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Titania immobilized polypropylene hollow fiber as a disposable coating for stir bar sorptive extraction–high performance liquid chromatography–inductively coupled plasma mass spectrometry speciation of arsenic in chicken tissues

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ABSTRACT

The bottleneck of applying stir bar sorptive extraction (SBSE) to elemental speciation analysis is lack of suitable extraction phases with good affinities to different elemental species. In this paper, a newly high polar extraction phase of titania immobilized polypropylene hollow fiber (TiO_2-PPHF) was prepared by sol–gel immersion and low temperature hydrothermal process and the obtained TiO_2-PPHF inherits the adsorption properties of TiO_2 and the toughness of PPHF. With a suitable size of stainless steel magnetic bar inserted into the prepared TiO_2-PPHF, a disposable TiO_2-PPHF coating stir bar was obtained. The prepared TiO_2-PPHF was characterized by X-ray diffraction spectrometry and scanning electron microscopy and the significant parameters affecting the extraction efficiency of different arsenic species were studied. Based on the above facts, a new method of SBSE combined with high performance liquid chromatography (HPLC)–inductively coupled plasma mass spectrometry (ICP-MS) was developed for the speciation of phenyl arsenic compounds and their possible transformation products in chicken tissues. Under the optimal conditions, limits of detection (LODs) of the developed method for eight target arsenic species were in the range of 11.4–64.6 ng L^{-1} with enrichment factors of 8.5–22.3 (theory enrichment factor was 50), and the relative standard deviations (RSDs) were varying from 6.3 to 12.6% ($c_{\text{AsIII/V}} = 5\,\mu g\,L^{-1}$, $c_{\text{MMA,DMA,p-ASA,4-OH,3-NHPAA,PA,4-NPAA}} = 10\,\mu g\,L^{-1}$, $n = 7$). The proposed method was successfully applied to the speciation of arsenic in chicken meat/liver samples and the recoveries for the spiked samples were in the range of 78.5–120.4%. In order to validate the accuracy of the proposed method, a certified reference material of BCR-627 tuna fish tissue was analyzed and the determined values were in good agreement with the certified values. The TiO_2-PPHF was demonstrated to be a highly selective coating for the target arsenic species, and could be easily prepared in batches with low cost. In addition, with the disposable coating, the carry-over effect commonly encountered in conventional SBSE was avoided.

1. Introduction

Arsenic, as a ubiquitous element, exists as many different chemical species in the environment and organisms. The chemical form and oxidation state of arsenic play a very important role in its toxicity and bioavailability. Inorganic arsenic compounds (arsenite As(III) and arsenate As(V)) are strong carcinogenic substances. Simple methylated arsenic species such as monomethylarsonic acid (MMA) and dimethyl arsinic acid (DMA) are identified as possible cancer promoters. Arsenobetaine (AsB), arsenocholine (AsC), arsenic sugars and arsenolipids are considered to be non-toxic species [1]. Some phenylarsonic acid compounds, for example, p-amino phenyl arsenic acid (p-ASA), 3-nitro-4-hydroxyphenylarsonic acid (3-NHPAA, Roxarsone), and 4-nitrophenylarsonic acid (4-NPAA), are capable of controlling intestinal parasites, improving feed efficiency, and promoting rapid growth of the poultry. Thus, phenylarsonic acid compounds are extensively used in the poultry industry [2]. However, the abuse of those feed additives containing arsenic will bring potential hazards to human health and environment. Most of the phenylarsonic acid compounds are excreted virtually unchanged in the manure [3], but could be eventually converted to toxic arsenic compounds (such as As(V)) to contaminate water and soil in the role of sunlight and micro-organisms [4,5]. Therefore, it is of great significance to develop rapid, sensitive and simple arsenic speciation methods for further investigation and better understanding of arsenic toxicity and bioavailability in biological and environmental systems.

At the end of 1970s in the 20th century, hyphenation technique by coupling chromatographic separation with element-specific detection was proposed by Van Loon [6] and Suzuki for trace ele-

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Abbreviations: As(III), arsenite; As(V), arsenate; MMA, monomethylarsonic acid; DMA, dimethyl arsinic acid; 4-OH, 4-hydroxyphenylarsonic acid; 3-NHPAA, 3-nitro-4-hydroxyphenylarsonic acid; PA, phenylarsonic acid; p-ASA, 4-aminophenylarsonic acid; 4-NPAA, 4-nitrophenylarsonic acid.

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ment speciation analysis. Afterwards, the hyphenation technique has been rapidly developed and become one of the most commonly used approaches for elemental speciation. This is especially the case for arsenic speciation. Nowadays, different separation techniques (gas chromatography (GC), capillary electrophoresis (CE), high performance liquid chromatography (HPLC), etc.) coupled with highly sensitive and element specific atomic spectrometry or atomic mass spectrometry (such as inductively coupled plasma mass spectrometry (ICP-MS)) has been proven to be one of the most effective means for the speciation of arsenic in different samples with complex matrix [7]. GC provides excellent separation capacity for volatile arsenicals, but most naturally occurring arsenic species are non-volatile which should be derivatized into volatile species prior to GC analysis. Derivatization complicates the analytical process and results in possible analyte loss or species transformation, which greatly limits the application of GC in the field of arsenic speciation [8]. CE is a high efficiency separation method but lacks of sensitivity and selectivity for real samples with complex matrix. CE–ICP-MS provides higher selectivity and improved sensitivity compared with CE–UV detection for arsenic species, but is usually limited by complicated interface and poor relative detection limits [9]. HPLC–ICP-MS has been demonstrated to be the most effective method in arsenic speciation due to the advantages of no derivatization required, simple interface and the flow rate of HPLC effluent matching with the sample uptake rate of the ICP pneumatic nebulizer. Different HPLC separation modes including ion exchange (IE) [2], reversed phase (RP) [10], reversed phase ion pair (RP-IP) [11] and micellar HPLC [12] have been employed for arsenic speciation, but IE HPLC is one of the most used separation techniques for arsenic speciation.

For elemental speciation in real-world samples, appropriate sample pretreatment techniques are often required because of the extremely low concentration of single species for a given element and very complicated matrix in the samples. In recent years, different sample pretreatment techniques have been employed for arsenic speciation, such as solid phase extraction (SPE) [13] and solid phase microextraction (SPME) [8]. SPME offers numerous advantages in sample preparation for speciation analysis, such as easy to combine with virtually any detection system, quick achievement of sample-matrix separation, solvent free and miniaturization of manipulation in sample pretreatment techniques. The combination of in-tube SPME with HPLC for arsenic speciation analysis can obviously exhibit the advantages of simple operation and good sensitivity [14]. Stir bar sorptive extraction (SBSE) which was first developed in 1999 [15] is a sample preparation technique derived from SPME, and its extraction mechanism and advantages are similar to those of SPME. Generally, the volume of extraction phase of SBSE is 50–250 times larger than that of SPME fiber, thus, better reproducibility and higher sensitivity than SPME are expected when SBSE is used. Therefore, SBSE is especially suitable for trace/ultra-trace analysis. The SBSE extraction process and its analytical applications have been thoroughly described in recent reviews [16–18]. Like SPME, the further development and application of SBSE are highly dependent on the exploration of new extraction coatings. However, to the best of our knowledge, polydimethylsiloxane (PDMS), as the most commonly used coating for extraction of non-polar and weak polar organic compounds by SBSE [19], is the only commercially available coating. To improve the extraction performance of SBSE for polar compounds, some novel extraction coatings with good capability have been explored extensively, including dual-phase stir bar (PDMS/activated carbons) [20], restricted access material (RAM) alkyl-diol-silica (ADS) [21], polyurethane foams (PU) [22], PDMS/β-cyclodextrin (β-CD) [23], polyphthalazine ether sulfone ketone (PPESK) [24], nylon-6 polymer imprinted with L-glutamine [25], vinylpyrrolidone (VPL)/divinylbenzene (DVB) monolithic material [26], and PDMS/polyvinylalcohol (PVA) [27], etc. However, very few reports on the application of SBSE to the trace elements and their species analysis have been published until present, mainly due to lacking of suitable coatings and coating techniques. Pu et al. [28] proposed a zirconia coated graphite bar sorptive extraction for electrothermal vaporization (ETV)–ICP-MS determination of trace Cd, Hg and Pb with limits of detection at 0.05, 0.42 and 0.06 pg mL^{-1}, respectively. Vercauteren et al. [29] have determined ppq-level traces of organotin compounds in environmental samples using SBSE combined with thermal desorption-capillary GC–ICP-MS. Similarly, Prieto et al. [30] has utilized headspace stir bar sorptive extraction (HS-SBSE)–thermal desorption–GC–MS to the speciation of methylmercury and butyltin species in environmental samples. Duan et al. [31] employed HS-SBSE–GC–ICP-MS for the speciation of dimethylselenide and dimethyldiselenide in biological samples.

A few high polar inorganic metallic oxides, such as titania, alumina, and zirconia, have been extensively used in SPE for trace elements and their speciation analysis [32,33], indicating an application possibility of inorganic metallic oxides as the coating for stir bar sorptive extraction of high polar target analytes. Unfortunately, it is difficult to coat or bond the inorganic metallic oxides powder on the surface of glass stirring rod and even through sol–gel coating technique, the coating will easily peel off during the process of preparation and stirring extraction. To obtain an inorganic metallic oxide coated stir bar with good stability, an appropriate preparation technique is required. Employing polypropylene hollow fiber (PPHF) as template and combined with sol–gel process, Xu and Lee et al. [34] synthesized a zirconia hollow fiber by repeatedly impregnating PPHF in zirconia sol precursor and calcinating it to burn off the template. The prepared zirconia hollow fiber had been demonstrated to be lack of mechanical strength, and therefore, a shaker instead of a stirrer was used to facilitate the extraction process to prevent its possible damage. As the template PPHF itself has good toughness, it is assumed that the obtained material would inherit the toughness advantage of PPHF if the template is not burned off.

In this work, using PPHF as the support and template, a novel high polar SBSE extraction phase of titania (TiO_2) immobilized PPHF was prepared by sol–gel immersion and low temperature hydrothermal process. With a suitable size of stainless steel magnetic bar inserted into the prepared TiO_2-PPHF, a disposable TiO_2-PPHF coating stir bar was obtained and a new method of TiO_2-PPHF SBSE coupled with HPLC–ICP-MS was developed for simultaneous speciation of phenylarsonic acids and their possible transformation products in biological samples.

2. Experimental

2.1. Instrument

A quadrupole (Q) ICP-MS (Model Agilent 7500a, Hewlett-Packard, Yokogawa Analytical Systems, Tokyo, Japan) with a Babington nebulizer was used for the determination of arsenic species with a single-ion-monitoring mode (m/z 75). An HPLC system consisting of a LC-10AD high-pressure pump, CTO-10A column oven, SPD-10AV UV–vis spectrometry detector, C-R6A chromatopac (Shimadzu, Japan) and CAPCELL PAK C18 MG column (5 μm, 250 mm × 4.6 mm i.d., Shiseido, Japan) was used for the separation of arsenic species. ICP-MS was used as an on-line detector for HPLC by connecting HPLC column outlet (1.0 mL min^{-1}) to the Babington nebulizer situated in the spray chamber via a minimum length piece of Teflon tubing (i.d. 0.5 mm). Optimization of the ICP-MS instrument (i.e., lens settings, sampling depth, and carrier gas flow rate) was performed with conventional pneumatic nebulization (PN)-ICP-MS prior to being connected with HPLC. Typical