Talanta 192 (2019) 24–31

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Sensitive determination of perfluoroalkane sulfonamides in water and urine samples by multiple monolithic fiber solid-phase microextraction and liquid chromatography tandem mass spectrometry

Yanmei Huang[a,b,1], Min Lu[a,b,1], Haiyan Li[a,b], Mindong Bai[a,b], Xiaojia Huang[a,b,*]

[a] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
[b] Key Laboratory of the Ministry of Education for Coastal and Wetland Ecosystems, College of the Environment and Ecology, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Keywords:
Perfluoroalkane sulfonamides
Solid-phase microextraction
Fluorophilicity
Boronate affinity
Water
Urine

ABSTRACT

To extract perfluoroalkane sulfonamides (PFASAs) in water and urine samples effectively, a new adsorbent based on poly (1H,1H,2H,2H-nonafluorohexyl acrylate/vinyboronic anhydride pyridine complex-*co*-ethylenedimethacrylate) monolith (FBE) was synthesized and used as the extraction phase of multiple monolithic fiber solid-phase microextraction (MMF-SPME). Because there are abundant fluorinated (*F*-) alkyl chains and boron atoms in the adsorbent, the FBE/MMF-SPME displays satisfactory extraction performance for PFASAs by means of fluorophilic and B-N coordination interactions. Under the most favorable conditions, the FBE/MMF-SPME was combined with HPLC-MS/MS for the sensitive monitoring of ultra-trace PFASAs in environmental water and human urine samples. The limits of detection and limits of quantification achieved for target analytes were in the range of 0.13–1.45 ng/L and 0.44–4.80 ng/L, respectively. The developed FBE/MMF-SPME-HPLC-MS/MS method was successfully applied to quantify the level of PFASAs in water and human urine samples, and ultra-trace target PFASAs were detected in the real samples. The recoveries at different fortified concentrations ranged from 80.3% to 119% with RSD in the range of 0.9–11%. Compared with reported methods, the proposed method exhibits some merits such as high sensitivity, good method precision, low consumption of sample and environmental friendliness.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFSs) are a class of anthropogenic organofluorine chemicals characterized by hydrogen atoms on alkylated chains were replaced by fluorine atoms. Because of the unique properties such as good chemical and thermal stability, satisfactory surface activity and superhydrophobicity, PFSs have been widely used in many fields such as fabric protection, photolithography, chromium plating and fire fighting foams [1,2]. Perfluoroalkane sulfonamides (PFASAs) are an important class of PFSs. Because it displays wide applications, PFASAs are ubiquitous in various environmental waters such as tap water [3–5], canal water [6], river water [7,8] and waste water [9,10]. Studies well indicate that PFASAs can induce adverse health effects to biota [11,12] and humans [13]. For example, Slotkin's study evidenced that PFASAs could injure pheochromocytoma cells, and thus to be considered as developmental neurotoxicant [14]. In addition, previous studies have evidenced that urine was the primary elimination route for PFSs [15,16]. Monitoring the concentrations of PFASAs in human urine is necessary for toxicological study. Therefore, it is especially important to develop highly sensitive, reliable determination method for the monitoring of ultra-trace PFASAs in water and urinary specimens.

Compared to other classes of PFSs such as perfluoroalkyl acids and perfluoroalkyl sulfonic acids, there are only a few analytical methods are available for the determination of PFASAs in various matrices [17–22]. Due to the high sensitivity and selectivity, high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) has become the popular analytical method of PFASAs. However, considering the low concentrations of PFASAs in real samples and the complexity of sample matrices, suitable sample pretreatment is necessary before chromatographic detection. So far, several technologies have been utilized to extract PFASAs [18–23]. Solid-phase extraction (SPE) is the main sample preparation method for the analysis of PFASAs [18–21]. However, SPE requires large volume of sample and a certain

* Correspondence to: Xiamen University, P. O. Box 1009, Xiamen 361005, China.
E-mail address: hxj@xmu.edu.cn (X. Huang).
[1] Note: Yanmei Huang and Min Lu paid the same contribution to the work.

https://doi.org/10.1016/j.talanta.2018.09.004
Received 6 June 2018; Received in revised form 26 July 2018; Accepted 2 September 2018
Available online 04 September 2018
0039-9140/

amount of organic solvent. At the same time, the operation procedure of SPE is inconvenient, several steps including conditioning, loading sample, elution of interferences and analytes are involved. Liquid-phase extraction (LPE) is another method for the enrichment of PFASAs [22]. However, large amount of organic solvent is needed. Recently , headspace solid-phase microextraction (HP-SPME) was developed for the extraction of PFASAs and other PFSs [23]. After the optimization of extraction parameters, the HP-SPME was combined with gas chromatography/mass spectrometry (GC/MS) to detect PFSs in tap and surface waters. The HP-SPME is environmentally friendly. However, the sensitivity should be further improved. For PFASAs, the limits of detection (LODs) were as high as 20 ng/L. The reason may be that the extraction capacity of SPME is limited because a low quantity of adsorbent is utilized. Hence, developing sample pre-concentration procedure with simple operation, high extraction capacity, cost-effectiveness and eco-friendliness is highly urgent for the sensitive monitoring of PFASAs.

Based on the same extraction principle as solid-phase microextraction (SPME), a new extraction format named as multiple monolithic fiber SPME (MMF-SPME) was developed in our lab [24–26]. Typically, MMF-SPME contains four thin monolithic fibers. As a result, the MMF-SPME possesses higher extraction capacity than conventional SPME because more extraction phase is involved in the extraction. Furthermore, the MMF-SPME characterized by simple operation, easy preparation of monolithic fibers, fast mass-transfer, various chemical properties, low consumptions of sample and organic solvent. Based on the unique advantages, MMF-SPME is an ideal sample preparation method for the analysis of PFASAs. As other adsorbent-based extraction, extraction medium (adsorbent) is the key of MMF-SPME. On the basis of the principle of “similarity dissolves similarity”, to enrich target analytes effectively, multiply interactions should be involved in the extraction. In this work, PFASAs including perfluoro-1-octanesulfonamide (PFOSA), N-methylperfluoro-1-octanesulfonamide (MFOSA), N-ethylperfluoro-1-octanesulfonamide (EFOSA) and 2-(N-methylperfluoro-1-octanesulfonamido) ethanol (MFOSE) were selected as target analytes. In these compounds, there are abundant fluorinated (*F*-) alkyl chains and sulfonamide groups which can be utilized to produce multiply interaction. For this reason, 1H,1H,2H,2H-nonafluorohexyl acrylate (NF) and vinyboronic anhydride pyridine complex (VB) were selected as dual functional monomers to *in-situ* copolymerize with ethylenedimethacrylate (ED) to synthesize a new monolithic adsorbent (FBE) and used as the extraction phase of MMF-SPME (FBE/MMF-SPME). In the FBE, there are ample *F*-alkyl and boron atoms. According to the principles of fluorophilicity [27,28] and boronate affinity [29,30], the FBE can produce fluorophilic and B-N coordination interactions with PFASAs. As a result, it is reasonable to expect that the FBE/MMF-SPME can enrich target PFASAs effectively. To the best of our knowledge, this is the first time that combining fluorophilic and B-N coordination interactions to realize the effective extraction of PFASAs. After optimization of the preparation conditions of FBA and extraction parameters of FBE/MMF-SPME, a sensitive method for the determination of ultra-trace PFASAs in environmental water and human urine samples was developed by the combination of FBE/MMF-SPME with HPLC-MS/MS.

2. Experimental

2.1. Chemical reagents

The functional monomers NF (≥ 98%) and VB (95%) were purchased from TCI Ltd. (Shanghai, China) and Alfa Aesar Ltd.(Tianjin, China), respectively. Cross-linker ED (97%) was supplied by Alfa Aesar Ltd. (Tianjin, China). 1-Propanol (97%), 1,4-butanediol (98%), azobis (isobutyronitrile) (AIBN) (97%) and trifluoroacetic acid (TFA) were bought from Xilong Chemical Co. (Guangzhou, China). HPLC-grade acetonitrile (ACN) and methanol were obtained from Tedia Company (Fairfield, USA). Milli-Q grade water utilized throughout the present study was purified by an ultrapure water system (Millipore, USA). Fused-silica capillary with 530 μm i.d. was got from Ruifeng Instrumental Co. (Hebei, China).

The standards of PFOSA (≥ 98%), MFOSA (≥ 98%), EFOSA (≥ 98%) and MFOSE (≥ 98%) were purchased from Well-labs (wellington, Kansas, USA). The chemical properties of the target analytes are shown in Supporting information (Table S1). Individual stock solutions of each PFASA at a concentration of 10.0 mg/L were prepared in HPLC-grade methanol and stored in the dark at 4 °C. Mixtures of target analytes standard solutions were prepared at a concentration of 5.0 μg/L and were applied to optimize the extraction parameters and validate the method.

2.2. Instruments and chromatographic analysis

Analysis of PFASAs was accomplished on an HPLC-MS/MS (Agilent 1290, Foster City, CA, USA) consisting of an auto sampler and coupled to an Agilent 6460 triple quadrupole mass spectrometer (MS/MS). The Agilent Masshunter workstation software (Foster City, CA, USA) was used to control the whole HPLC-MS/MS system. A Phenomenex Kinetex C_{18} LC column (100 mm × 3.0 mm, 2.6 μm particle size) with guard from Phenomenex (Aschaffenburg, Germany) was used for separations. The mobile phase consisted of ACN containing 0.1% formic acid (v/v) (solvent A) and ultrapure water with 0.1% (v/v) FA (solvent B). The LC was run under gradient elution mode and the optimized program was as follows: 0.0–3.0 min = 40% A, 3.0–4.0 min = 40–60% A and kept for 2.0 min, 6.0–6.1 min = 60–90% A and kept for 7.0 min, 13.0–13.1 min = 90–40% A and kept for 9.0 min. At the same time, the flow rate, column temperature and injection volume were 0.25 mL/min, 40 °C, 10 μL, respectively.

To enhance the sensitivity and selectivity for the detection of the target analytes, MS analysis was performed using multiple reaction monitoring (MRM) with negative ESI mode. The mass parameters including precursor ion, PI; fragmentor voltage, FV; daughter ions, DI; collision energy, CE, for each analyte were optimized and showed in Table S2. The parameters of the mass spectrometer were as follows: desolvatation temperature, 300 °C; capillary voltage, 4.0 kV; desolvatation gas, 11 L/min; Delta EMV, 200 V; nebulizer, 15 psi; MS1 Heater, 100 °C; MS2 Heater, 100 °C. The desolvatation and collision gases were high-purity nitrogen (99.9% purity, Air Liquid).

Elemental analysis (EA), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and pore size distribution (PSD) were utilized to characterize the synthesized FBE. The detailed information about these equipments can be found in the Supporting information.

2.3. Preparation of FBE/MMF

The preparation of FBE/MMF is quite simple. Firstly, thin monolithic fibers were *in-situ* synthesized in capillaries according to the polymerization method of monolith. In this work, the mixture of NF/VB (w/w = 1/1) was selected as dual functional monomers. ED and AIBN (2% (w/w) of the total amount of polymerization solution) were used as cross-linker and initiator, respectively. To obtain the satisfactory extraction performance and longevity of the new adsorbent, the ratio of NF/VB to ED and the amount of porogenic solvent (1-propanol/1,4-butanediol, w/w = 3/2) in polymerization solution were investigated in detail (Table 1). Briefly, 18 mg NF, 18 mg VB, 84 mg ED and 4.0 mg AIBN were dissolved in 80 mg the mixture of 1-propanol (48 mg) and 1,4-butanediol (32 mg). The oxygen in the solution was removed with high purity nitrogen. After that, the polymerization solution was infused into a fused-silica capillary (10 cm lengthy), then using two silicon rubbers to seal the both ends of the capillary and put it in an oven to conduct the polymerization reaction (70 °C for 12 h). After the polymerization, 2.0 cm length of capillary was removed to obtain elastic thin FBE fiber (0.53 mm in diameter and 2.0 cm in length). According to above-mentioned process, more thin FBE fibers could be fabricated. In the following step, four FBE fibers were tied up at the