



# Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS

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## ARTICLE INFO

### Article history:

Received 8 November 2011  
Received in revised form 20 March 2012  
Accepted 22 March 2012  
Available online 2 April 2012

### Keywords:

Schiff base-chitosan grafted multiwalled carbon nanotubes  
Solid-phase extraction  
Metals ions  
Inductively coupled plasma mass spectrometry

## ABSTRACT

A novel Schiff base-chitosan-grafted multiwalled carbon nanotubes (S-CS-MWCNTs) solid-phase extraction adsorbent was synthesized by covalently grafting a Schiff base-chitosan (S-CS) onto the surfaces of oxidized MWCNTs. The adsorbent was characterized by Fourier-transform infrared spectroscopy, transmission electron microscopy, and thermal gravimetric analysis. The results showed that S-CS was successfully grafted onto the surfaces of MWCNTs. A method was developed for the determination of heavy metals, namely V(V), Cr(VI), Cu(II), As(V) and Pb(II) in biological and environmental samples by inductively coupled plasma mass spectrometry coupled with preconcentration with S-CS-MWCNTs. The parameters influencing preconcentration of target ions, such as the pH of the sample solution, the flow rate of sample loading, the eluent concentration, and eluent volume, were investigated and optimized. Under the optimal conditions, the enrichment factors of V(V), Cr(VI), Cu(II), As(V), and Pb(II) reached 111, 95, 60, 52, and 128, respectively, and the detection limits were as low as 1.3–3.8 ng L<sup>-1</sup>. The developed method was successfully applied to the determination of trace-metal ions in herring, spinach, river water, and tap water with good recoveries ranging from 91.0% to 105.0%.

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## 1. Introduction

Rapid industrial development is resulting in increasing levels of heavy metal residues in biological and environmental samples, and this problem has been receiving much attention because of the toxic effects of such residues on human health and plant growth [1–3]. These metal ions can gradually accumulate in the human body through the food chain. When the amounts are excessive, the metals can be hazardous to human health [4,5]. Quantifications of trace metals in biological and environmental samples using advanced instrumental techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) [6,7], inductively coupled plasma mass spectrometry (ICP-MS) [8,9], electrothermal atomic adsorption spectrometry (ETAAS) [10,11], and flame atomic absorption spectrometry (FAAS) [12,13] have been reported. Compared with other techniques, ICP-MS has advantages such as accuracy, speed, multi-elemental determination and low determination limits [14,15]. However, low concentrations of metal ions and matrix interference in samples make direct determination using ICP-MS very difficult. Preconcentration procedures are

therefore necessary to improve the sensitivity and selectivity in trace-metal determination.

It is well known that solid-phase extraction (SPE) not only has many advantages such as high enrichment factors, low reagent consumption, simplicity, and environmental friendliness, but it can also be combined with different detection techniques in on-line or off-line modes [16]. The adsorbent plays a key role in SPE procedures. Research on new adsorbents that can preconcentrate and separate metal ions from complex samples has therefore been attracting increasing attention in the analytical sciences.

Since they were first reported in 1991, carbon nanotubes (CNTs) have attracted great interest because of their unique mechanical properties, high chemical stability, large specific surface area, and large number of potential applications [17,18]. CNTs are considered to be superior materials for adsorbing different analytes from samples because of their outstanding structural and chemical stabilities [19]. Some SPE methods using multiwalled carbon nanotubes (MWCNTs) or modified MWCNTs as adsorbents for preconcentration and separation of metal ions and organic compounds in real samples have been reported [20–24]. MWCNTs modified using special functional groups or polymers have proved to be more selective than raw or oxidized MWCNTs because of their exceptional properties [3,25]. CNTs modified with polymers such as 2-aminobenzothiazole [3], iminodiacetic acid [5], ethylenediamine [25], L-cysteine [26] and chitosan (CS) [27], by covalent or

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non-covalent interactions, have been applied for metal ion pre-concentration. However, covalent functionalization of CNTs with polymers has proved to be an effective way to improve their dispersion stability and make the resulting composites more stable and controllable [28]. CS, a natural polysaccharide with similar structural characteristics to cellulose, obtained by the deacetylation of chitin. It is a biocompatible, biodegradable, and non-toxic natural biopolymer and has excellent film-forming abilities [28]. CS can selectively adsorb some metal ions, and has been successfully used in wastewater treatment [31]. However, because CS is very sensitive to the pH of ionic solutions, its applications are limited. Several strategies [32] have been devised to prepare CS derivatives that are insoluble in acid solutions and to preserve the adsorption capacity of CS. In order to increase the chemical stability of CS in acid solutions and improve its metal-ion-adsorbing properties, Schiff base-chitosan (S-CS) was produced by grafting aldehydes onto the CS backbone [33]. Although the preparation of CS-modified MWCNTs via covalent interactions have been reported by a few groups [29,30], so far no work has been published on the application of MWCNTs covalently modified with CS derivatives to SPE column preconcentration for ICP-MS determination of trace metals.

In this study, we describe the synthesis and characterization of the composite S-CS-grafted MWCNTs (S-CS-MWCNTs) prepared by covalent modification of MWCNTs with S-CS. We also developed a method for the determination of heavy metals, namely V(V), Cr(VI), Cu(II), As(V), and Pb(II), in biological and environmental samples using ICP-MS coupled with preconcentration using S-CS-MWCNTs.

## 2. Experimental

### 2.1. Instrumentation

The detection system used for the determination of heavy-metal ions was an Agilent model 7500cx ICP-MS (Agilent Technologies, Santa Clara, CA, USA). All the operating parameters were those recommended by the manufacturer. The optimum operating conditions and measurement parameters for ICP-MS are listed in Table 1. The S-CS-MWCNTs were characterized using a Vector 22 Fourier-transform infrared (FT-IR) spectrometer (Bruker, Germany), a JEM-2010 FEF transmission electron microscope (TEM) (JEOL, Tokyo, Japan), and an SDTA851 thermogravimetric analyzer (TGA) (Mettler, Zurich, Switzerland). The pH values were controlled using a pH meter (Mettler Toledo Instruments Co., Ltd., China) supplied

**Table 1**  
Operating conditions for ICP-MS.

Nebulizer	Babington
Spray chamber	Quartz, double pass
RF power (kW)	1.5
Carrier gas flow rate (L min <sup>-1</sup> )	0.9
Makeup gas flow rate (L min <sup>-1</sup> )	0.15
Sample uptake rate (mL min <sup>-1</sup> )	0.3
Detection mode	Auto
Integration time (s)	0.1
Analytical masses	<sup>51</sup> V, <sup>53</sup> Cr, <sup>63</sup> Cu, <sup>75</sup> As, <sup>208</sup> Pb

with a combined electrode. A DBIII hot plate (Jia De Instruments Co., Ltd., China) was used in the preparation of sample solutions.

### 2.2. Reagents and solutions

High-purity doubly deionized water (DDW) obtained using a Milli-Q system (Millipore Corporation, Billerica, MA, USA) was used throughout the experiments. The tubes and glassware used in the experiments were soaked in 10% (v/v) HNO<sub>3</sub> solutions overnight and rinsed with DDW before use.

CS (Sangon Biotech Co., Ltd., Shanghai, China) and 4-methylbenzaldehyde (Aladdin Reagent Co., Ltd., Shanghai, China) were used in this work. Oxidized MWCNTs (MWCNTs-COOH) were provided by the Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). The lengths of the MWCNTs-COOH were in the range 10–30 μm, and their outer diameters were in the range 20–30 nm.

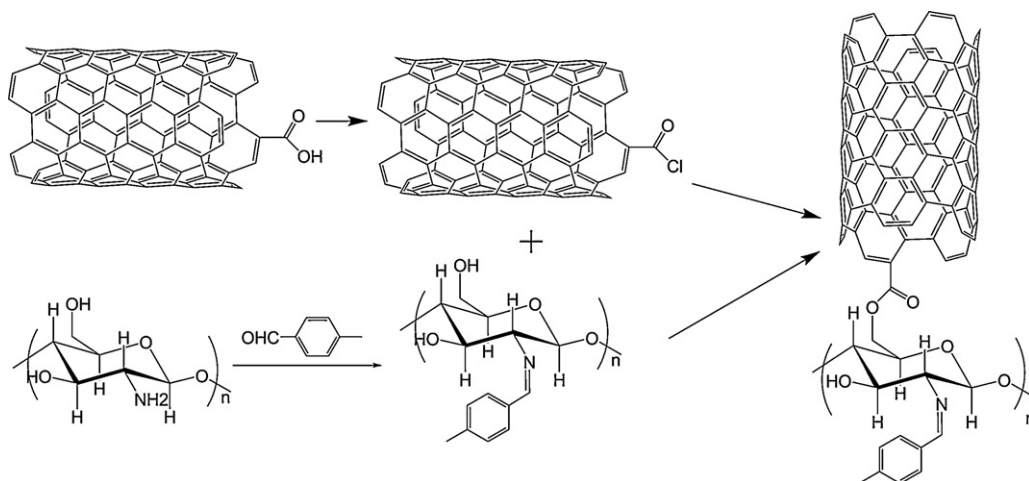
Stock standard solutions (10 mg L<sup>-1</sup>) of V(V), Cr(VI), Cu(II), As(V), and Pb(II), were obtained from the National Research Center for Certified Reference Materials (Beijing, China). Working solutions were prepared daily by appropriate dilutions of stock solutions. HNO<sub>3</sub> and NH<sub>3</sub>·H<sub>2</sub>O were used to adjust the pHs of the solutions. Standard reference materials (GBW10024 scallop sample and GBW08607 water sample) were purchased from the National Research Center for Certified Reference Materials (Beijing, China). All the other reagents used were of at least analytical reagent grade (the Fifth Reagent Factory, Tianjin, China).

### 2.3. Synthetic procedures

The synthesis of the S-CS-MWCNTs is illustrated in Fig. 1.

#### 2.3.1. Synthesis of S-CS

Purified CS was obtained according to the method reported in the literature [28]. CS (1000 mg) was dissolved in 80.0 mL of



**Fig. 1.** Synthesis and structure of S-CS-MWCNTs.

0.2% (w/w) aqueous acetic acid solution. The solution was allowed to stand overnight, and then 4.0 mL of 4-methylbenzaldehyde in methanol (2:1, v/v) were slowly added. After stirring for 24 h at room temperature, the resulting mixture was washed with ethanol several times, filtered, and dried in a vacuum oven at 40 °C for 8 h. The obtained yellow powder was S-CS.

### 2.3.2. Synthesis of acyl-chloride-modified MWCNTs (MWCNTs-COCl)

MWCNTs-COOH (80 mg) were dispersed in 40.0 mL of thionyl chloride. The suspension was stirred for 24 h at 70 °C. The residue was separated by filtration, washed with *N,N*-dimethylformamide (DMF), and dried under a vacuum at 80 °C for 8 h to obtain MWCNTs-COCl.

### 2.3.3. Synthesis of S-CS-grafted MWCNTs-COOH

MWCNTs-COCl (50 mg) and S-CS (400 mg) were added in 30.0 mL of DMF. The mixture was stirred at 100 °C for 48 h under a nitrogen atmosphere and filtered through a 0.22- $\mu\text{m}$  microporous membrane. To remove the physically adsorbed compounds, the residue was washed with 0.2% acetic acid, ethanol, and DDW. The S-CS-MWCNTs adsorbent was obtained after drying overnight in an oven at 40 °C.

## 2.4. Column preparation

S-CS-MWCNTs (40 mg) were packed into an SPE mini-column (6.0 cm  $\times$  9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and DDW were passed through the column to clean it.

## 2.5. Preconcentration procedure

A standard or sample solution (20.0 mL) containing V(V), Cr(VI), Cu(II), As(V), and Pb(II) was prepared, and the pH was adjusted to 7.0 with HNO<sub>3</sub> or NH<sub>3</sub>·H<sub>2</sub>O. The obtained solution was passed through the column at a flow rate of 1.0 mL min<sup>-1</sup>. The metal ions retained on the column were then eluted with 2.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and directly determined by ICP-MS. After use, the SPE column was regenerated using 2.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and 5.0 mL of DDW.

## 2.6. Sample preparation

A certified reference material (GBW10024, scallop, 40 mg) was added to a 100-mL beaker. After adding 5.0 mL of HNO<sub>3</sub> and 1.0 mL of HClO<sub>4</sub>, the mixture was covered with a watch glass and left overnight at room temperature. The mixture was heated on a hot plate until the temperature reached 200 °C. The temperature was maintained until the volume of acid solution in the beaker was about 1.0 mL. The digested sample was diluted in DDW to 20.0 mL and the pH was adjusted to 7.0 with NH<sub>3</sub>·H<sub>2</sub>O. A blank sample was prepared using the same procedure but without addition of the certified reference material.

Herring and spinach were obtained from a local supermarket (Tianjin, China). The spinach was cleaned with DDW and dried naturally. Digestion and spiking at different concentrations of the samples were performed using the same procedure as that used for the certified reference material (GBW10024, scallop).

The two environmental water samples used were river water (Haihe River, Tianjin, China) and tap water (Tianjin University of Science & Technology, Tianjin, China). Their pH values were adjusted to 7.0 by adding HNO<sub>3</sub> or NH<sub>3</sub>·H<sub>2</sub>O prior to analysis. The

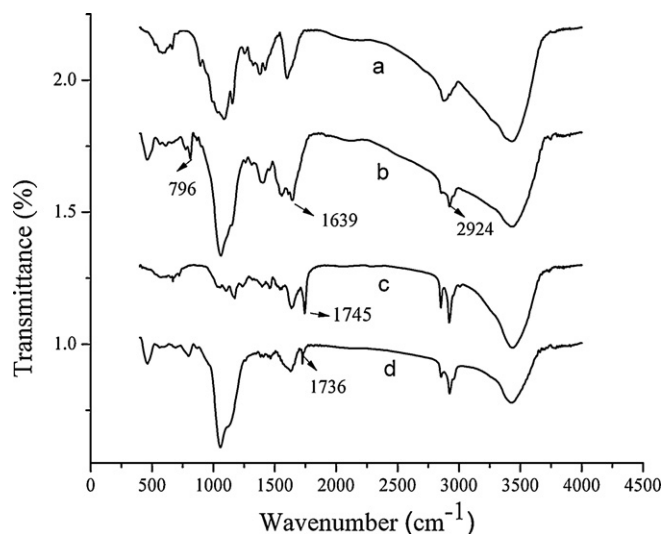


Fig. 2. FT-IR spectra of CS (a), S-CS (b), MWCNTs-COOH (c), and S-CS-MWCNTs (d).

preconcentration procedure described above was applied to the samples.

## 3. Results and discussion

### 3.1. Characterization of S-CS-MWCNTs

The FT-IR spectra of pure CS, S-CS, MWCNTs-COOH, and S-CS-MWCNTs were recorded. Their IR adsorption frequencies are shown in Fig. 2a–d. A comparison of the FT-IR spectra of CS and S-CS showed that a new band at 1639 cm<sup>-1</sup> appeared in the S-CS spectrum. This band was attributed to the C=N stretching vibration and indicated that the Schiff base had been successfully prepared. As a result of CS reacting with 4-methylbenzaldehyde, several new peaks also appeared in the S-CS, and they were assigned as follows. The peak observed at 2924 cm<sup>-1</sup> was attributed to the stretching vibration of C–H in CH<sub>3</sub>. The peak at 796 cm<sup>-1</sup> resulted from the C–H bending vibration of the benzene ring. In the MWCNTs-COOH spectrum, there was a strong absorbance at 1744 cm<sup>-1</sup>, which corresponds to the C=O of –COOH. However, in the S-CS-MWCNTs, the absorbance at 1744 cm<sup>-1</sup> was absent, and there was an absorbance at 1736 cm<sup>-1</sup>, which indicated that the –OH of the CS had reacted with the MWCNTs to form ester bonds. The results confirmed the successful immobilization of S-CS on the surfaces of the MWCNTs.

The surface microstructures of the grafted composites were observed using TEM. The TEM image of the MWCNTs-COOH is shown in Fig. 3a. The average diameters of the MWCNTs-COOH were 20–30 nm. The TEM image of the S-CS-MWCNTs (Fig. 3b) shows that their diameters were obviously larger than those of the MWCNTs, and we could clearly see that some of the S-CS was grafted onto the MWCNTs. In the higher-magnification TEM image (Fig. 3c), a core-shell structure of S-CS-MWCNTs was clearly observed. The core of MWCNTs in the center was wrapped in grafted S-CS, proving that the MWCNTs were coated with the polymer. These coated polymer layers could reduce the strong attractive interactions among the nanotubes and prevent aggregation of the MWCNTs, and could also increase the number of adsorption sites for metal ions.

To estimate the S-CS contents of the S-CS-MWCNTs, the structural properties of S-CS and S-CS-MWCNTs powders were determined by TGA. The TGA curves of MWCNTs-COOH, S-CS, and S-CS-MWCNTs are presented in Fig. 4. The TGA curve of the MWCNTs-COOH (Fig. 4a) showed a weight loss of less than 1% from 25 to 600 °C. In the TGA curve of the S-CS-MWCNTs (Fig. 4b), the

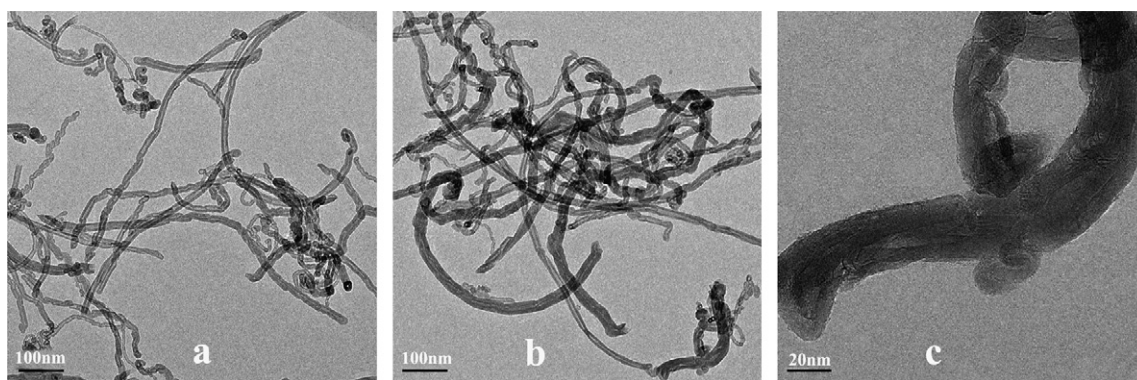


Fig. 3. TEM images of MWCNTs-COOH (a), S-CS-MWCNTs (b), and S-CS-MWCNTs magnification (c).

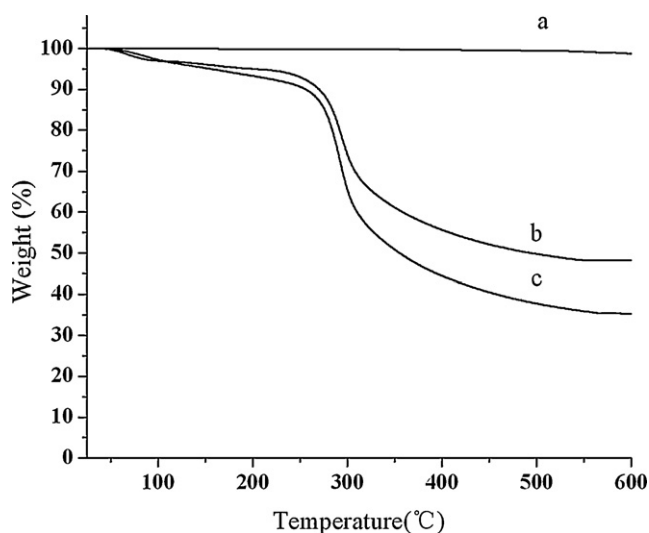


Fig. 4. TGA curves of MWCNTs-COOH (a), S-CS-MWCNTs (b), and S-CS (c). The scanning temperature ranged from 25 °C to 600 °C, with a 10 °C min<sup>-1</sup> heating rate, under a nitrogen atmosphere.

first region showed a 5% weight loss between 30 and 100 °C, which was probably the result of evaporation of the absorbed water. The second region showed a sharp 35% weight loss between 250 °C and 330 °C, which could be ascribed to thermal degradation of the S-CS. The thermal analytical trends observed for the S-CS-MWCNTs were the same as those of S-CS (Fig. 4c). Based on the TGA curves, using a previously established protocol for the determination of functional group loading on MWCNTs [34], the content of grafted S-CS on the surfaces of the MWCNTs was about 70%.

### 3.2. Optimization of the mass of adsorbent

To evaluate the effect of adsorbent mass on the recovery of metal ions, different amounts of adsorbent (10–50 mg), packed into an SPE column, were investigated, following the preconcentration procedure. As shown in Fig. 5, the recoveries of metal ions increased with increasing amounts of adsorbent in the range 10–40 mg. When the amount was less than 20 mg, low recoveries of metal ions were obtained because of by-passing of the liquid in the SPE column. When the amount was 30 mg, the recovery of As(V) did not reach the quantitative recovery level ( $\geq 95\%$ ). Quantitative recoveries of target ions were obtained in the range 40–50 mg. Therefore, 40 mg of S-CS-MWCNTs was the amount selected for further studies.

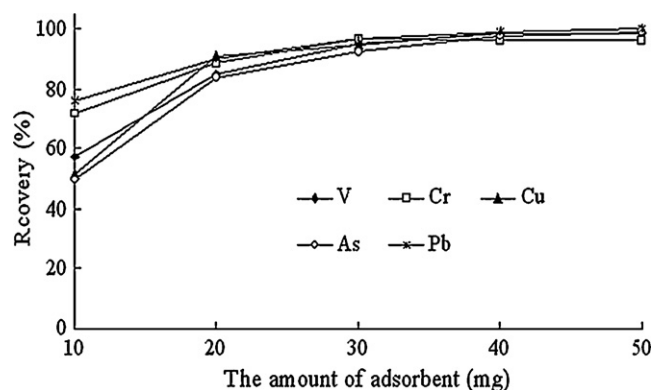


Fig. 5. Effects of adsorbent mass on the preconcentration of analytes (other conditions: sample volume, 20.0 mL; flow rate, 1 mL min<sup>-1</sup>; eluent, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>; pH 7;  $n=3$ ).

### 3.3. Optimization of parameters affecting target ions preconcentration

#### 3.3.1. pH of the sample solution

In SPE, the pH of the sample solution plays a key role in preconcentration of metal ions [19,35]. The effect of pH on preconcentration was investigated in the pH range 2.0–8.0. Fig. 6 shows quantitative recoveries ( $\geq 95\%$ ) for each analyte in the pH range 6.0–8.0. For V(V), Cu(II) and Pb(II), strong protonation of the S-CS-MWCNTs at pH < 6.0 probably accounted for the decreases in the recoveries of metal ions. These ions were quantitatively recovered in the pH range 6.0–8.0. When the pH of the solution was higher

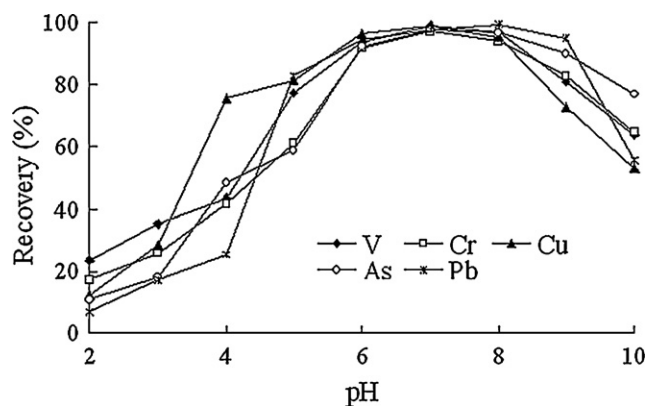
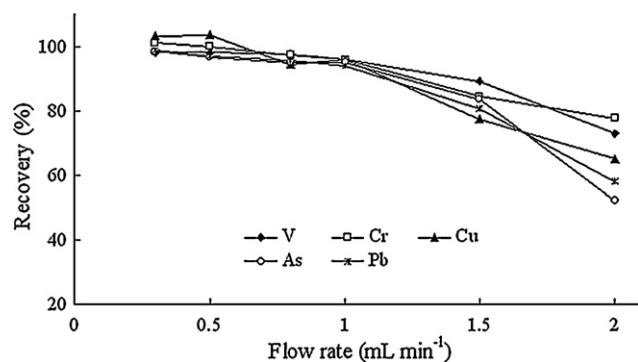


Fig. 6. Effects of pH on the preconcentration of 1.0  $\mu\text{g L}^{-1}$  V(V), Cr(VI), Cu(II), As(V), and Pb(II) on S-CS-MWCNTs (other conditions: sample volume, 20.0 mL; flow rate, 1 mL min<sup>-1</sup>; eluent, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>;  $n=3$ ).

**Table 2**  
Analytical figures of merit of the developed method.

Element	Enrichment factor	Detection limit ( $3\sigma$ ) ( $\mu\text{g L}^{-1}$ )	RSD % ( $1 \mu\text{g L}^{-1}$ , $n=11$ )	Linear range ( $\mu\text{g L}^{-1}$ )	$R^2$
V	111	0.0021	3.8	0.005–10	0.9993
Cr	95	0.0038	1.4	0.005–10	0.9998
Cu	60	0.0035	3.1	0.005–10	0.9994
As	52	0.0013	4.6	0.005–10	0.9996
Pd	128	0.0036	1.6	0.005–10	0.9995



**Fig. 7.** Effects of sample solution flow rates on the preconcentration of analytes (other conditions: sample volume, 20.0 mL; eluent,  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ ; pH 7;  $n=3$ ).

than 8.0, the decreases in recoveries of metal ions might result from the hydrolysis of metal ions in solution. In aqueous solutions, the Cr(VI) exists mainly as  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$ . In our research, the recovery of Cr(VI) increased with increasing pH, and quantitative adsorption was obtained in the pH range 6.0–8.0. At low pH,  $\text{HCrO}_4^-$  would be converted to neutral  $\text{H}_2\text{Cr}_2\text{O}_7$ , and this would lower the adsorption capacity. At high pH, more  $\text{OH}^-$  in the solution could create competition with Cr(VI) in the adsorption process, thereby decreasing the preconcentration efficiency. The pH value strongly affects the distribution of As(V) in aqueous solutions [36]. With an increase in pH from 3.0 to 6.0,  $\text{H}_3\text{AsO}_4$  is converted to  $\text{H}_2\text{AsO}_4^-$ , leading to higher recovery. When the pH was controlled to 6.0–8.0, the  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  could combine with  $-\text{OH}$  and  $-\text{C}=\text{N}-$  on the S-CS-MWCNTs by coordination complexation or electrostatic interaction, and the highest recovery of As(V) was obtained. Above pH 8.0,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  are the major species and competition with  $\text{OH}^-$  tends to reduce As adsorption. Therefore, pH 7.0 was chosen as the optimum pH for the loading samples in all subsequent experiments.

### 3.3.2. Flow rate of sample loading

In an SPE system, the flow rate of the sample loading not only affects the preconcentration of the analytes but also controls the analysis time. The flow rate was therefore examined in the range  $0.3\text{--}2.0 \text{ mL min}^{-1}$ . The results are shown in Fig. 7. Quantitative recoveries were achieved when the flow rate of the sample solutions was in the range  $0.3\text{--}1.0 \text{ mL min}^{-1}$ . However, when the sample loading rate was higher than  $1.0 \text{ mL min}^{-1}$ , low recoveries of analytes were obtained as a result of by-passing of liquid in the SPE column. To decrease the analysis time for the experiments, a flow rate of  $1.0 \text{ mL min}^{-1}$  was selected for the sample solutions.

## 3.4. Optimization of parameters affecting target ions elution

### 3.4.1. Eluent concentration

$\text{HNO}_3$  was chosen as the eluent for ICP-MS.  $\text{HNO}_3$  solutions ( $2.0 \text{ mL}$ ) of various concentrations ( $0.1$ ,  $0.2$ ,  $0.5$  and  $1.0 \text{ mol L}^{-1}$ ) were investigated for eluting the metal ions adsorbed on the column. The results indicated that the retained metal ions were quantitatively eluted with  $\text{HNO}_3$  concentrations higher than

$0.5 \text{ mol L}^{-1}$ , so  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  was selected as the eluent for further experiments.

### 3.4.2. Eluent volume

The influence of eluent volume on analyte recovery was studied in the range  $1.0\text{--}5.0 \text{ mL}$ . It was found that the recoveries increased as the volume of  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  added increased. The results showed that the quantitative recoveries of the analytes ( $\geq 95\%$ ) could be obtained when the volume exceeded  $2.0 \text{ mL}$ . Therefore,  $2.0 \text{ mL}$  of  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  were used in further experiments.

## 3.5. Evaluation of interferences

The effects of interference by common coexisting ions with the preconcentration and determination of analytes were investigated under the optimum conditions described above. In these experiments, solutions containing analyte ions ( $1.0 \mu\text{g L}^{-1}$  of each ion) and a series of interfering ions were examined. The tolerance limit was set as the amount of ions reducing recoveries of the examined ions to less than 90%. From the experimental results, it can be seen that excesses of 20,000-fold K(I) and Na(I), 5000-fold Ca(II) and Mg(II), 4000-fold Mn(II), Ni(II) and Hg(II), and 500-fold Al(III) and Fe(III) did not result in significant interference with the preconcentration and determination of  $1.0 \mu\text{g L}^{-1}$  of analytes ions. This demonstrated that the method had a good tolerance to matrix interference, and the presence of other ions normally present in biological and environmental samples did not influence determination of the target ions under the selected conditions.

## 3.6. Analytical figures of merit

The analytical parameters of the proposed method, such as the enrichment factors, the detection limits, relative standard deviations (RSD), linear ranges, and correlation coefficients ( $R^2$ ) for each analyte are summarized in Table 2.

Using the optimum SPE conditions, calibration curves were prepared at concentrations of V(V), Cr(VI), Cu(II), As(V), and Pb(II) between  $0.001$  and  $10 \mu\text{g L}^{-1}$ . Linear ranges were obtained for the target ions in the concentrations range  $0.005\text{--}10 \mu\text{g L}^{-1}$ , with good correlation coefficients ( $R^2 > 0.9990$ ). The enrichment factors, obtained by comparing the slopes of the linear portion with those in direct detection of the target ions in standard solutions [37,38], were 111, 95, 60, 52, and 128 for V(V), Cr(VI), Cu(II), As(V), and Pb(II), respectively.

Under the optimum conditions, the detection limits of the method for the target ions were calculated as three times the standard deviation ( $3\sigma$ ) of 11 runs of a blank solution. The detection limits were found to be  $2.1$ ,  $3.8$ ,  $3.5$ ,  $1.3$ , and  $3.6 \text{ ng L}^{-1}$  for V(V), Cr(VI), Cu(II), As(V), and Pb(II), respectively. The precisions (RSD) of 11 replicated extractions and determinations of  $1.0 \mu\text{g L}^{-1}$  of target ions were calculated to be in the range  $1.4\text{--}4.6\%$

These results clearly showed the merits of SPE using the prepared S-CS-MWCNTs as the adsorbent, and indicated that the developed method had high efficiency and sensitivity, and could be used for trace-metal determination.

**Table 3**  
Results for determination of V, Cr, Cu, As, and Pb in certified reference materials (GBW10024 scallop and GBW08607 water).

Certified reference material	Analytes	Certified Value ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ ) (mean $\pm$ SD, $n=3$ )	Recovery (%)
GBW10024 scallop	V	0.36 $\pm$ 0.1	0.354 $\pm$ 0.012	98.3
	Cr	0.28 $\pm$ 0.07	0.269 $\pm$ 0.009	96.1
	Cu	1.34 $\pm$ 0.18	1.380 $\pm$ 0.124	102.9
	As	3.6 $\pm$ 0.6	3.535 $\pm$ 0.237	98.2
	Pb	0.12	0.117 $\pm$ 0.004	97.5
GBW08607 water	Cr	0.525 $\pm$ 0.010	0.521 $\pm$ 0.016	95.4
	Cu	1.045 $\pm$ 0.010	1.044 $\pm$ 0.036	98.9
	Pb	1.045 $\pm$ 0.020	1.030 $\pm$ 0.015	99.5

**Table 4**  
Results for determination of V, Cr, Cu, As, and Pb in biological samples (mean  $\pm$  SD,  $n=3$ ).

Samples	Analytes	Add ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ )	Recovery (%)
Herring	V	0	0.032 $\pm$ 0.005	
		0.05	0.081 $\pm$ 0.023	98.0
		0.1	0.135 $\pm$ 0.003	103.0
	Cr	0	0.277 $\pm$ 0.064	
		0.2	0.487 $\pm$ 0.041	105.0
		0.3	0.570 $\pm$ 0.091	97.7
	Cu	0	0.176 $\pm$ 0.094	
		0.2	0.369 $\pm$ 0.142	96.5
		0.5	0.633 $\pm$ 0.133	91.4
	As	0	0.080 $\pm$ 0.087	
		0.05	0.128 $\pm$ 0.042	96.0
		0.1	0.171 $\pm$ 0.022	91.0
Pb	0	ND		
	0.05	0.051 $\pm$ 0.030	104.0	
	0.1	0.980 $\pm$ 0.124	99.0	
Spinach	V	0	0.051 $\pm$ 0.005	
		0.05	0.102 $\pm$ 0.006	102.0
		0.1	0.148 $\pm$ 0.019	97.0
	Cr	0	0.339 $\pm$ 0.056	
		0.2	0.529 $\pm$ 0.078	95.0
		0.3	0.619 $\pm$ 0.093	93.3
	Cu	0	0.773 $\pm$ 0.074	
		0.2	0.963 $\pm$ 0.104	95.0
		0.5	1.255 $\pm$ 0.211	96.4
	As	0	ND	
		0.05	0.058 $\pm$ 0.004	98.0
		0.1	0.107 $\pm$ 0.092	98.0
Pb	0	0.005 $\pm$ 0.010		
	0.05	0.052 $\pm$ 0.010	94.0	
	0.1	0.104 $\pm$ 0.024	99.0	

ND: not detected.

### 3.7. Column reuse

The stability and potential regeneration of the column packed with S-CS-MWCNTs were also important factors in evaluating the adsorbent and the method. It was found that the S-CS-MWCNTs show good stability. After 20 repeated cycles, the average

**Table 6**  
Comparison of the analytical parameters of the developed method with those of other reported adsorbents.

Adsorbent	Detection	Element	Enrichment factor	Detection limit ( $\mu\text{g L}^{-1}$ )	Reference
MWCNTs modified with 2-aminobenzothiazole	ICP-AES	Pb	100	0.27	[3]
MWCNTs using iminodiacetic acid	ICP-MS	V, Cr, Pb, Cd, Co, Cu, As	66–101	0.0004–0.0034	[5]
The hemimicelle capped CMMWCNTs	FI-AFS	As	62.8	0.002	[19]
Ethylenediamine-modified MWCNTs	ICP-OES	Cr, Fe, Pb	200	0.35	[25]
MWCNTs impregnated with D2EHPA-TOPO mixture	FAAS	Cu, Ni, Zn	25	40–60	[35]
MWCNTs/o-cresolphthalein complexone	FAAS	Cu, Co, Ni, Pb	40	1.64–5.68	[39]
MWCNTs-APDC	FAAS	Cu, Cd, Pb, Zn, Ni, Co	80	0.30–0.60	[40]
Oxidized MWCNTs	FAAS	Cu, Zn, Mn, Pb	15.2–20.6	0.28–1.00	[41]
Chitosan/Silica	ICP-OES	V, Cu, Pb, Cd, Hg	20	0.05–0.39	[4]
Schiff base-chitosan grafted MWCNTs	ICP-MS	V, Cr, Cu, As, Pb	52–128	0.0013–0.0038	This work

**Table 5**  
Results for determination of V, Cr, Cu, As, and Pb in environmental water samples (mean  $\pm$  SD,  $n=3$ ).

Samples	Analytes	Add ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
River water	V	0	1.299 $\pm$ 0.014	
		0.5	1.808 $\pm$ 0.012	101.7
		1.0	2.272 $\pm$ 0.013	97.2
	Cr	0	0.311 $\pm$ 0.006	
		0.5	0.809 $\pm$ 0.008	99.7
		1.0	1.306 $\pm$ 0.014	99.6
	Cu	0	3.207 $\pm$ 0.028	
		0.5	3.722 $\pm$ 0.067	103.0
		1.0	4.220 $\pm$ 0.159	101.3
	As	0	1.824 $\pm$ 0.011	
		0.5	2.302 $\pm$ 0.043	95.7
		1.0	2.792 $\pm$ 0.027	96.8
Pb	0	0.458 $\pm$ 0.041		
	0.5	0.953 $\pm$ 0.015	99.0	
	1.0	1.426 $\pm$ 0.048	96.8	
Tap water	V	0	0.577 $\pm$ 0.003	
		0.5	1.081 $\pm$ 0.005	100.6
		1.0	1.611 $\pm$ 0.049	103.3
	Cr	0	0.292 $\pm$ 0.013	
		0.5	0.782 $\pm$ 0.020	98.0
		1.0	1.252 $\pm$ 0.057	96.0
	Cu	0	1.675 $\pm$ 0.010	
		0.5	2.155 $\pm$ 0.117	96.0
		1.0	2.655 $\pm$ 0.048	98.0
	As	0	0.802 $\pm$ 0.004	
		0.5	1.283 $\pm$ 0.022	96.2
		1.0	1.758 $\pm$ 0.055	95.7
Pb	0	0.243 $\pm$ 0.004		
	0.5	0.735 $\pm$ 0.018	98.5	
	1.0	1.260 $\pm$ 0.025	101.7	

recoveries of V(V), Cr(VI), Cu(II), As(V), and Pb(II) were 97.3  $\pm$  5.0%, 95.1  $\pm$  3.2%, 96.4  $\pm$  3.5%, 95.2  $\pm$  4.1%, and 96.7  $\pm$  4.7%, respectively.

### 3.8. Analysis of real samples

The certified reference materials, i.e., scallop (GBW10024) and water (GBW08607), were analyzed using the column procedure to evaluate the validity of the developed method. The results listed

in Table 3 show that good agreement was obtained between the experimentally measured values and the certified values for V(V), Cr(VI), Cu(II), As(V), and Pb(II).

The developed method was used for the determination of V(V), Cr(VI), Cu(II), As(V), and Pb(II) in herring, spinach, river water, and tap water samples. The accuracy of the method was verified by the analysis of samples spiked with known amounts of the five analytes. The results are given in Tables 4 and 5, as shown, the recoveries of the target ions ranged from 91.0% to 105.0%. Some of the recoveries were more than 100%. This was probably the result of instrumental errors and experimental operating errors. For ICP-MS, the instrumental error in determining the metal ions was less than 4%, which means that the recoveries could be more than 100%.

#### 4. Conclusions

A novel material was synthesized by covalently grafting S-CS onto the surfaces of MWCNTs, and used for preconcentration of V(V), Cr(VI), Cu(II), As(V), and Pb(II) in various samples, namely herring, spinach, river water, and tap water, using an SPE method. The results demonstrated that the proposed multi-element enrichment method can be successfully used for analysis of V(V), Cr(VI), Cu(II), As(V), and Pb(II) in environmental water and biological samples. The method is fast and has good sensitivity and excellent precision. Compared with previously reported procedures (Table 6), the present method has high enrichment factors and sensitivity. In short, the proposed method is suitable for preconcentration and separation of trace/ultra-trace metal ions in real samples.

#### Acknowledgments

The authors are grateful for financial support from the National Natural Science Foundation of China (Project nos. 31171683 and 31071547), and the Ministry of Science and Technology of China (Project nos. 2011AA100806 and 2009BADB9B07).

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