Solid Phase Extraction of Mn, Co, Cr, Zn, and Pb on Titanium Dioxide Nanotubes for Their Determination by Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Due to their natural and anthropogenic sources, environmental pollution caused by metals, especially heavy metals, has received considerable attention around the world. Unlike organic pollutants, metals are non-biodegradable and hence, are accumulated by living organisms. Mn is a micronutrient for the function of the central nervous system and normal bone growth (1). Co is an essential trace element in human dietary intake, possessing anti-anemic properties and acting as the central atom of vitamin B₁₂, which is widely responsible for the production of red blood cells (2). The toxicity of Cr depends on its chemical forms (3). Zn plays an important role in the human metabolism (4). Pb is classified as a prevalent toxic metal, which constitutes a major environmental health problem (5). It is worth noting that at higher concentrations, all of the metals are recognized as potentially toxic (2, 6-8). Therefore, accuracy in the determination of trace metals in biological and environmental samples is very important.

It is well known that inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry, and inductively coupled plasma atomic emission spectrometry still represent the most important routine methods for elemental analysis. However, the direct determination of trace/ultra-trace elements in biological and environmental samples often suffers from the following problems:

ABSTRACT

In this paper, the use of titanium dioxide nanotubes (TDNTs) as solid-phase extraction adsorbent for on-line microcolumn separation and preconcentration of trace metals (Mn, Co, Cr, Zn, and Pb) was investigated by inductively coupled plasma mass spectrometry (ICP-MS). The effects of the experimental parameters, including pH, sample flow rate and volume, elution conditions and interfering ions on the recoveries of the analytes were investigated systematically. The experimental results showed that the analytes were adsorbed quantitatively on TDNTs in the pH range from 7.0 to 9.0 and then eluted completely with 1.5 mol L⁻¹ HNO₃ solution. Under the optimum conditions, the detection limits of this method ranged from 0.3 pg mL⁻¹ (Co) to 15 pg mL⁻¹ (Zn) with a 150-fold enrichment factor; the relative standard deviations (RSDs) for the analytes were less than 4.5% (n=9, c=1.0 ng mL⁻¹). The linear range of the calibration curve spanned three orders of magnitude. This method was applied to the determination of trace elements (Mn, Co, Cr, Zn, and Pb) in natural water samples with recoveries of 94.8–104%. In order to validate this method, the certified reference material GBW 07601 Human Hair was analyzed, and the determined values were in good agreement with the certified values.

(i) extremely low concentration, (ii) complicated sample constituent, and (iii) remarkable matrix effects. In order to achieve an accurate and reliable analytical result, an effective separation and preconcentra-

tion technique is usually mandatory before analysis (9-10). Several of these procedures, including solvent extraction, coprecipitation, ion exchange, cloud point extraction, solid phase extraction (SPE), capillary microextraction and chromatography, have been commonly used for sample pretreatment (11-17). Among them, SPE has attracted considerable practical interest because of major advantages such as convenience, time savings, low cost, reduced solvent utilization, high concentration factor, possible miniaturization, and ease of automation (18-20). In addition, SPE is often classified into two operation modes: batch operation and column operation, followed by the on-line or off-line operation mode. The on-line operation technique has become increasingly popular because of its merits of low blank values, high preconcentration factor, simple operation, and improvement in the detection limits (21). It should be pointed out that adsorbent material packed in a microcolumn plays a fundamentally crucial role in on-line SPE for the separation and preconcentration of different substances.

In recent years, the development of a new adsorbent material with high selectivity and sensitivity for SPE has been of interest to analysts (22, 23). Owing to their small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties, some nanostructure materials for preconcentration and separation of substances have drawn growing attention in the analytical sciences (24-32). Titanium dioxide nanotubes (TDNTs), as a new and excellent material, have

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attracted great attention in the fields of photocatalysis and dye-sensitized solar cells (33, 34). It was proven that TDNTs have a larger surface area than titanium dioxide nanoparticles and carbon nanotubes (35). In addition, they provide very attractive features, such as high chemical stability, durability, corrosion resistance, low or no toxicity, and low cost. All of these facts mentioned above reveal that TDNTs may be a promising candidate as adsorbers for the preconcentration and separation of different substances. To the best of our knowledge, however, studies on the use of TDNTs for the analysis of elements and their forms have not received enough attention.

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

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA) with a concentric nebulizer (Meinhard) and a standard low-volume glass impact-bead spray chamber was used for analyte determination. The optimum operating conditions for the ICP-MS are given in Table I. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R. China) coupled to a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.) packed with TDNTs was used for the preconcentration/separation process. A minimum length of

PTFE tube with an inner diameter of 0.5 mm was used for all connections. The pH values of the solution were measured with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode. An Ethos T microwave digestion device (Milestone, Italy) was used for sample digestion.

Standard Solutions and Reagents

The stock standard solutions (1.0 mg mL⁻¹) of Mn, Co, Cr, Zn, and Pb were obtained from the National Analysis Center of Iron & Steel (Beijing, P.R. China). The working solutions were prepared by dilution from the stock solutions. Quantification of the elemental concentrations was performed using external calibration with aqueous standard solutions with ¹¹⁵In as the internal standard. The TDNTs were synthesized and characterized in our laboratory. All reagents used were ultrapure or at least of analytical grade. High purity deionized water (18.2 MΩ) obtained from a Milli-Q® A10 system (Millipore Corporation, USA) was used throughout this work.

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 60 milligrams of TDNTs. Before use, 1.5 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 NH₃•H₂O.

Sample Pretreatment

A certified reference material (CRM) sample of 0.1000 g GBW 07601 Human Hair (obtained from the Institute of Geophysical and Geochemical Prospecting, Langfang, P.R. China) was accurately weighed into a 100-mL Teflon® vessel, and then 4.0 mL concentrated HNO₃ and 2.0 mL H₂O₂ (30%, w/w) were added, respectively. The solid particles attached to the wall of the Teflon vessels were rinsed with digestion reagents. After about 5 minutes, the digestion vessels were closed and placed into a microwave oven. The samples were digested in a microwave oven at 180 °C (ramp, 10 minutes; hold, 15 minutes) at 1.0 kW power. After cooling, the solutions were transferred to Teflon beakers, 0.5 mL HClO₄ was added, then heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 0.1 mol L⁻¹ HNO₃ solution and diluted to the desired volume.

TABLE I
ICP-MS Operating Parameters

Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 L min ⁻¹
Auxiliary Argon Flow Rate	0.80 L min ⁻¹
Nebulizer Argon Flow Rate	0.91 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	⁵⁵ Mn, ⁵⁹ Co, ⁵² Cr, ⁶⁶ Zn, ²⁰⁸ Pb, and ¹¹⁵ In

A water sample (collected from the Yangtze River, Wuhan, P.R. China) was filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling. Procedural blanks were treated in the same way.

General Procedure

To study the adsorption of the analytes on TDNTs under dynamic conditions, a portion of aqueous sample solution containing the analytes was prepared, and the pH adjusted to the desired value. The solution was passed through a column by using a peristaltic pump at the desired flow rate. Afterwards, the retained analytes were eluted with 2.0 mL of 1.5 mol L⁻¹ HNO₃ solution. The analytes in the effluents were determined by ICP-MS. The microcolumn could be used repeatedly after regeneration with 1.5 mol L⁻¹ HNO₃ solution and deionized water. The recoveries of the analytes were calculated from the ratio of the concentration found by ICP-MS to that of the initial sample.

RESULTS AND DISCUSSION

Effect of pH on Adsorption

Owing to the effect on chemical composition and surface charge of

the adsorbents (36,37), the pH value plays a very important role in the adsorption of the analytes on the TDNTs. For this reason, the effect of pH on the adsorption of the studied ions on the TDNTs was investigated under dynamic conditions. The sample solutions were adjusted to the pH range of 1.0–9.0 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 effects of pH on the recoveries of the analytes are shown in Figure 1. As can be seen, the quantitative recoveries of the analytes (>90%) were found in the pH range from 7.0 to 9.0. Thus, a pH of 8.0 was used in the following experiments.

The adsorption behaviors of the analytes on the TDNTs in the pH range mentioned above can be explained in terms of surface charge of the TDNTs. According to the literature (38, 39), the TDNTs exist mainly as H₂Ti₂O₄(OH)₂ at a lower pH value, but might convert to H[Ti₂O₄(OH)₂]⁻ and [Ti₂O₄(OH)₂]²⁻ with an increase in pH value, which leads to the increase of cation adsorption.

Selection of Eluent Conditions

The choice of eluent is very important for the successful coupling of a microcolumn preconcentration system to ICP-MS. From Figure 1, it can be seen that the adsorption of the analytes on the TDNTs is negligible at pH <1.0. Thus, various concentrations of HNO₃ were studied for desorption of the retained analytes from the microcolumn. The results in Table II show that 1.2 mol L⁻¹ HNO₃ was sufficient for the quantitative elution of the analytes (>90%). The effect of eluent flow rate on the recovery of the analytes was examined by keeping the eluent volume at 2.0 mL and a concentration of 1.2 mol L⁻¹ eluent, respectively. The experimental results indicated that any flow rate between 0.2 and 0.8 mL min⁻¹ can be used for the quantitative elution of the analytes. To obtain as short an analysis time as possible, the flow rate of the eluent was set at 0.6 mL min⁻¹ in this work.

The effect of eluent volume on the recoveries of the analytes was also investigated by keeping the concentration of the 1.2 mol L⁻¹ HNO₃ solution at a 0.6 mL min⁻¹ flow rate. The experimental results demonstrated that quantitative recoveries (>90%) could be obtained with 1.0 mL of 1.2 mol L⁻¹ HNO₃ solution. Taking the required

Fig. 1. Effect of pH on the recovery of analytes on TDNTs. Mn²⁺, Co²⁺, Cr³⁺, Zn²⁺, and Pb²⁺: 5.0 ng mL⁻¹; sample volume: 25 mL.

TABLE II
Effect of Eluent Concentration
on the Recoveries of the Analytes

Eluent ^a (HNO ₃ , mol L ⁻¹)	Mn ²⁺	Co ²⁺	Cr ³⁺	Zn ²⁺	Pb ²⁺
0.3	46.3	51.6	38.9	40.1	53.1
0.6	70.1	64.3	57.6	61.3	71.3
0.9	82.9	87.9	79.8	85.7	89.2
1.2	98.7	101	93.7	97.2	99.6
1.5	95.2	98.5	97.1	102	95.3
1.8	103	96.2	98.2	99.1	101

^a Eluent volume: 2.0 mL

Analytes: 5.0 ng mL⁻¹

sampling volume for ICP-MS into account, a 2.0-mL eluent volume was adopted for this work.

Effect of Sample Solution Flow Rate

The flow rate of the sample solution is an important factor for the quantitative extraction of analytes since it controls the analysis time and affects the retention of the analytes on the microcolumn. Therefore, the flow rate of the sample solution was optimized in the range of 0.3 to 2.1 mL min⁻¹. The results in Figure 2 indicate that at a flow rate higher than 1.5 mL min⁻¹, there was a decrease in the recoveries of the studied ions. The reason for this is insufficient contact between the analytes and the adsorbent to reach equilibrium. Therefore, all subsequent experiments were performed at a flow rate of 1.2 mL min⁻¹.

Effect of Sample Solution Volume

In order to explore the possibility of enriching low concentrations of analytes from a large sample volume, the effect of sample volume on the adsorption of the analytes was studied. For this purpose, 25, 50, 100, 150, 200, and 250 mL of the sample solutions containing 10 ng of the analytes were passed

through the microcolumn at a 1.2 mL min⁻¹ flow rate. The results from Figure 3 show that quantitative recoveries (>90%) were obtained for sample volumes up to 150 mL. Because the elution volume was 1.0 mL, a 150-fold enrichment factor was obtained for the studied ions. Considering the analysis time, a 25-mL sample volume was used for the analysis of real samples in this study.

Adsorption Capacity

The adsorption capacity is an important parameter for the evaluation of the adsorbent and was investigated by a method provided in the literature (40). For this purpose, 20-mL aliquots of a series of concentrations (2.5–20 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 adsorption capacity calculated from the breakthrough curve was 4.2, 3.6, 8.4, 2.9, and 5.1 mg g⁻¹ for Mn, Co, Cr, Zn, and Pb, respectively.

Effect of Interfering Ions

The effect of potential interfering ions in biological and environmental samples on the preconcentration and determination of the

analytes was examined. In the experiments, a solution of 5.0 ng mL⁻¹ analytes containing the added interfering ions was tested according to the recommended procedure under the optimum conditions. The tolerance limit of coexisting ions is defined as the largest amount making the recovery of the analyte less than 90%. The experimental results are summarized in Table III. As can be seen, the presence of major cations and anions has no obvious influence on the preconcentration and determination of the studied ions under the selected conditions.

Column Reuse

To test the long-term stability of the TDNTs, the column was subjected to successive adsorption and desorption cycles by passing 25 mL

TABLE III
Effect of Coexisting Ions

Coexisting Ion	Mass Ratio ^a
Na ⁺ , K ⁺	20,000 ^b
Ca ²⁺ , Mg ²⁺	10,000 ^b
Fe ³⁺ , Al ³⁺	300 ^b
SO ₄ ²⁻ , SiO ₃ ²⁻	2,000 ^b
PO ₄ ³⁻	2,000 ^b

^a Mass ratio: Foreign ion/Analytes

^b Maximum amounts tested.

Fig. 2. Effect of flow rate on the recovery of the analytes on TDNTs. Mn²⁺, Co²⁺, Cr³⁺, Zn²⁺, and Pb²⁺: 5.0 ng mL⁻¹; sample volume: 25 mL.

Fig. 3. Effect of sample volume on the recovery of analytes on TDNTs. Mn²⁺, Co²⁺, Cr³⁺, Zn²⁺, and Pb²⁺: 5.0 ng mL⁻¹; 10 ng; pH: 8.0.

of the sample solution through the column. The stability and potential reuse of the column containing the TDNTs was assessed by monitoring the changes in the recoveries of the analytes. The experimental results showed that the column was reused after being regenerated with 5.0 mL of 1.5 mol L⁻¹ HNO₃ solution and 10 mL deionized water, respectively, and is stable for up to 50 adsorption-elution cycles without an obvious decrease in the recoveries of the analytes.

Analytical Performance

The analytical performance characteristics of this method, including precision, linear range of calibration curve, and detection limits, were carried out under the optimum experimental conditions. The detection limits of Mn, Co, Cr, Zn, and Pb, based on three times the standard deviation of the blank solution, were found to be 9.0, 0.3, 5.7, 15, and 4.7 pg mL⁻¹, respectively. The linear range of this method was from 0.1 to 100 ng mL⁻¹ with the correlation coefficient better than 0.9993. The precision for the nine determinations of 1.0 ng mL⁻¹ of Mn, Co, Cr, Zn, and Pb were 2.5, 4.3, 3.7, 2.0, and 4.0%, respectively.

Sample Analysis

In order to identify the accuracy of this procedure, a certified reference material GBW 07601 Human Hair and natural water samples were analyzed under the selected conditions. The obtained results are summarized in Tables IV and V, respectively. As can be seen, the determined values were in good agreement with the certified values, and the recoveries of the analytes were in the 94.8–104% range.

TABLE IV
Analytical Results of Analytes in CRM GBW 07601 Human Hair

Element	Found ^a (μg g ⁻¹)	Certified ^b (μg g ⁻¹)
Mn	6.0±0.4	6.3±0.5
Co	0.064±0.007	0.071±0.008
Cr	0.45±0.06	0.37±0.05
Zn	190±8	190±5
Pb	7.9±0.5	8.8±0.9

^a Mean value±standard deviation, n=3.

^b Reference values.

TABLE V
Analytical Results and Recoveries of the Analytes in Natural Water Samples

Element	Added (ng mL ⁻¹)	Found ^a (ng mL ⁻¹)	Recovery (%)
Mn	-	5.15±0.24	-
	5.0	9.97±0.43	96.4
Co	-	1.65±0.12	-
	1.0	2.67±0.11	102
Cr	-	1.47±0.09	-
	1.0	2.45±0.15	98.0
Zn	-	6.47±0.21	-
	5.0	11.21±0.46	94.8
Pb	-	2.31±0.10	-
	1.0	3.35±0.19	104

^a Mean value ± standard deviation, n=3.

CONCLUSION

In conclusion, titanium dioxide nanotubes (TDNTs) as a solid phase extraction adsorbent packed in a microcolumn provide an effective preconcentration and separation procedure for the determination of trace elements (Mn, Co, Cr, Zn, and Pb) in biological and environmental samples by inductively coupled plasma mass spectrometry (ICP-MS). The adsorption behavior of the analytes on the TDNTs was investigated systematically. The analytes were retained on the TDNTs in the pH range of 7.0–9.0, and desorbed quantitatively with 1.0 mL of 1.2 mol L⁻¹ HNO₃ solution. In addition, no carryover was observed in the next analysis. An enrichment factor of 150 was achieved. It can be stated that TDNTs have great potential as an adsorbent for the preconcentration and determination of trace/ultra-trace elements in real samples.

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