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Solid-phase extraction of Cu, Co and Pb on oxidized single-walled carbon nanotubes and their determination by inductively coupled plasma mass spectrometry

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ABSTRACT

A novel method using a microcolumn packed with single-walled carbon nanotubes (SWNTs) as a new adsorption material was developed for the preconcentration of trace Cu, Co and Pb in biological and environmental samples prior to their determination by inductively coupled plasma mass spectrometry (ICP-MS). SWNTs oxidized with concentrated nitric acid have been proved to possess an exceptional adsorption capability for the analytes due to their surface functionalization. The adsorption behaviors of the analytes on SWNTs under dynamic conditions were studied systematically. The main factors influencing the preconcentration and determination of the analytes (pH, sample flow rate and volume, eluent concentration and interfering ions) have been examined in detail. Under the optimum conditions, the detection limits for Cu, Co and Pb were 39, 1.2 and 5.4 pg mL^{-1}, respectively; the relative standard deviations (RSDs) were found to be less than 6.0% ($n = 9$, $c = 1.0$ ng mL^{-1}). This method was validated using a certified reference material of mussel, and has been successfully applied for the determination of trace Cu, Co and Pb in real water sample with the recoveries of 96.0–109%.

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1. Introduction

It is well known that trace elements play an important biochemical and physiological role in the regulation of metabolism and influence human growth, development, health and disease. Co is essential trace element, having a complex role in many body functions, but it is toxic in large amount; Cu has a great influence on arterial strength; Pb is classified as prevalent toxic metal, which constitutes a major environmental health problem [1,2]. Therefore, sensitive, reproducible and accurate analytical methods are required for the determination of trace Cu, Co and Pb in environmental and biological samples. Although the detection power of instruments has been improved greatly due to the rapid development of modern science and technology, direct determination of trace elements at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences. For these reasons, an efficient separation and preconcentration procedure is often required prior to the measurement step [3–6].

Of many sample pretreatment procedures, solid-phase extraction has received an increasing attention in the separation/preconcentration of trace elements and elimination of matrix interference because of (i) high concentration factor, (ii) simple operation, (iii) the ability to handle large volume samples in a closed system free from contamination, (iv) rapid phase separation, and (v) the possibility of combination with different analytical techniques [7–9]. Being a most key factor of separation and preconcentration, sorbent material for solid-phase extraction determines the sensitivity and selectivity of analytical method. Various substances, including chelating resin, modified silica, alumina, cross-linked polymer, active carbon, cellulose and biological adsorbent, have been proposed and applied as the solid-phase extractants [10–17]. In recent years, nanometer-size material has drawn growing attention in analytical sciences because of its special properties. One of them is that most of the atoms of nanoparticle are on their surface. The surface atoms are unsaturated, possess highly chemical activity, and can easily bind with other atoms. Consequently, interesting in adapting nanometer material as a new adsorbent for the preconcentration and separation of substance has increased significantly [18–24]. Single-walled carbon nanotubes (SWNTs), as an interesting member in carbon family, have been predicted and experimentally proved to possess exceptional mechanical properties, high chemical stability and a large specific surface area, which make them a promising candidate as adsorbers [25]. Especially, their surface properties can be modified through chemical treatments to satisfy some special needs [26,27]. All of the facts

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mentioned above reveal to us that SWNTs may have a great analytical potential as an effective adsorbent. To our knowledge, however, studies on SWNTs as a solid-phase extraction adsorbent for the preconcentration and determination of trace elements have received little attention.

The aim of this work is to check the possibility of SWNTs as solid-phase extractant packed into a microcolumn for the preconcentration of trace elements under dynamic conditions. On the basis of the experimental results obtained, a novel method using a microcolumn packed with SWNTs coupled with ICP-MS was developed for the determination of trace Cu, Co and Pb in the biological and environmental samples.

2. Experimental

2.1. Apparatus

An X-7 ICP-MS system (Thermo Elemental Corporation, America) was used for the determination. The optimum operation conditions for ICP-MS are summarized in Table 1. An Ethos T microwave digestion device (Milestone, Italy) was used for sample digestion. This device is pressure and temperature controlled, so that on reaching maximum pressure and temperature the microwave energy input is restricted automatically.

A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, China) coupled with a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.), packed with SWNTs, were used for the preconcentration/separation process. A minimum length of PTFE tube with an i.d. of 0.5 mm was used for all connections. The pH values of solution were controlled with a pH meter (Thermo Orion Corporation, America) supplied with a combined electrode.

2.2. Standard solution and reagents

The stock standard solutions (1.0 mg mL^{-1}) of Cu, Co and Pb were obtained from the National Analysis Center of Iron & Steel (Beijing, China). Working solutions were prepared daily by appropriate dilution of stock solutions. All reagents used were ultrapure or at least of analytical grade (The First Reagent Factory, Shanghai, China). High purity deionized water (18.2 MΩ) obtained from Milli-Q® A10 system (Millipore Corporation, America) was used throughout this work. The pH values of solution were achieved by adding to the solution an appropriate amount of HNO_3 or $NH_3{\cdot}H_2O$.

SWNTs were kindly provided by Shenyang Metal Institute of Chinese Academy (Shenyang, China). The method of preparation and character of SWNTs were reported previously [28]. Before use, SWNTs were oxidized with a concentric HNO_3 according to the literature [29]. The treated SWNTs were dried at 100 °C and stored for future use.

Table 1
Operating conditions for ICP-MS.

Plasma power (kW)	1.3
Plasma argon flow rate (L min^{-1})	14.5
Auxiliary argon flow rate (L min^{-1})	0.78
Nebulizer argon flow rate (L min^{-1})	0.95
Sampler orifice (nickel) (mm)	1.1
Skimmer orifice (nickel) (mm)	0.7
Acquisition mode	Peak-jumping
Number of sweep	100
Dwell time (ms)	10
Acquisition time (s)	40
Number of measurements per peak	3
Isotopes	^{63}Cu, ^{59}Co and ^{208}Pb

2.3. Column preparation

Twenty milligrams of the treated SWNTs was filled into a PTFE microcolumn (20 mm × 3.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 1.0 mol L^{-1} HNO_3 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 HNO_3 or $NH_3{\cdot}H_2O$.

2.4. Sample pretreatment

A sample portion (0.1000 g of mussel) was accurately weighed into Teflon vessel of 100 mL, and then 6.0 mL of concentrated HNO_3 and 2.0 mL of $HClO_4$ were added, respectively. After about 5 min, when the first vigorous reaction had taken place, the digestion vessels were closed and placed into the microwave oven. The samples were digested in microwave oven at 120 °C (ramp, 10 min; hold, 15 min) with a power 1.0 kW. When the digestion programs were complete, the vessels were cooled to room temperature. The vessels were then opened carefully, and a clear acid phase was observed. The analytes were heated on a hot plate at 140 °C to evaporate excess reagents. After reaching near dryness, the residue was dissolved in 0.1 mol L^{-1} HNO_3, and diluted to 50.0 mL with deionized water. A blank digest was carried in the same way. Then the preconcentration procedure given above was applied to the final solution.

Natural water sample (from East Lake of Wuhan, China) was collected in pre-washed (with doubly distilled, dilute HNO_3 and deionized water, respectively) polyethylene bottles. The water sample was filtered through a membrane filter of 0.22 μm pore size prior to analysis. The pH of the samples was adjusted to 8.0 with buffer solution. The blanks were prepared in the same way as the sample, but omitting the samples. The preconcentration procedure described above was applied to the samples. The levels of analytes in the samples were determined by ICP-MS.

2.5. General procedure

Sample solutions were prepared by appropriate dilution of the stock solutions and adjusted to the desired pH with HNO_3 or $NH_3{\cdot}H_2O$ before use. The obtained solution was passed through the microcolumn with a peristaltic pump at a desired flow rate. Afterwards, the retained metal ions were eluted with 2.0 mL of 0.5 mol L^{-1} HNO_3. The analytes in the effluents were determined by ICP-MS. The column could be used repeatedly after regeneration with 0.5 mol L^{-1} HNO_3 and deionized water, respectively.

3. Results and discussion

3.1. Effect of pH on adsorption

After oxidization with concentrated HNO_3, some acidic groups such as –COOH and –OH can form on the surface of SWNTs. Hence, the adsorption of ions on SWNTs is highly dependent on the solution pH value, which affects the surface charge of the adsorbent and degree of ionization and speciation of the adsorbates. The pH at which the zeta potential equals to zero is called the isoelectric point (IEP), and it is used to assess the adsorbent surface charge quantitatively. Because of the surface functionalization, the IEP of SWNTs shifts to lower pH values [29]. At pH > IEP, SWNTs surfaces, covered by the negative charges, attract cations. The decrease of pH leads to the neutralization of SWNTs surfaces, so cation adsorption decreases quickly.

In order to evaluate the pH dependence of the adsorption, the pH values of sample solution were adjusted to a range of 1.0–9.0. The adsorption percentage was calculated based on a difference between the amounts of the metal ions in the starting sample and

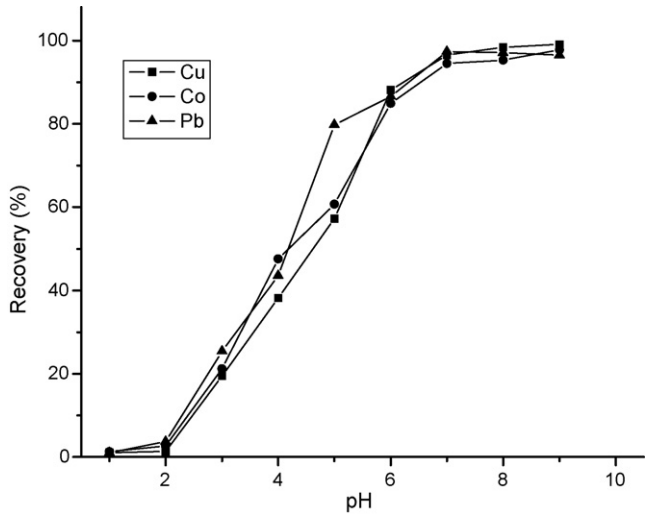

Fig. 1. Effect of pH on recovery of the analytes from SWNTs ($N = 3$). Cu^{2+}, Co^{2+} and Pb^{2+}: 5.0 ng mL^{-1}; sample volume: 20 mL.

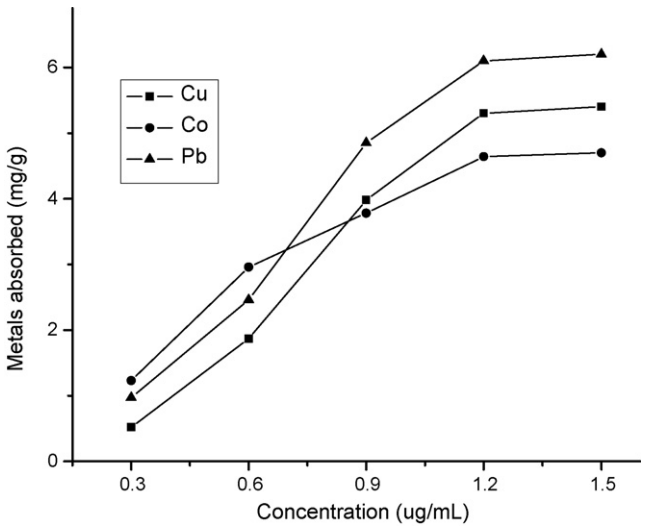

Fig. 2. The breakthrough curve of the analytes on SWNTs ($N = 3$). pH = 8.0; sample volume: 20 mL.

the solution from the column. The effects of pH value on the recoveries of analytes are shown in Fig. 1. It can be seen that the studied ions were absorbed poorly at pH < 2.0. A quantitative recovery (>90%) for the analytes was obtained in the pH ranging from 7.0 to 9.0. Thus, a pH of 8.0 was used throughout. It should be pointed out here that under the selected experimental conditions, there is no any hydroxide precipitate in the sample solution.

3.2. Effect of eluent concentration and volume

The elution of the absorbed analytes could be achieved by using an appropriate eluent solution capable of effectively striping them from the SWNTs and bring them into the solution. From Fig. 1, it can be found that the adsorption of the analytes on SWNTs could be negligible at pH < 2.0. For this reason, various concentrations of HNO_3 were studied for the desorption of the retained analytes from the microcolumn. The results in Table 2 show that 0.5 mol L^{-1} HNO_3 was sufficient for quantitative elution, the good recoveries could be obtained (>90%).

The effect of the eluent volume on the recoveries of analytes was also studied by keeping HNO_3 concentration of 0.5 mol L^{-1}. It was found that the quantitative recoveries (>90%) could be obtained with 2.0 mL of 0.5 mol L^{-1} HNO_3.

3.3. Influence of sample flow rate

The sample flow rate through the column packed with SWNTs is a very important parameter, since it affects the retention of cations on the adsorbent and the duration of complete analysis. The effect of sample flow rate on adsorption percentage of analytes was investigated by passing 20 mL of sample solution through the microcolumn with a peristaltic pump at flow rate between 0.2 and 2.0 mL min^{-1}. The experimental results showed that quantitative recoveries of the studied ions (>90%) were obtained in the flow rate range of 0.2–1.2 mL min^{-1}. However, the recoveries of the studied ions will decrease by further increasing the flow rate above 1.2 mL min^{-1} because of a decrease in adsorption kinetics. Thus, all subsequent experiments were performed at a flow rate of 1.2 mL min^{-1}.

3.4. Effect of sample solution volume

The preconcentration and separation of the analytes were usually performed at a lower concentration. In order to improve the relative sensitivity of the procedure when determining very low concentration of analytes, a relative large sample volume is usually suggested. For this purpose, sample volumes of 25, 50, 100, 150, 200 and 250 mL were adopted to investigate effect of sample volume. Mixed sample solutions containing the analytes (Cu: 20 ng; Co: 10 ng; Pb: 15 ng) were passed through the microcolumn at a 1.2 mL min^{-1} flow rate, and the results showed that the quantitative recoveries (>90%) were obtained for sample volume up to 100 mL. As described previously, 2.0 mL of 0.5 mol L^{-1} HNO_3 was sufficient to elute the analytes adsorbed on the SWNTs. Thus, an enrichment factor of 50 could be obtained with 100 mL of sample solution in this work.

3.5. Adsorption capacity

Adsorption capacity, as an important parameter for the evaluation of adsorbent, was investigated by a method provided in the literature [30]. For this purpose, 20 mL aliquots of a series of concentrations (0.3–1.5 μg mL^{-1}) were adjusted to the appropriate pH, then preconcentrated and eluted. The amount of metal ions adsorbed at each concentration level was determined by ICP-MS. The breakthrough curves were obtained by plotting the metal

Table 2
Effect of eluent concentration on the recoveries of the analytes ($N = 3$).

Eluent[a] (HNO_3, mol L^{-1})	Cu^{2+}	Co^{2+}	Pb^{2+}
0.1	81.7	83.5	82.1
0.2	87.5	86.1	85.9
0.5	98.1	103	98.7
1.0	102	97.1	99.1
2.0	96.7	101	98.7

[a] Eluent volume: 2.0 mL.

Table 3
Effect of the coexisting ions on the recoveries of the analytes ($N = 3$).

Coexisting ion	Concentration ratio[a]
Na^+, K^+	10,000
Ca^{2+}, Mg^{2+}	5,000
Al^{3+}, Fe^{3+}	300
SiO_3^{2-}, SO_4^{2-}	5,000
PO_4^{3-}	1,500

[a] Concentration ratio: foreign ion/determined ions.

Table 4
Comparative data of the analytical performance with those in the literature.

Adsorbent	Method	Element	Enrichment factor	D.L. (ng mL^{-1})	RSD (%)	Reference
Nanometer-sized alumina	ICP-MS	Cu, Co and Pb	5.0	0.0082–0.045	3.0–4.2	[31]
Multiwalled carbon nanotubes-APDC	FAAS	Cu, Co and Pb	80	0.3–0.6	<5	[23]
Nanometer-sized TiO_2	ICP-AES	Cu, Mn, Cr and Ni	50	0.34–1.78	2.4–5.5	[32]
Nanometer-sized sol–gel zirconia coating	ICP-MS	Cu, Cr, Cd and Pb	6.25	0.0037–0.018	2.0–4.9	[1]
Oxidized SWNTs	ICP-MS	Cu, Co and Pb	50	0.0012–0.039	3.9–5.2	This work

ion concentrations (μg mL^{-1}) *versus* the milligrams of metal ions adsorbed on per gram of adsorbent (Fig. 2). The adsorption capacity calculated from the breakthrough curve is 5.4, 4.7 and 6.2 mg g^{-1} for Cu, Co and Pb, respectively. Further work on systematic investigation of adsorption mechanism is being undertaking.

3.6. Effect from coexisting ions

The effects of common coexisting cations and anions, as commonly expected in biological and environmental samples, on the preconcentration and determination of the analytes were examined. The tolerance limit of coexist ions is defined as the largest amount making the recovery of the analyte less than 90%. Sample solutions of 10 ng mL^{-1} Cu, Co and Pb containing the added ions with 20 mL sample volume were treated according to the recommended procedure. The effects of the interfering ions on the recoveries of analytes are shown in Table 3. It can be seen that the major cations and anions were not found to interfere with the determination in the range of their amounts tested.

3.7. Column reuse

In order to examine the long-term stability of SWNTs, it was subject to successive adsorption and desorption cycles by passing 20 mL of the solutions containing the analytes through the column. The stability and potential regeneration of the column was assessed by monitoring the changes in the recoveries of the analytes. The column can be reused after regenerated with 5.0 mL of 0.5 mol L^{-1} HNO_3 and 20 mL deionized water, respectively, and stable up to 40 adsorption–elution cycles without obvious decrease in the adsorption capacity and the recoveries for the analytes.

3.8. Detection limits and precisions

Under the optimized conditions, the detection limits of this method for Cu, Co and Pb, based on three times the standard deviation of 11 runs of the blank solution, were found to be 39, 1.2 and 5.4 pg mL^{-1}, respectively. The relative standard deviation (RSD) of this method, obtained for the nine determinations of 1.0 ng mL^{-1} of Cu, Co and Pb, were 4.8%, 5.2% and 3.9%, respectively. The comparison of the analytical performances in the present work with those reported in the literature [23,31,32,1] was given in Table 4. Generally, the results obtained by this method are comparable to those of reported method or better than them.

Table 5
Analytical results of the analytes in standard reference material of mussel (GBW 08571).

Element	Added (μg g^{-1})	Found[a] (μg g^{-1})	Certified (μg g^{-1})	Recovery (%)
Cu	0	7.3 ± 1.0	7.7 ± 0.9	–
	5.0	12.5 ± 0.8	–	104
Co	0	0.91 ± 0.07	0.94 ± 0.06	–
	1.0	1.87 ± 0.11	–	96.0
Pb	0	2.05 ± 0.14	1.96 ± 0.09	–
	1.0	3.14 ± 0.16	–	109

[a] Mean value ± standard deviation, $n = 3$.

Table 6
Analytical results of the analytes in natural water samples.

Element	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)
Cu	0	3.57 ± 0.14	–
	1.0	4.54 ± 0.19	97.0
	2.0	5.69 ± 0.17	106
Co	0	1.32 ± 0.08	–
	0.5	1.84 ± 0.08	104
	1.0	2.40 ± 0.12	108
Pb	0	2.34 ± 0.11	–
	0.5	2.82 ± 0.10	96.0
	1.0	3.39 ± 0.15	105

[a] Mean value ± standard deviation, $n = 3$.

3.9. Sample analysis

In order to establish the validity of the proposed method, a certified reference material of mussel (GBW 08571) and water sample were analyzed by this procedure. The results were summarized in Table 5. The determined values are in good agreement with the certified values for the analytes. The proposed method was also applied to the determination of analytes in the natural water sample. Various amounts of analytes were also spiked to the water sample. The results were given in Table 6. A good agreement was obtained between the added and measured analyte amounts. The recoveries of the analytes were in a range of 96.0–109%.

4. Conclusions

In this research, single-walled carbon nanotubes (SWNTs) were treated with concentrated nitric acid to introduce some functional groups, such as carboxyl, hydroxyl and carbonyl, on their surfaces, which improve their adsorption capability of ions in solution. Furthermore, the microcolumn separation and preconcentration system using SWNTs as a sorbent material for ICP-MS were evaluated, and demonstrated to be promising for routine determination of trace/ultra-trace elements. The adsorption behavior of the analytes on SWNTs was investigated systematically. The analytes retained on SWNTs can be easily desorbed and no carryover is observed in the next analysis. An enrichment factor of 50 was achieved. It is expected that SWNTs have great potential as an adsorbent for the preconcentration and determination of trace/ultra-trace elements in various samples.

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