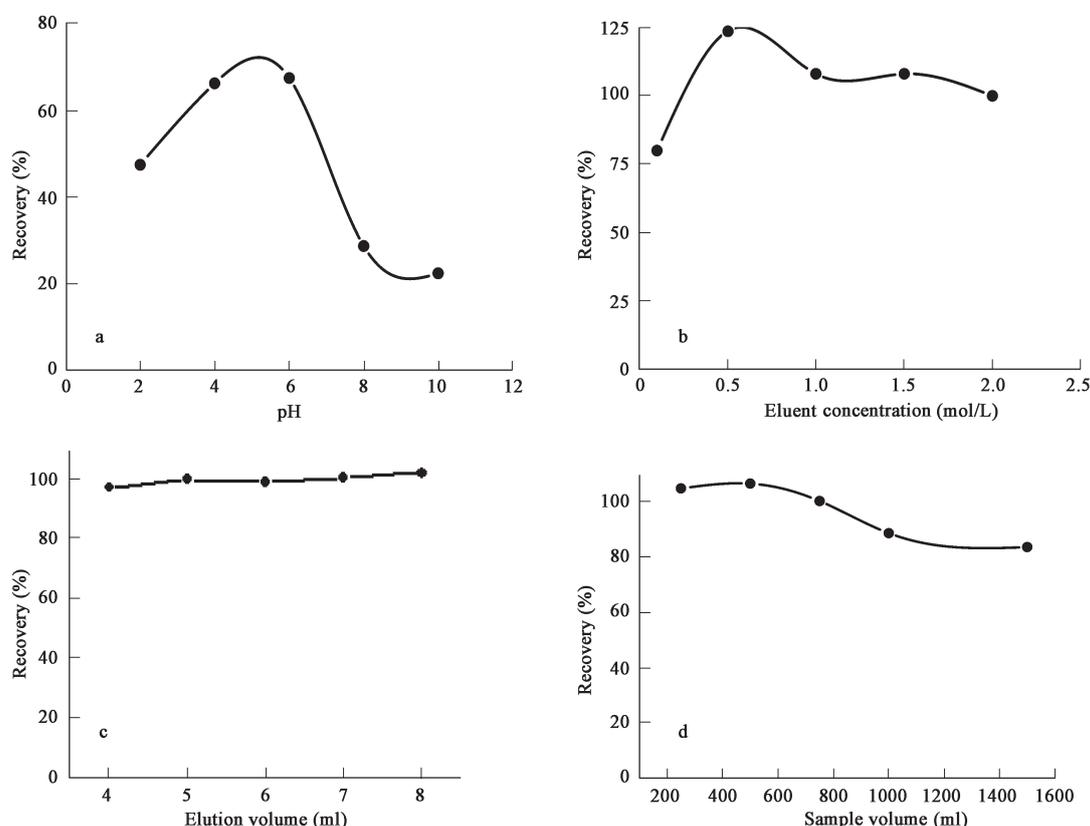


Fig. 1 Effect of pH (a), eluent concentration (b), eluent volume (c), and sample volume (d) on the recovery of  $\text{Cd}^{2+}$  using functionalized MWCNTs.  $\text{Cd}^{2+}$ : 16 ng/ml.

were between 4 and 6, the recoveries of Cd<sup>2+</sup> on adsorbent were higher under other conditions. In order to control the condition easily, the pH of working solution was selected as 6.

### 2.1.2 Eluent concentration and volume

An appropriate eluent should elute the target analyte efficiently and also have no interference in the subsequent determination of ion. Five different concentrations of nitric acid was compared for this purpose in the process (Fig.1b). It can be seen that the retention was relative strong, the recovery of target analyte was low and cannot be eluted completely when the concentration of eluent was 0.1 mol/L. But the recovery of Cd<sup>2+</sup> was increased sharply when the concentration of nitric acid was increased to 0.5 mol/L. The concentration of nitric acid was thus selected as 0.5 mol/L. Usually, the concentration of Cd<sup>2+</sup> in environmental samples is very low, to acquire the maximal enrichment factor and meet the requirement of injection volume for F-AAS, the eluent volume was optimized between 4 and 8 ml. The results measured by F-AAS are presented in Fig.1c. From the data it can be seen that when the eluent volume was up to 4 ml and more, the recoveries did not significantly change. Finally, 5 ml was selected to obtain an ultimate balance between the eluting time and injection volume for F-AAS.

### 2.1.3 Sample flow rate

The flow rate of sample is an important parameter that controls the time of analysis and affects the retention of target analyte on the minicolumn. In order to reach the requirement of rapid throughput, the sample flow rate was investigated. We found that when the flow rate of sample was increased, there was no significant impact on the recoveries of Cd<sup>2+</sup> and thus in the following study (data not shown here), the maximal flow rate was used.

### 2.1.4 Sample volume

As is well known, the adsorption capacity of materials used as adsorbent is an important factor for achieving a high enrichment factor, however, a more direct way to enhance the detection limit of a method is to increase the sample volume. The sample volume was investigated over the range of 250–1500 ml. The results in Fig.1d show that the recoveries of Cd<sup>2+</sup> were between 106.7% and 100.4% for sample volumes up to 750 ml. For sample volumes up to 1000 and 1500 ml, the recoveries of Cd<sup>2+</sup> were down to 88.8% and 83.8%. For achieving the quantitative absorption of Cd<sup>2+</sup>, the sample volume should be selected between 250 and 750 ml. Because a large volume would be time consuming to process, 250 ml was selected for further use.

## 2.2 Effect of coexisting ions

Tuzen and Soylak (2007) reported that many metal ions can be adsorbed by MNCNTs. Due to the existence of the competitive adsorption the influence of concomitant ions on the adsorption of Cd<sup>2+</sup> on the adsorbent in solution should be investigated. In this research, the concentration of Cd<sup>2+</sup> in the working solution was maintained at 16

ng/ml. Solutions containing different ions of different concentration were passed through the column under the optimum conditions chosen from the earlier experiments. The results are given in Table 2. The results suggested that the presence of large amounts of coexisting ions have no obvious influence on the recovery of Cd<sup>2+</sup>.

**Table 2 Effect of coexisting ions on the recovery of Cd<sup>2+</sup> (Cd<sup>2+</sup>: 16 ng/ml)**

Coexisting ion	Concentration of coexisting ions (µg/ml)	Recovery Cd <sup>2+</sup> (%)
Na <sup>+</sup>	80	98.8
K <sup>+</sup>	48	101
Mg <sup>2+</sup>	16	87.5
Ca <sup>2+</sup>	16	91.3
Ni <sup>2+</sup>	0.8	109
Cu <sup>2+</sup>	0.8	97.5
Al <sup>3+</sup>	0.4	95.0
Fe <sup>3+</sup>	0.4	106
SO <sub>4</sub> <sup>2-</sup>	80	98.8
Cl <sup>-</sup>	48	101

## 2.3 Analytical performance

A series of experiments were designed to investigate other parameters, including linear range, correlation coefficients and detection limit for obtaining better analytical performance. These procedures were carried out under the optimal conditions. The results indicated that there was an excellent linear correlation between ABS and the Cd<sup>2+</sup> concentration from 0.5 to 50 ng/ml. The correlation coefficient is 0.9992. The detection limit (calculated as the concentration corresponding to three times the standard deviation of 11 runs of the blank samples) of this method for cadmium is 0.15 ng/ml, and the precision of the proposed method is 2.06% (*n*=6) at 5 ng/ml.

## 2.4 Analytical application

In order to demonstrate the applicability and reliability of the proposed method for realworld samples, four environmental samples, including snow, two industrial wastewaters and that from a waterspout in a sewage treatment plant were collected. Three spiked and two blank for each real water sample were passed through the column according to the above-mentioned procedure. The contents of cadmium in blank solution of four samples were found, they were 0.5, 2.8, 1.3 and 0.6 ng/ml, respectively. Subsequently extraction step to four samples spiked with cadmium at 5 ng/ml were processed as the described above. The concentration of Cd<sup>2+</sup> was determination by F-AAS and the results were given in Table 3. The recoveries of Cd<sup>2+</sup> were in the range of 91.3%–108.0%. All these

**Table 3 Recoveries of Cd<sup>2+</sup> spiked into environmental samples (5 ng/ml)**

Samples	Blank (ng/ml)	Recovery (%)
Snow water	0.5	91.3±4.6
Waste water 1	2.8	108.0±4.0
Waste water 2	1.3	104.7±4.6
Waster water 3	0.6	101.3±4.6

results indicate that this proposed method can be used to determine the content of cadmium in real water samples.

### 3 Conclusions

A simple and reliable method for the separation, pre-concentration and determination of trace cadmium in real samples was established using MWCNTs functionally oxidized by potassium permanganate used as a solid-phase adsorbent. The results obtained showed that these functional MWCNTs possess high analytical potential for pre-concentration of trace cadmium from environmental waters and can be reused many times. Compared with the MWCNTs oxidized by nitric acid, this oxidation procedure (refluxing with potassium permanganate) was very safe. A very low detection limit of 0.15 ng/ml was obtained and precision better than 2.06% was achieved. The experimental results from the analysis of the content of Cd<sup>2+</sup> in real samples demonstrated that satisfactory recoveries (between 91.3% and 108.0%) were achieved. All data proved that the established method could be effectively applied to the analysis of trace cadmium in environmental waters.

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