Graphene oxide–silica composite coating hollow fiber solid phase microextraction online coupled with inductively coupled plasma mass spectrometry for the determination of trace heavy metals in environmental water samples

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A B S T R A C T

In this work, a novel graphene oxide–silica (GO–silica) composite coating was prepared for hollow fiber solid phase microextraction (HF-SPME) of trace Mn, Co, Ni, Cu, Cd and Pb followed by on-line inductively coupled plasma mass spectrometry (ICP-MS) detection. The structure of the prepared graphene oxide and GO–silica composite was studied and elucidated by atomic force microscopy (AFM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The GO–silica composite coated hollow fiber was characterized by scanning electron microscope (SEM), and the results show that the GO–silica composite coating possessed a homogeneous and wrinkled structure. Various experimental parameters affecting the extraction of the target metal ions by GO–silica composite coated HF-SPME have been investigated carefully. Under the optimum conditions, the limits of detection (LODs, 3σ) for Mn, Co, Ni, Cu, Cd and Pb were 7.5, 0.39, 20, 23, 6.7 and 28 ng L^{-1} and the relative standard deviations (RSDs, $c_{Mn, \ Co, \ Cd}=0.05$ µg L^{-1}, $c_{Ni, \ Cu, \ Pb}=0.2$ µg L^{-1}, $n=7$) were 7.2, 7.0, 5.6, 7.3, 7.8 and 4.6%, respectively. The accuracy of the proposed method was validated by the analysis of Certified Reference Material of GSBZ 50009-88 environmental water and the determined values were in a good agreement with the certified values. The proposed method has been successfully applied for the determination of trace metals in real environmental water samples with recoveries ranging from 85 to 119%.

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1. Introduction

Heavy metals, which have been widely used in industry of plating, steel, electronics and metallurgy and so on, are inevitably discharged into the environmental waters. They are non-biodegradable and can enter into human body through food chain, thus cause various damages to human's health even if in low dose [1,2]. Therefore, it is urgent to develop a rapid, sensitive and reliable monitoring technique for heavy metals in the environmental waters. Inductively coupled plasma mass spectrometry (ICP-MS) is considered to be one of the most appropriate techniques for trace and ultra-trace elements' analysis because of its low limits of detection and isotopes capability. However, when the conventional ICP-MS was employed for real-world sample analysis, it still suffered from the mass spectroscopic interference and matrix effects [3]. Although the spectroscopic interference in

ICP-MS can be minimized by using high-resolution (HR) ICP-MS and collision/reaction cell (CRC) ICP-MS [4], these techniques are rarely used in routine analysis due to the high cost and complicated instruments, and what is more, they still suffer from matrix effects. Therefore, a sample pretreatment step, which can separate the analytes from the matrix and preconcentrate them before their measurement, is often mandatory [5].

Among various sample pretreatment techniques [5–8], in-tube solid phase microextraction (in-tube SPME), also called capillary microextraction (CME), has the advantages of low cost, simple operation, fast speed, high selectivity, low sample/reagent consumption as well as easy-to-automate and has been widely used for analysis of trace organic and inorganic analytes by on-line coupling with different detection instrumentations [5,9–13]. The extraction principle of in-tube SPME is based on the distribution equilibrium of target analytes between the sample and the coating material. Thus, the coating material plays a fundamentally important role in in-tube SPME which determines its selectivity and extraction efficiency. Up to now, besides the conventional organic poly(dimethyl siloxane) (PDMS) and poly(ethylene glycol) (PEG)

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coatings [14], a large number of new in-tube SPME coatings have been increasingly developed, such as polypyrrole (PPY) [15], human low-density lipoprotein (LDL) [16], single-walled carbon nanotubes [17], chitosan [18], alumina [5] and silica modified coating [9]. However, the amount of the coatings on the inner surface of the fused-silica capillary is limited, which leads to a relatively low adsorption capacity of in-tube SPME. It has been demonstrated that the use of newly developed hollow fiber supported in-tube SPME (called in-tube hollow fiber solid phase microextraction, in tube HF-SPME) was one of the simplest ways to solve this problem, due to its high porosity [19,20]. Chen et al. [19] prepared a new hollow fiber coating by mixing partially sulfonated poly(styrene) (PSP) with mixed-sol of 3-mercapto propyltrimethoxysilane (MPTS) and N-(2-aminoethyl)-3-amino-propyltrimethoxysilane (AAPTS) and developed a novel method based on in-tube HF-SPME on-line coupled with ion pair reversed phase-high performance liquid chromatography (HPLC)–ICP-MS for arsenic speciation. Compared with fused-silica capillary supported in tube SPME, higher extraction efficiency was obtained by HF supported in-tube SPME.

Since discovered in 2004 [21], graphene, a new two-dimensional material comprising a single layer of sp^2-hybridized carbon atoms [22], has become one of the hottest research topics and gained much attention in material sciences due to its various unique properties [23–25]. It was reported that graphene possesses a high theoretical specific surface area (2630 m^2/g) [23], suggesting a high sorption capacity. In addition, due to its large delocalized π-electron system, graphene can form a strong π–π stacking interaction with the benzene ring [26]. These unique properties make graphene superior for the adsorption of benzenoid compounds [27–31]. However, the research about graphene as an adsorbent for heavy metals is scarce [32,33], owning to the lack of functional groups on its surface for effective binding with metal ions.

Graphene oxide (GO), a precursor to graphene after reduction, consists of a hexagonal carbon network bearing hydroxyl and epoxide functional groups on its "basal" plane, whereas the edges are mostly decorated by carboxyl and carbonyl groups [34,35]. These oxygen-containing functional groups can bind with metal ions, especially the multivalent metal ions, through both electrostatic and coordinate approaches. It can be estimated that GO is an ideal adsorbent for metal ions. Recently, the utilization of GO as a sorbent for the removal of heavy metal ions from water has been reported [36,37]. Yang et al. [36] found that the adsorption capacity of Cu(II) on GO was 10 times higher than that of Cu(II) on active carbon. Wang et al. [37] prepared a few-layered GO (FGO) and found that the maximum adsorption capacities of Pb(II) ion on FGO were higher than any currently reported materials. However, to the best of our knowledge, there were no reports on the use of GO as the adsorbent for the separation/preconcentration of metal ions. The possible reason was that the GO was highly hydrophilic due to the oxygen-containing functional groups in its structure and could be easily lost during extraction. Therefore, the successful application of GO as an adsorbent for trace metal analysis is highly dependent on the breakthroughs in improvement of its stability in aqueous solution.

The purpose of this work was to prepare GO–silica composite coating and develop a novel method of GO–silica composite coated HF-SPME on-line coupled to ICP-MS for the determination of trace metals in environmental waters. GO–silica composite was prepared with the addition of silica to enhance the coating stability. In another aspect, hollow fiber supported in-tube SPME instead of capillary supported in-tube SPME was employed in order to obtain high adsorption capacity due to the porosity of hollow fiber. The adsorption behaviors of various metal ions, including Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} on the GO–silica composite coated HF,

were examined, and the optimal experimental conditions were established. The developed method was validated by the determination of trace metals in the environmental water samples.

2. Experimental

2.1. Instrumentations

An Agilent 7500a ICP-MS (Agilent, Tokyo, Japan) with a Babington nebulizer was applied and the optimal operating conditions are summarized in Table 1. The pH values were controlled by a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode (LE438). An IFIS-C flow injection system (Ruimai Tech. Co. Ltd., Xi'an, China) was used for on-line coupling HF-SPME with ICP-MS. Polypropylene hollow fiber (600 µm i.d. × 800 µm o.d., pore size: 0.2 µm) was obtained from Membrana (Wuppertal, Germany). PTFE tubing with 0.5 mm i.d. was used for all connections. These connections were kept as short as possible to minimize the dead volume.

2.2. Standard solutions and reagents

The stock standard solutions (1.000 g L^{-1}) of Cd, Co, Mn, Ni, Pb and Cu were prepared by dissolving appropriate amounts of Cd $(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $MnSO_4$, $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, Pb $(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$ (all of analytical grade, The First Reagent Factory, Shanghai, China) in 1% (v/v) diluted HNO_3, respectively. Working solutions were prepared daily by appropriate dilutions of their stock solutions. Graphite powder (325 mesh, 99.9995%) was obtained from Alfa Aesar (MA, USA). P_2O_5, $K_2S_2O_8$, H_2O_2, $KMnO_4$, HCl and H_2SO_4 were purchased from Sinopharm Chemistry Reagent Co. Ltd, China (Shanghai, China). Tetramethoxysilane (TMOS) was purchased from Organic Silicon Material Company of Wuhan University (Wuhan, China). High purity water (18.2 MΩ cm) obtained from Milli-Q Element system (Millipore, Molsheim, France) was used throughout this work. All reagents were of analytical grade unless otherwise specified. Plastic and glass containers and all other laboratory materials that could come into contact with samples and standards were stored in 20% (v/v) nitric acid over 24 h and rinsed with high purity water prior to use.

2.3. Synthesis and characterization of graphene oxide, graphene oxide–silica composite and silica coated hollow fiber

Graphite oxide was synthesized according to the modified Hummers' method [38,39]. Briefly, 3 g of graphite powder was added into a 25 mL 3-necked round-bottom flask containing 12 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5, and the

Table 1
Operating conditions of ICP-MS.

ICP-MS plasma	parameters
Rf power	1250 W
Plasma gas (Ar) flow rate	14 L min^{-1}
Auxiliary gas (Ar) flow rate	0.88 L min^{-1}
Carrier gas (Ar) flow rate	1.08 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	50 ms
Integration mode	Peak area
Points per spectral peak	1
Isotopes	[55]Mn, [59]Co, [60]Ni, [63]Cu, [111]Cd, [208]Pb