Chromium Speciation Analysis by Solid-Phase Extraction on Titanium Dioxide Nanotubes and Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

In recent years, chemical speciation of an element has been drawing growing attention in the fields of environmental, toxicological, nutritional, medical, and analytical science (1). Chromium speciation is of great interest because its toxicity depends upon its oxidation state. Cr(III) is considered to be essential to mammals for the maintenance of the glucose, protein and lipid metabolism (2,3). On the other hand, Cr(VI) is reported to be toxic for biological systems even at relatively low levels (4). Therefore, it is of increasing importance to monitor the concentration of individual chromium species.

Up to now, the direct determination of chromium species has not been possible 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 perform speciation, a chemical separation and pre-concentration step is often required prior to analysis. A variety of methods, including solvent extraction, coprecipitation, ion exchange, solid-phase extraction, chelating resin adsorption, chromatography, and catalytic cathodic stripping voltammetry, have been developed for Cr speciation (5-12). Among these procedures, solid-phase extraction has attracted considerable practical interest in

ABSTRACT

A novel method was developed for the speciation of inorganic chromium by titanium dioxide nanotubes as a solid phase extractant and inductively coupled plasma mass spectrometry (ICP-MS). In order to achieve the quantitative separation of Cr(III) and Cr(VI), experiments were performed to optimize conditions such as pH, sample flow rate, sample volume, and concentration of the eluent. During the separation steps, Cr(III) was selectively sorbed on the column packed with TiO₂ nanotubes in the pH range of 5.0-8.0, while Cr(VI) was found to remain in solution. The retained Cr(III) was subsequently eluted with 2.0 mL of 1.5 mol L⁻¹ nitric acid.

The detection limit of Cr(III) for this method was 0.023 ng mL⁻¹, and the relative standard deviation (RSD) for Cr(III) was 3.8% (n=9, c= 0.5 ng mL⁻¹). The linear range of the calibration curve spanned three orders of magnitude. The proposed method was applied to the determination of Cr(III) and Cr(VI) in water samples with the recovery of 94.2-102%.

comparison to the traditional liquid-liquid extraction methods because of its major advantages: (i) simplicity of operation, (ii) high concentration factor, (iii) rapid phase separation, and (iv) ability to combine with different detection techniques (13). It should be noted that the adsorbent material plays a fun-

damentally important role in this technique, and the development of a new adsorbent material with high selectivity and sensitivity is forever of interest to analysts. Owing to the small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties, nanostructure materials as a new adsorbent for preconcentration and separation of a substance have drawn growing attention in the analytical sciences. Some nanometer-size substances, such as carbon nanotubes, carbon nanofibers, nanometer-size titanium dioxide, nanometer-size zirconium oxide, FeC nanoparticles, and nanometer-size silicon dioxide have been successfully used as solid-phase extractants for preconcentration/separation of metal and nonmetal ions (14-19), as well as adsorption of organic compounds (20).

TiO₂ nanotubes have been used for the photodegradation as the photocatalyst. However, they should have much higher adsorption capacity than that of TiO₂ nanoparticles because they have been shown to have a large surface area, which makes them promising candidates as adsorbents (21,22). To the best of our knowledge, however, studies on the application of TiO₂ nanotubes to the analysis of elemental speciation have received little attention. The main aim of this work was to develop TiO₂ nanotubes as a new adsorbent for the simultaneous separation and determination of inorganic chromium speciation by ICP-MS. The adsorption characteristics of TiO₂ nanotubes for the analytes were investigated in detail. The proposed

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method was applied to the speciation of inorganic chromium in water samples with satisfactory results.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA) was used for the analysis. The optimum operating conditions for the ICP-MS are summarized in Table I.

The pH values of the solutions were measured with a pH meter (Thermo Orion Corporation, USA), supplied with a combined electrode. An HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R.China), coupled with a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.) packed with TiO₂ nanotubes, was used for the preconcentration/separation process. A minimum length of PTFE tube with a 0.5 mm i.d. was used for all connections.

Standard Solutions and Reagents

The stock standard solution (1.0 mg mL⁻¹) of Cr(III) was obtained from the National Analysis Center of Iron & Steel (Beijing, P.R. China); Cr(VI) was prepared by dissolving K₂Cr₂O₇ (Tianjin Reagent Factory, Tianjin, P.R. China) in 0.1 mol L⁻¹ nitric acid. Working solutions were prepared daily 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, USA) was used throughout this work.

Sample Preparation

Water samples were collected from Wuhan (P.R. China) and stored in prewashed polyethylene bottles. Before analysis, the water

samples were filtered through a cellulose membrane filter of 0.22 μm pore size. The pH of the samples was adjusted to the desired value with HNO₃ and NH₃·H₂O. 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.

Column Preparation

A PTFE microcolumn (20 mm × 3.0 mm i.d.), plugged with a small portion of glass wool at both ends, was filled with 100 mg of TiO₂ nanotubes. 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 with HNO₃ and NH₃·H₂O.

General Procedure

An aliquot of aqueous sample solution containing Cr(III) and Cr(VI) was prepared, and the pH was adjusted to the desired pH with HNO₃ and NH₃·H₂O before use. The obtained solution was passed through the column by using a peristaltic pump at the desired flow rate. Cr(III) was retained on the column, while Cr(VI) was collected in the effluent. Afterwards, the sorbed Cr(III) was

eluted with 2.0 mL of 1.5 mol L⁻¹ HNO₃. The Cr concentration was determined in the two fractions by ICP-MS.

RESULTS AND DISCUSSION

Effect of pH on Adsorption of Cr(III) and Cr(VI)

In this work, the pH value plays an essential role with respect to the adsorption of different species of chromium on TiO₂ nanotubes since it affects the surface charge of the adsorbent and speciation of the adsorbates. Thus, the effect of the pH on the retention of Cr(III) and Cr(VI) on the column of TiO₂ nanotubes was studied. The sample solutions were adjusted to a pH range of 1.0–8.0 with HNO₃ and NH₃·H₂O, and then passed through the microcolumn. The retained ions were stripped off the column and measured by ICP-MS, as described in the recommended procedure. The effect of pH on the recoveries of Cr(III) and Cr(VI) are shown in Figure 1. As can be seen, the quantitative recovery (>90%) was found for Cr(III) in part of the pH range 5.0–8.0, whereas that of Cr(VI) was less than 6.0%. This suggests that it is possible to separate Cr(III) and Cr(VI): Cr(III) is retained on the column, while Cr(VI) is not. A pH of 6.0 was selected for this experiment.

TABLE I.
ICP-MS Operating Parameters

Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 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 (number of replicates)
Isotopes	⁵² Cr and ¹¹⁵ In

Elution of Cr(III)

As can be seen in Figure 1, the Cr(III) ions were not retained on the TiO₂ nanotubes at a higher acidity (pH <1.0). Hence, nitric acid was used as the eluent reagent to elute the retained Cr(III) on the microcolumn packed with TiO₂ nanotubes following the above procedure. The effect of eluent concentrations on the recoveries of the analytes was evaluated under the selected experimental conditions. The experimental results show that the elution of Cr(III) was quantita-

tively removed with 2.0 mL of 1.5 mol L⁻¹ HNO₃, and good recoveries were obtained (>90%).

In addition, the effect of eluent volume on the recovery of the analytes was also studied in the 0.5–3.0 mL range. The results showed that quantitative recoveries for Cr(III) (>90%) were obtained when the volume exceeded 1.5 mL. Taking the required sampling volume for ICP-MS into account, 2.0 mL of 1.5 mol L⁻¹ HNO₃ was used for all subsequent experiments to ensure complete elution.

Influence of Sample Flow Rate

The flow rate of the sample solution is also a very important parameter for the quantitative separation of Cr(III) and Cr(VI) on TiO₂ nanotubes, including the length of the complete analysis. Therefore, the effect of the sample solution flow rate on the retention of Cr(III) on TiO₂ nanotubes was examined under the optimum conditions (pH, eluent, etc.). The flow rate was adjusted in the 0.4–2.0 mL min⁻¹ range. It can be seen from Figure 2 that the retention of Cr(III) was practically unchanged up to 1.2 mL min⁻¹, but its retention decreases with higher flow rates due to a decrease in the adsorption kinetics. Accordingly, all subsequent experiments were performed at a flow rate of 1.2 mL min⁻¹.

Effect of Sample Solution Volume

The effects of sample volume on the retention behaviors of Cr(III) on TiO₂ nanotubes was investigated by varying the sample volume containing 10 ng of Cr(III) from 20 to 200 mL. The results in Figure 3 indicate that when the sample volumes of Cr(III) were lower than 100 mL, the recoveries of Cr(III) were all above 90% and remained constant,

Fig. 1. Effect of pH on recovery of Cr(III) and Cr(VI) on TiO₂ nanotubes. Cr(III) and Cr(VI): 4.0 ng mL⁻¹ and sample volume: 20 mL.

Fig. 2. Effect of flow rate of sample solution on the recovery of Cr(III) on TiO₂ nanotubes. pH: 6.0, Cr(III): 4.0 ng mL⁻¹, and sample volume: 20 mL.

Fig. 3. Effect of sample volume on recovery of Cr(III) on TiO₂ nanotubes. pH: 6.0; Cr(III): 10 ng.

whereas a decrease of the recovery was observed with the continuous increase of sample volume. As described in the previous section, the analytes were quantitatively recovered using a volume of 2.0 mL of 1.5 mol L⁻¹ HNO₃. Thus, an enrichment factor of 50-fold was obtained for the ions studied in this work. Considering the analysis time, a 20-mL sample volume was used for the analysis of real samples.

Adsorption Capacity

The capacity study used was adapted from that recommended in the literature (23). For this purpose, 20-mL aliquots of a series of concentrations (5.0–30.0 µg mL⁻¹) were adjusted to the appropriate pH, and then the preconcentration and separation procedure described above

was applied. The breakthrough curves were obtained by plotting the metal ion concentrations (µg mL⁻¹) versus the milligrams of metal ions adsorbed on per gram of adsorbent. The adsorption capacity calculated from the breakthrough curve was 8.7 mg g⁻¹ for Cr(III).

Effect of Interfering Ions

The effects of common coexisting ions on the adsorption of Cr(III) on TiO₂ nanotubes were investigated. In these experiments, various salts and ions were added individually to a solution containing 4.0 ng mL⁻¹ Cr(III), and the test procedure described above was applied. The tolerance limit was set as the coexisting ion amount required to cause ±5.0% error in the determination of the analytes. The results listed in Table II show 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 TiO₂ nanotubes was studied by monitoring the changes in the recoveries of Cr(III). It was found that the column can be reused after regeneration with 10 mL of 1.0 mol L⁻¹ HNO₃ and 20 mL deionized water, respectively, and is stable up to 40 adsorption-elution

cycles without an obvious decrease in the recovery of the analytes.

Detection Limits and Precision

According to the definition of IUPAC (30), the detection limits of this method for Cr(III), calculated from three times the standard deviation of the blank signal, was 0.023 ng mL⁻¹ with the relative standard deviation of 3.8% (n=9, c=0.5 ng mL⁻¹).

Analysis Application

The feasibility of the determination for Cr(III) and Cr(VI) on TiO₂ nanotubes was explored in water samples including reference material (obtained from P.R. China), groundwater from the market, and wastewater from an industrial site in Wuhan City. The proposed preconcentration and separation technique was applied to the analysis of Cr species by the internal standard method (using In as the internal standard element). The reliability was checked by spiking the experiments. The results listed in Table III indicate that the recoveries are reasonable for trace analysis, in a range of 94.2–102%.

CONCLUSION

In this work, the adsorption behavior of Cr(III) and Cr(VI) on TiO₂ nanotubes has been investigated systematically. The experimental results indicate that Cr(III)

TABLE II
Tolerance Limits of Coexisting Ions

Coexisting Ion	Concentration Ratio ^a
Na ⁺ , K ⁺	5000 ^b
Ca ²⁺ , Mg ²⁺	2000 ^b
Fe ³⁺ , Al ³⁺	500 ^b
PO ₄ ³⁻ , SiO ₃ ²⁻ , SO ₄ ²⁻	5000 ^b

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

^b Maximum concentrations tested (each interference ion was added into the solution, separately).

Table III
Analytical Results and Recoveries of Cr(III) and Cr(VI) in Water Samples

Sample	Added (ng mL ⁻¹)		Found ^a (ng mL ⁻¹)		Total	Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI) ^b		Cr(III)	Cr(VI)
GSBZ 5009-88 ^c	-	-	-	-	668±45	-	-
	500	-	-	-	1150±72	96.4	-
Ground Water	0	0	0.98±0.06	0.52±0.04	1.50±0.11	-	-
	1.0	1.0	1.93±0.13	1.54±0.11	3.47±0.29	95.0	102
Wastewater	0	0	6.72±0.56	2.75±0.19	9.47±0.42	-	-
	5.0	5.0	11.6±0.57	7.46±0.37	19.06±1.23	97.6	94.2

^a Mean value ± standard deviation, n=5.

^b Calculated value.

^c National reference material (China): the certified value of Cr concentration is 640±36 ng mL⁻¹.

was almost quantitatively retained in the pH range of 5.0-8.0, while Cr(VI) remained in the solution. The Cr(III) retained on TiO₂ nanotubes can be easily desorbed, and no carryover is observed in the next analysis. An enrichment factor of 50-fold was achieved. Based on the high adsorption selectivity of the TiO₂ nanotubes for Cr(III) and Cr(VI), a simple, rapid, and reliable method was developed for the pre-concentration, separation, and determination of chromium species in environmental water samples by the microcolumn packed with TiO₂ nanotubes coupled with ICP-MS.

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