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Automated bundled hollow fiber array-liquid-phase microextraction with liquid chromatography tandem mass spectrometric analysis of perfluorinated compounds in aqueous media

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HIGHLIGHTS

- Full automation of hollow fiber-mediated liquid-phase microextraction was explored.
- A bundled hollow fiber array was used as a novel extraction device.
- Improved analytical performance was achieved for perfluorinated compounds.
- Only low sample volumes were required.

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ABSTRACT

An automated bundled hollow fiber array (BHF)-liquid-phase microextraction (LPME) methodology in combination with ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) has been developed for the determination of perfluorinated compounds (PFCs) in environmental aqueous matrices. Eight PFCs were considered, including perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid, perfluorotridecanoic acid, perfluorotetradecanoic acid. Experimental parameters influencing extraction efficiency, such as number of hollow fibers in the BHF extraction device, type of extraction and desorption solvent, extraction conditions (stirring rate, temperature and duration), elution conditions and the salting out effect were examined. Under the most favourable conditions, enrichment factors of between 9 and 40 were achieved for the target compounds when extracting from 10 mL of sample. Good intra and inter-day precision were obtained with relative standard deviations of less than 12%. The linearity range investigated was between 5 and 10,000 ng L⁻¹, with coefficients of determination (r^2) ≥ 0.991 . The developed method was applied for the UHPLC-MS/MS determination of environmental PFCs in industrial water discharge samples. The automation of BHF-LPME together with UHPLC-MS/MS rendered the method efficient, rapid and sensitive to determine PFCs, with the possibility of on-site real-time monitoring of contaminants in environmental waters.

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1. Introduction

The occurrence of perfluorinated compounds (PFCs) in the environment is of great concern since they have been documented as contaminants of emerging concern in recent years [1]. Over the

past few decades, PFCs have been employed extensively in numerous industrial applications such as surface coatings for textiles, furniture and paper packaging, pesticides, additives, surfactants, ion-pair reagents in liquid chromatography-mass spectrometry (LC-MS), and fire-fighting foam, etc [2]. Due to the presence of the highly electronegative fluorine atom and its small covalent radius, the covalent bond between carbon and fluorine is exceptionally strong, conferring PFCs with properties such as thermal stability and resistance to hydrolysis, metabolism, and

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biodegradation [3]. This results in these compounds being environmentally persistent.

Longer chain PFCs are known to bioaccumulate and induce adverse health effects on humans and wildlife [4,5]. They are ubiquitous in both rural and urban environments [3]. In particular, they have been detected in various environmental waters such as river water [6–10], seawater [11–14], tap water [8,15,16], wastewater [6,14,17–19], as well as textiles [20–22], packaging materials [20,22,23], house dust [24], air samples [25], and biota [26,27] at concentrations varying from parts per trillion to parts per billion levels. It is important to develop sensitive and accurate methods to detect these contaminants and monitor their levels in the environment, particularly with respect to the Stockholm Convention on Persistent Organic Pollutants [28]. It is especially important to ensure that sources of water for human and wildlife consumption are not contaminated.

Most of the conventional sample preconcentration procedures for PFCs are based on sorbent-based extraction such as solid-phase extraction (SPE) [2,6,11,12,16–19,29], ion-pair sorptive extraction [30], ultrasonic probe-assisted extraction [23], magnetic SPE [7,31,32]. Only a few studies have reported on solvent-based extraction, for instance, pressurised liquid extraction [20] and liquid-liquid extraction (LLE) [29,33].

Considering the limitations of SPE and LLE where large sample volumes are often required with moderate to lengthy processing time, recent research work has been geared towards developing efficient, automated and miniaturised sample preparation methods. This would be advantageous as PFCs are known to potentially adsorb on glass vials during sample preparation; hence, samples have to be processed as quickly as possible after collection to minimise any analyte loss [1]. Alternatively, polypropylene containers should be used. Automation of miniaturised sample preparation procedures can help to reduce the time taken to process these samples and therefore, their contact with glass apparatus. In addition, human labour is reduced, and higher sample throughput can be attained. Repetitive processes are also best operated by machines so as to obtain repeatable and reproducible data.

Of the existing microextraction techniques for PFCs, most focus on micro-SPE [9,27] and solid-phase microextraction (SPME) in complex environmental and biological samples [14,34–38]. There have also been some reports on the use of liquid-phase microextraction (LPME) for the preconcentration of PFCs [10,26,39–41].

The separation and determination of PFCs is commonly carried out with LC-MS [6,12,15,22,36,38] or LC-tandem mass spectrometry (MS/MS) [7,9,16–19,21,23,24,27,29–33,37,39,40], with the latter being more sensitive and selective. Capillary zone electrophoresis [8] methods with indirect ultraviolet detection are usually not as sensitive and their detection limits are at the parts per million levels. Gas chromatography (GC)-MS [14,20,25] or GC-MS/MS [10] methods require that the analytes be derivatised prior to analysis.

The concept of using a bundled hollow-fiber array (BHF) for LPME was recently reported [42]. Nine HF were held together compactly in a bundle, and sealed at their ends with the mid-cross-sectional area of the device resembling a cylindrical honeycomb. This alternative approach of HF-based LPME was applied to capitalise on the maximum volume capacity of the wall pores for extraction of PFCs. The BHF extraction device was dipped in the extractant solvent for the impregnation of the wall pores of the HFs, without deliberately introducing the solvent into the lumen [42].

To the best of our knowledge, this is the first study of HF-mediated LPME of PFCs, and especially of automated BHF-LPME of these compounds, and it should add to the currently limited literature on the use of LPME in general on the analysis of PFCs, particularly those of longer alkyl chains, in water.

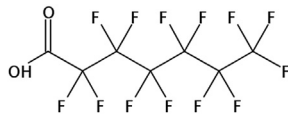
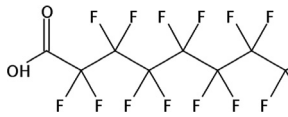
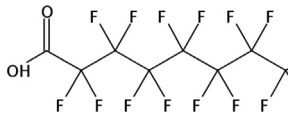
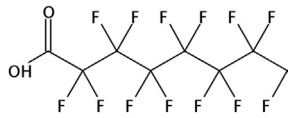
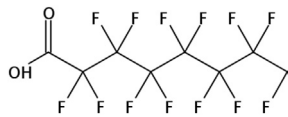
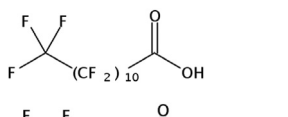
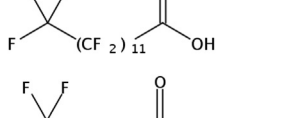
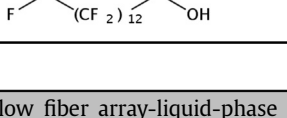
2. Experimental

2.1. Reagents, standards and materials

High purity perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTTrDA), perfluorotetradecanoic acid (PFTeDA) standards were purchased from Sigma–Aldrich (St. Louis, MO, USA). The chemical structures of the PFCs are shown in Table 1. LC-MS grade methanol (MeOH) acetonitrile (ACN), ethyl acetate (EA), toluene, pipette tips of 200 μ L capacity and polypropylene syringe filters of pore size 0.45 μ m were purchased from Fisher Scientific (Pittsburgh, PA, USA). Ultrapure water was prepared on a Milli-Q water purification system (Millipore, Billerica, MA, USA). 1-Octanol (>99%), butanol, dodecane, dioctyl ether, dibutyl ether, hydrochloric acid (HCl), sodium chloride (NaCl) sodium hydroxide and ammonium formate (HCO_2NH_4 ; >98%) were obtained from Sigma–Aldrich. Accurel Q3/2 polypropylene HF membrane (inner diameter: 600 μ m, wall thickness: 200 μ m, pore size: 0.2 μ m) was purchased from Membrana (Wuppertal, Germany).

Stock solutions of individual standards were prepared by dissolving each compound in MeOH at a concentration of 100 mg L^{-1} . They were stored at 4 $^{\circ}\text{C}$ in polypropylene bottles. Working standard solutions were prepared by spiking ultrapure water to give the

Table 1
Structures, pK_a values and log D values of target PFCs.

Analyte	Structure	pK_a	log P
PFHpA		0.47	5.71
PFOA		0.50	6.44
PFNA		0.52	7.17
PFDA		0.52	7.90
PFUdA		0.52	8.63
PFDoA		0.52	9.36
PFTTrDA		0.52	10.1
PFTeDA		0.52	10.8

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