

Separation and chromium speciation by single-wall carbon nanotubes microcolumn and inductively coupled plasma mass spectrometry

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Abstract Microcolumn packed single-walled carbon nanotubes (SWCNTs) were used as solid phase extraction adsorbent for chromium speciation coupled to inductively coupled plasma mass spectrometry for detection. The effects of the experimental parameters, including pH of the solution, sample flow rate, volume and concentration of eluent, sample volume and interfering ions, on separation and determination of Cr(III) and Cr(VI) were investigated in detail. It was found that Cr(III) was selectively sorbed on the microcolumn packed with SWCNTs in the pH range from 2.0 to 4.0, while Cr(VI) remained in solution. The retained Cr(III) was subsequently eluted with 2.0 mL of 1.2 mol L⁻¹ nitric acid. Under the optimum conditions, the detection limits based on 3 σ criterion were 0.01 ng mL⁻¹ and 0.024 ng mL⁻¹ for Cr(III) and Cr(VI), respectively. The relative standard deviations were less than 5.0% ($n=9$, $c=1.0$ ng mL⁻¹). The method was successfully applied to the speciation of chromium in real samples including natural and waste water. The recoveries of spiked samples were higher than 92.5%.

Keywords Single-wall nanotubes · Preconcentration and separation · Inductively coupled plasma mass spectrometry · Chromium · Speciation

Introduction

In recent years, there is a growing interest in the determination of chemical forms of an element owing to their quite different effects on human health [1–4]. Chromium is one such element which exists mainly in the environment as two oxidation states, namely Cr(III) and Cr(VI). The biological and toxicological behavior of the two species, however, differs significantly. Cr(III) is an essential element in human body and plays an important role in the metabolism of glucose, protein and lipid, whereas Cr(VI) is detrimental to health even at relatively low levels as it may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers [5–7]. The toxicity of Cr(VI) is attributed to its ability to migrate across the cell membrane, as a result of increasing intracellular chromium concentrations [8]. Release of Cr into the environment is due to its extensive use in many technology fields ranging from electroplating, dyeing, steel, leather, wood preservation in industry to artificial fertilizers in agriculture. Therefore, it is of increasing importance to monitor the total concentration of chromium, especially the concentration of the individual chromium species.

In general, the determination of chromium species is not possible directly by instrumental methods including inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). To solve this problem, separation and preconcentration steps are usually required prior to the determination. A number of methods such as solvent extraction, coprecipitation, ion exchange, cloud point extraction, solid extraction, capillary microextraction and chromatography have been reported in the literatures for speciation of chromium [9–17]. In comparison with the methods mentioned above,

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solid phase extraction has become increasingly popular because of its major advantages: (1) simple to operate; (2) high concentration factor; (3) rapid phase separation, and (4) the ability to combine with different detection techniques [18, 19]. It should be noted that the adsorbent material plays a fundamentally important role in this technique, and the development of a new adsorbent material with high selectivity and sensitivity is forever of interests to analysts. Owing to its small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties, nanostructure material as new adsorbent for preconcentration and separation of substance has drawn growing attention in analytical sciences. Some nanometer-size substances, such as multi-walled carbon nanotubes, carbon nanofibers, nanometer-size titanium dioxide, nanometer-size aluminum dioxide, nanometer-sized zirconium oxide, FeC nanoparticles, nanometer-size silicon dioxide and titanium dioxide nanotubes have been successfully used as solid-phase extractants for preconcentration/separation of metal and nonmetal ions [20–27], as well as adsorption of organic compounds [28].

Single-walled carbon nanotubes (SWCNTs), a fascinating member in carbon material family, have exceptional mechanical properties, high chemical stability and large specific surface area [29]. Especially, SWCNTs can be modified with chemical treatments to introduce some special functional groups on their surfaces [30]. These facts reveal that SWCNTs may be a promising candidate as adsorbents for solid phase extraction. Up to now, however, to the best of our knowledge, studies on the application of SWCNTs to the analysis of element and its speciation have received little attention. The main aim of this work was to develop SWCNTs as a new adsorbent for simultaneous separation and determination of speciation of inorganic chromium by ICP-MS. The adsorption characteristics of SWCNTs for the analytes were investigated in detail. The proposed method has been applied to the speciation of inorganic chromium in water samples with satisfactory results.

Experimental

Instrumentation

A Thermo Elemental X-7 ICP-MS (Thermo Elemental Corporation, USA, <http://www.thermo.com>), equipped with a standard low-volume glass impact-bed spray chamber (Peltier-cooled to +3 °C), a concentric glass nebulizer and Fassel-type torch, was used in this work. The ICP-MS operating conditions and measurement parameters are listed in Table 1. The ion lens settings, nebulizer flow rate, and

Table 1 Operating parameters for ICP-MS

Plasma power	1,300 W
Plasma argon flow rate	14.0 L min ⁻¹
Auxiliary argon flow rate	0.75 L min ⁻¹
Nebulizer argon flow rate	0.92 L min ⁻¹
Sampler orifice (nickel)	1.1 mm
Skimmer orifice (nickel)	0.7 mm
Acquisition mode	Peak-jumping
Number of sweep	100
Dwell time	10 ms
Acquisition time	40 s
Number of measurements per peak	3
Isotopes	⁵² Cr and ¹¹⁵ In

torch position of the instrument were optimized daily in order to obtain the maximum ¹¹⁵In count rate. The samples and standards were spiked with 2.0 ng mL⁻¹ of indium internal standard before measurement for the elimination of matrix effects.

The pH values of the solutions were controlled with a pH meter (Thermo Orion Corporation, USA, <http://www.thermo.com>), supplied with a combined electrode. A Model Ethos T microwave system (Milestone, Italy, <http://www.milestonesci.com>) was used for sample digestion. A Model HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, China, <http://www.qphuxi.com>), coupled to a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm×3.0 mm i.d.), packed with SWCNTs, was used for the preconcentration/separation process. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connections.

Reagents

The stock standard solution (1.0 mg mL⁻¹) of Cr(III) was obtained from the National Analysis Center of Iron & Steel (Beijing, China); Cr(VI) was prepared by dissolving K₂Cr₂O₇ (Tianjin Reagent Factory, Tianjin, China, <http://www.tjsgsc.com>) in 0.1 mol L⁻¹ nitric acid. Working solutions were prepared daily from by appropriate dilution of stock solutions. All reagents used were ultrapure or at least of analytical grade. High purity deionized water (18.2 MΩ) obtained from Milli-Q® A10 system (Millipore Corporation, America, <http://www.millipore.com>) was used throughout this work.

SWCNTs were kindly provided by Shenyang Metal Institute of Chinese Academy (Shenyang, China, <http://www.imr.ac.cn>). Before use, SWCNTs were oxidized with concentrated HNO₃ according to the literature [31]. The treated SWCNTs were dried at 100 °C and stored for future use.

Column preparation

A PTFE microcolumn (20 mm×3.0 mm id) plugged with a small portion of glass wool at both ends was filled with twenty milligrams of the treated SWCNTs. Before use, 1.0 mol L⁻¹ HNO₃ solution and high purity deionized water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH value with HNO₃ and CH₃COONa.

General procedure

Certain volume of sample solution containing Cr(III) and Cr(VI) was prepared, and the pH was adjusted to the desired value with HNO₃ and CH₃COONa before use. The obtained solution was passed through the column by using a peristaltic pump at a desired flow rate. Cr(III) was retained on the microcolumn, while Cr(VI) was collected in the effluent. Afterwards, the sorbed Cr(III) was eluted with 2.0 mL of 1.2 mol L⁻¹ HNO₃. Cr(III) was determined in the eluate by ICP-MS; Cr(VI) was determined in the effluent. In addition, taking the presence of organic matter (humic compounds) into account in natural water, the effects of a representative organic matter, sodium humate, on the adsorption characteristics of Cr(III) and Cr(IV) on SWCNTs was investigated in the preliminary experiment. The results show that no effect was observed at the selected conditions.

Sample preparation

Waste water (pH 5.5) and lake water (pH 6.7) were collected from Wuhan (China), and stored in prewashed polyethylene bottles. Mineral drinking water (pH 6.8) was purchased in the market (Wuhan, China). Before analysis, water samples were filtered through a cellulose membrane filter of 0.22 μm pore size. The pH of samples was adjusted to the desired value with HNO₃ and CH₃COONa. Then the procedure given above was applied to the samples. The blanks were prepared in the same way as the sample, but omitting the sample. It should be pointed out here that chromium exists mainly in samples as Cr(III) and Cr(VI) in the pH range of 2–8 [32, 33].

Results and discussion

Surface functionalization of SWCNTs

Owing to their large specific surface, high chemical stability and unique mechanical properties, carbon nanotubes (CNTs) have attracted great attention in the applications such as gas adsorption and catalyst support [29, 34]. What is more, some investigations have shown that the

treatment of CNTs with oxidized acids can introduce many functional groups, such as carboxyl (—COOH), hydroxyl (—OH) and carbonyl (>C=O), on the surface of CNTs [31]. The oxygen-containing groups attached on the surfaces of CNTs can improve their adsorption capability of ions in solution. In this work, SWCNTs were treated with concentrated nitric acid according to the literature [31].

Effect of pH on adsorption

After the oxidization treatment with concentrated HNO₃, some acidic groups could form on the surface of SWCNTs. Thus, the pH value plays an essential role with respect to the adsorption of different species of chromium on SWCNTs, since it affects the surface charge of the adsorbent and degree of ionization and speciation of the adsorbates. In this work, the effect of pH on the adsorption behavior of Cr(III) and Cr(VI) was investigated, and the results was shown in Fig. 1. The adsorption percentage was calculated based on a difference between the amounts of Cr speciation in the starting sample and ones in the eluent. It was obvious that in the pH range of 2.0–4.0, Cr(III) was retained in SWCNTs with an adsorption percentage above 90%, while that of Cr(VI) was less than 5.0%. This suggests that it is possible that by selection of a proper pH, Cr(III) could be effectively separated from Cr(VI) on SWCNTs. All further works were carried out at pH 3.0 for speciation of chromium.

Elution of Cr(III)

As can be seen in Fig. 1, Cr(III) ions were not retained on SWCNTs at a higher acidity (pH<1.0). Hence, nitric acid

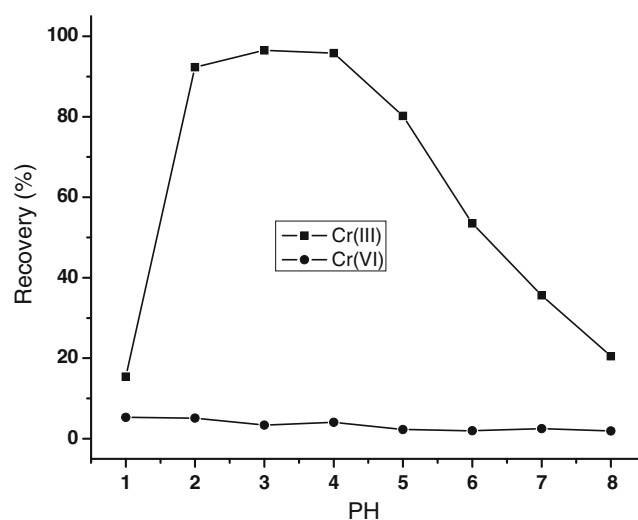


Fig. 1 Effect of pH on the adsorption of Cr(III) and Cr(VI) on SWCNTs. Cr(III) and Cr(VI): 4.0 ng mL⁻¹; sample volume: 20 mL; flow rate of sample solution: 1.2 mL min⁻¹

Table 2 Effect of interfering ions

Coexisting ion	Concentration ratio ^a
Na ⁺ , K ⁺	10,000
Ca ²⁺ , Mg ²⁺	2,000
Fe ³⁺ , Al ³⁺	200
PO ₄ ³⁻ , SiO ₃ ²⁻ , SO ₄ ²⁻ , Cl ⁻	5,000

^a Concentration ratio: Foreign ion / Cr(III)

was used as eluent reagent to elute the retained Cr(III) on microcolumn packed with SWCNTs according to the general procedure. The effect of eluent concentrations on the recoveries of the analytes was evaluated under the selected experimental conditions (Cr(III) and Cr(VI): 4.0 ng mL⁻¹; sample volume: 20 mL; flow rate of sample solution: 1.2 mL min⁻¹; pH=3.0). The results indicated that the retained species could be eluted quantitatively with the concentration of HNO₃ higher than 0.9 mol L⁻¹. In addition, the effect of eluent volume on the recoveries of analytes was also studied in the range of 0.5–3.0 mL. The results showed that the quantitative recoveries for Cr(III) (>90%) could be obtained when the volume exceed 1.5 mL. Taking the required sampling volume for ICP-MS into account, 2.0 mL of 1.2 mol L⁻¹ HNO₃ was used for all subsequent experiments to ensure the complete elution.

Effect of flow rate of sample solution

The flow rate of the sample solution affects the retention of analytes on the adsorbent and the duration of complete analysis. Thus, the effect of flow rate of sample solutions on the adsorption of Cr(III) on SWCNTs was examined in the range of 0.4–2.0 mL min⁻¹ (Cr(III) and Cr(VI): 4.0 ng mL⁻¹; sample volume: 20 mL; pH=3.0). The experimental results showed that the flow rate of the sample solutions had no obvious influence on the quantitative recoveries of Cr(III) up to 1.2 mL min⁻¹. All subsequent experiments were performed at a flow rate of 1.2 mL min⁻¹. However, the retention of Cr(III) will decrease with further

increase of the flow rate after it is over 1.2 mL min⁻¹ owing to a decrease in the contact time of solutions with the sorbent at a higher flow rate. Therefore, a flow rate of 1.2 mL min⁻¹ was selected in this work.

Effect of sample volume

The effects of sample volume on the retention behaviors of Cr(III) on SWCNTs was investigated by varying the sample volume containing 12 ng of Cr(III) from 50 to 200 mL. The results indicated that when the sample volumes of Cr(III) were lower than 125 mL, the recoveries of Cr(III) were all above 90% and remained constant, whereas a decrease of the recovery was observed with the continuous increase of sample volume. As described in previous section, the analytes were quantitatively recovered using a volume of 2.0 mL of 1.2 mol L⁻¹ HNO₃ (flow rate: 1.2 mL min⁻¹). Thus, an enrichment factor of 63-fold was obtained for the ions studied in this work. Considering the analyte time, 20 mL sample volume was used for the analysis of real samples.

Adsorption capacity

The adsorption capacity was studied by using the method recommended in the literature [35]. Under the optimized conditions, the detailed procedure was as follows: 20 mL sample solutions containing a series of concentrations (0.2–1.0 µg mL⁻¹) were passed through the column, and the analyte concentrations in the effluent were determined by ICP-MS, respectively. The breakthrough curves were obtained by plotting Cr(III) concentrations (µg mL⁻¹) versus the milligrams of metal ions adsorbed on per gram of adsorbent. The adsorption capacity calculated from the breakthrough curve is 0.73 mg g⁻¹ for Cr(III).

Effect of interfering ions

The effects of potentially interfering ions on the adsorption of Cr(III) on SWCNTs were investigated by determination of Cr(III) in the resulting column eluates. In these experiments,

Table 3 Comparison of the analytical performance of the published adsorbents with SWCNTs

Adsorbent	Method	Enrichment factor	DL (ngmL ⁻¹)		RSD (%)		Reference
			Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
Ordered mesoporous Al ₂ O ₃	ICP-MS	60	0.074	0.018	3.9	2.8	[16]
Titanium dioxide	ICP-MS	–	0.08	0.07	4.4	3.4	[32]
Immobilized moss	ICP-MS	20	0.15	–	1.0	–	[33]
Chelate resin	ICP-MS	–	0.02	–	1.9	–	[36]
Activated alumina	GFAAS	40	0.016	0.01	<10	<10	[37]
Modified SWCNTs	ICP-MS	63	0.01	0.24	2.1	4.0	This work

various salts and ions were added individually to a solution containing 4.0 ng mL^{-1} Cr(III) and the test procedure described above were applied. The results obtained were given in Table 2. It can be seen that the presence of major cations and anions has no obvious influence on the adsorption of Cr(III) under the selected conditions.

Column reuse

The stability and potential regeneration of the column packed with SWCNTs was studied by monitoring the changes in the recoveries of Cr(III) in this work. The column can be reused after regeneration with 10 mL of 1.0 mol L^{-1} HNO_3 and 20 mL deionized water, respectively, and is stable up to 35 adsorption-elution cycles without obvious decrease in the recoveries for the analytes.

Detection limits and precisions

According to the definition of IUPAC (3σ), the detection limits (DL) of this method, calculated from three times the standard deviation of the blank signal, were 0.01 ng mL^{-1} and 0.024 ng mL^{-1} for Cr(III) and Cr(VI) with an enrichment factor of 10-fold (sample volume: 20 mL), respectively. The linear range of this method was from 0.1 to 100 ng mL^{-1} with the correlation coefficient better than 0.9995. The relative standard deviations (RSD) were 2.1% and 4.0% for Cr(III) and Cr(VI), respectively ($n=9$, $c=1.0 \text{ ng mL}^{-1}$). Table 3 compares the analytical performances of SWCNTs with those of other adsorbents reported in the literatures [16, 32, 33, 36, 37]. Generally, the results obtained by the present method are comparable to those of reported method or better than them.

Sample analysis

The feasibility of the determination for Cr(III) and Cr(VI) on SWCNTs was explored in water samples including mineral drinking water from the market, lake water from Dongxi Lake and waste water from industrial activities in Wuhan City. The proposed preconcentration and separation procedure was applied to the analysis of Cr species by internal standard method. The reliability was checked by spiking experiments. The results were presented in Table S1 (Electronic Supplementary Material). The results indicate that the recoveries are reasonable for trace analysis, in a range of 92.5–105%.

Conclusions

In this study, a new kind of adsorbent of SWCNTs was developed for the separation, preconcentration and determi-

nation of inorganic chromium speciation in the environmental water samples by ICP-MS. The adsorption behavior of Cr(III) and Cr(VI) on SWCNTs was investigated systematically. The experimental results indicate that Cr(III) was almost quantitatively retained in the pH range of 2.0–4.0, while Cr(VI) remained in the solution. The Cr(III) retained on SWCNTs can be easily desorbed and no carryover is observed in the next analysis. An enrichment factor of 63-fold was achieved. Based on the obtained experimental results, it can be concluded that SWCNTs are likely to become an effective adsorbent of solid phase extraction for the speciation of chromium in various matrices other than water.

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