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A highly selective dispersive liquid–liquid microextraction approach based on the unique fluorous affinity for the extraction and detection of per- and polyfluoroalkyl substances coupled with high performance liquid chromatography tandem–mass spectrometry

Juan Wang[a,b], Yali Shi[a,*], Yaqi Cai[a,b]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

In the present study, a highly selective fluorous affinity-based dispersive liquid–liquid microextraction (DLLME) technique was developed for the extraction and analysis of per- and polyfluoroalkyl substances (PFASs) followed by high performance liquid chromatography tandem–mass spectrometry. Perfluoro-*tert*-butanol with multiple C-F bonds was chosen as the extraction solvent, which was injected into the aqueous samples with a dispersive solvent (acetonitrile) in a 120:800 (μL, v/v) mixture for PFASs enrichment. The fluorous affinity-based extraction mechanism was confirmed by the significantly higher extraction recoveries for PFASs containing multiple fluorine atoms than those for compounds with fewer or no fluorine atoms. The extraction recoveries of medium and long-chain PFASs ($CF_2 > 5$) exceeded 70%, except perfluoroheptanoic acid, while those of short-chain PFASs were lower than 50%, implying that the proposed DLLME may not be suitable for their extraction due to weak fluorous affinity. This highly fluoroselective DLLME technique can greatly decrease the matrix effect that occurs in mass spectrometry detection when applied to the analysis of urine samples. Under the optimum conditions, the relative recoveries of PFASs with $CF_2 > 5$ ranged from 80.6-121.4% for tap water, river water and urine samples spiked with concentrations of 10, 50 and 100 ng/L. The method limits of quantification for PFASs in water and urine samples were in the range of 0.6–8.7 ng/L. Furthermore, comparable concentrations of PFASs were obtained via DLLME and solid-phase extraction, confirming that the developed DLLME technique is a promising method for the extraction of PFASs in real samples.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic compounds that are widely used in various domestic and industrial products [1] due to their excellent surfactant properties. Since the late 1990s, these compounds have attracted attention as global contaminants because of their high persistence, bioaccumulation and toxicity [2]. Some long-chain PFASs ($CF_2 > 7$) were regulated under the Stockholm Convention [3] as well as other organizations [4] so that their production and usage were restricted. In this case, an efficient and selective analytical method is a prerequisite for their environmental management and prevention. Currently, high-performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS) is the most commonly used and popular method for the determination of PFASs [5]. Prior to analysis, the sample pretreatment plays a crucial role in decreasing the matrix effect and improving sensitivity [6,7]. For different environmental or biota samples, solid-phase extraction (SPE), alkali digestion, and ion-pair extraction were selected for PFASs extraction [6]. However, these pretreatment methods have disadvantages, such as high cost, tediousness and environmental unfriendliness with extensive amounts of organic solvent usage [8]. Dispersive liquid–liquid microextraction (DLLME) is a simple and highly efficient technique involving target analyte extraction into a microliter of extraction solvent by injecting a mixture of the extraction and dispersive solvents into aqueous samples [9]. Since its development in 2006, DLLME has been successfully applied to the preconcentration and determination of a wide range of analytes,

* Corresponding author.
E-mail address: shiyali@rcees.ac.cn (Y. Shi).

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including organic compounds in water, drugs in urine and plasma and metal in water or urine samples [8]. However, to the best of our knowledge, there is no available report for PFASs extraction using DLLME.

An interesting technique attracting our attention is the fluorous affinity-based separation method for the selective enrichment and/or analysis of biomolecules and related compounds [10]. The principle behind this technique is unique and depends on the strong noncovalent fluorine–fluorine (F-F) interaction between highly fluorinated materials [11]. Fluorous-tagged analytes such as oligonucleotides, peptides, triphenylphosphine oxide and fluoroalkyl-substituted phenyl bromides can be selectively extracted using a fluorinated adsorbent, nanographite or monolithic columns [10,12]. Also based on the unique fluorous affinity property, our group developed a sensitive colorimetric visualization method for the extraction of several PFASs using perfluorinated thiol-modified gold nanoparticles [13]. In addition, some commercial perfluoroalkyl-modified stationary phase LC columns exhibit a superior separation performance for PFASs and their isomers compared to common C18 reversed-phase columns [10]. Therefore, the fluorous affinity-based method may have great potential in the selective extraction of PFASs.

Another noteworthy technique is fluorous biphase systems that are widely used in green chemistry, in which some per- or polyfluorous solvents are used together with nonfluorous solvents to greatly improve the productivity, selectivity and simplicity of an organic reaction by combining the advantages of both homogeneous catalysis and heterogeneous catalysis [14,15]. The superior performance of per- or polyfluorous solvent as special extractant and reaction media is the foundation for the success of fluorous biphase systems. Given the high fluorination of these special solvents, the possibility of using them as fluorous affinity-based liquid extractants for PFASs has been speculated. Nevertheless, to date, the application of per- or polyfluorous solvents in DLLME for the analysis of PFASs has never been reported. In the present study, a novel DLLME technique based on the unique fluorous affinity property was established for the extraction of PFASs. Various parameters, such as the type and volume of dispersive and extraction solvents, were investigated regarding their effect on the extraction recovery for PFASs using DLLME. The developed technique coupled with HPLC–MS/MS was applied to determine PFASs in real environmental water and human urine samples.

2. Experiments and materials

2.1. Reagents and standards

The native and mass-labeled PFASs standards (PFAC-MXB, MPFAC-MXA), including thirteen native perfluoroalkyl carboxylic acids (PFCAs, $3 \leq CF_2 \leq 17$), seven native perfluoroalkyl sulfonic acids (PFSAs, $4 \leq CF_2 \leq 10$), three fluorotelomer sulfonates (4:2, 6:2 and 8:2 FTS) and three chlorinated polyfluoroether sulfonic acids (C8, C10 and C12 Cl-PFESA) were obtained from Wellington Laboratories (Ontario, Canada). Octanoic acid (OA) and octanesulfonic acid (OS) were purchased from J&K Scientific Co., Ltd, Beijing, China. HPLC-grade acetonitrile, methanol and acetone were obtained from Fisher Scientific (Hampton, NH, USA). Sodium chloride (NaCl), hydrochloric acid (HCl) and glucose were from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Human serum albumin (HSA, ≥99%) was purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). Perfluoro-*tert*-butanol (>98%, HPLC grade) and perfluorohexanes (>98%, HPLC grade) were purchased from J&K Scientific Co., Ltd, Beijing, China. Ammonium acetate (>97%, HPLC grade), acetic acid (>99.8%, HPLC grade) and an ammonium hydroxide solution (~50% v/v, HPLC grade) were purchased from Alfar (Ward Hill, MA, USA). Oasis WAX SPE cartridges (150 mg, 6 cc) and glass-fiber filter membranes (0.7 μm, 47 mm) were obtained from Waters Corporation (Milford, MA, USA) and Sartorius Stedim Biotech (Goettingen, Germany), respectively. Ultrapure water (>18.2 M Ω/cm) was produced using a Milli-Q Advantage A10 system (Millipore, Billerica, MA, USA).

2.2. Sample preparation

All solutions used for optimizing the parameters of DLLME were prepared by spiking PFASs in ultrapure water. Tap water, river water and urine samples for recovery studies were collected from Beijing, while for comparing the concentrations via two extraction methods, river and urine samples were collected from Xiaoqing River and from a population highly exposed to PFASs in Shandong Province, China, respectively. All samples were collected in polypropylene bottles and stored at 4 °C for water and −20 °C for urine until further pretreatment and analysis. All of the samples were filtered through 0.7 μm filter prior to extraction using the DLLME method as described in the following section.

2.3. Instrumentation

The target PFASs analysis was performed using a high-performance liquid chromatograph (Ultimate 3000 HPLC, ThermoFisher Scientific Co.) coupled with an electrospray ionization tandem mass spectrometer (API 3200, Applied Biosystems/MDS SCIEX, US) operated in negative mode. The mass spectrometry conditions of PFASs were shown in Table A.1. An Acclaim 120 C18 column (5 μm, 4.6 mm × 150 mm, ThermoFisher Scientific Co.) was used for separation of PFASs and a mobile phase of methanol (eluent A) and 50 mM of ammonium acetate in water (eluent B) was used to separate the targeted PFASs with the injection volume at 10 μL. The solvent gradient started at 28% B, a linear gradient was applied over 4 min to 5% B, was held for 3 min at 5% B, was increased to 28% B, and was held at this level for 10 min. The flow rate was 1.0 mL/min.

2.4. Dispersive liquid–liquid microextraction procedure

A 10 mL pure water sample free from PFASs was placed in a 15-mL screw cap polypropylene test tube with a conical bottom and spiked at the level of 50 ng/L of mixed PFASs standard solution; then, 20 ng/L of mixed internal standard was added, followed by the addition of 0.3 g of NaCl (3%, w/v) and adjusting the pH to 5 using HCl. The mixture solution of 800 μL of acetonitrile (as a dispersive solvent) and 120 μL of perfluoro-*tert*-butanol (as an extraction solvent) was rapidly injected into the sample solution using a 1.00-mL syringe, and then the mixture was gently shaken. A milky, cloudy solution (water, acetonitrile, and perfluoro-*tert*-butanol) was formed in the test tube. After the mixture was allowed to equilibrate for 5 min, it was centrifuged for 3 min at 4200 rpm, and the perfluoro-*tert*-butanol phase was sedimented at the bottom of the conical test tube. The sedimented phase was dried under a mild nitrogen stream after the supernatant was removed completely. The residue was dissolved in 100 μL of methanol, and 10.0 μL was injected into the HPLC–MS/MS system for analysis.

2.5. Solid-phase extraction (SPE) procedure

The samples were passed through Oasis WAX cartridges preconditioned with 4 mL of 0.5% ammonium hydroxide (in methanol), 4 mL of methanol and 8 mL of Milli-Q water. Then the cartridges were immediately washed off with 4 mL of 25 mmol/ L HAc-NH_4Ac buffer solution (pH 4) and 8 mL of Milli-Q water, and the residual moisture was removed by vacuum pump. The targeted PFASs

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