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# Simple and fast determination of perfluorinated compounds in Taihu Lake by SPE-UHPLC–MS/MS

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ABSTRACT

A simple and fast analytical method for determination of eleven Polyfluorinated Compounds (PFCs) in source water was developed in the present work. The water sample was prepared without filtered through microfiltration membrane and 500 mL of source water was enriched by the solid phase extraction (SPE). The targent compounds were analyzed by ultra high performance liquid chromatography–tandem mass spectrometry (UHPLC–MS/MS). The optimized analytical method was validated in terms of recovery, precision and method detection limits (MDLs). The recovery values after correction with the corresponding labeled standard were between 97.3 and 113.0% for samples spiked at 5 ng/L, 10 ng/L and 20 ng/L. All PFCs showed good linearity and the linear correlation coefficient was over 0.99. The precisions were 1.0–9.0% (n = 6). As the result of the enrichment, the MDL values ranged from 0.03 to 1.9 ng/L and were enough for analysis of the trace levels of PFCs in the Taihu Lake. The method was further validated in determining the source water and the results showed that PFHxS, PFHxA, PFOA and PFOS were the primary PFCs in Taihu Lake which might be different from the other researches. The method can be used for determination of PFCs in water with a stable recovery, good reproducibility, low detection limit, less solvent consumption, time saving and labor saving. To our knowledge, this is the first method that describes the effect of the filter membrane on the determination of PFCs in water which might acquire more accurate concentration of PFCs in Taihu Lake.



## 1. Introduction

Endocrine disrupting chemicals (EDCs) are environmental compounds (natural or synthetic), which impair the function of the endocrine system of animals and humans and pose a potential threat to human health [1]. Perfluorinated Compounds (PFCs) are useful artificial chemicals that have been widely used in several industrial applications and consumer products such as lubricants, paints, pesticides, surfactants, textiles, food packaging and nonstick cookware for more than 50 years [2]. PFCs are a new class of emerging organic pollutants for their high stable, bio-accumulative and resistant to degradation which mainly include perfluorosulfonates (PFSAs) and perfluorocarboxylic acids (PFCAs) [3]. PFCs are detected in blood samples of animals and humans worldwide [4–11]. Epidemiologic studies have indicated that the exposure of PFCs may be associated with the children's neurodevelopment, lipid level, testosterone levels, thyroid hormones levels [12–14]. Therefore, PFCs have attracted more and more attention from scientists and governments.

Although the application of PFCs has been restricted and even forbidden by many countries, PFCs are still widely used in commercial products due to their low cost and excellent properties of repelling the water and oil. PFCs are highly water-soluble in comparison with other persistent and bioaccumulative organic pollutants such as polychlorinated dioxins and PCB which have low water solubility [15]. The water is the major medium for the PFCs and some surface water in different countries is found to be contaminated with PFCs [2,3,7,16–22].

Due to the low concentrations of PFCs in the environmental water, enrich and purify of the source water is necessary. The methods for the quantitative analysis of PFCs mainly include the liquid chromatography–tandem mass spectrometry (LC–MS/MS) [3,16,23–25] and gas chromatography/chemical ionization mass spectrometry (GC/CI–MS) [26–28]. However, GC/CI–MS method needs the derivatization of PFCs which is tedious and toxicant, the LC–MS/MS has been the predominant method. Solid phase extraction (SPE) is the most widely used for enrichment of the PFCs in water which mainly include WAX and HLB. The sampling volume

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of the SPE is ranged from 500 mL to 1500 mL. In this study, HLB and LC–MS/MS will be used in the analysis of the PFCs in source water.

## 2. Experimental

### 2.1. Instruments

The ultra high performance liquid chromatography (UHPLC, Agilent, USA) with a C18 column (50 mm × 2.1 mm, 1.8 μm particle size, Agilent, USA) was connected to the triple quadrupole tandem mass spectrometer (3200QTrap, Applied Biosystems-Sciex, USA). The entire system from sample injection to data acquisition was computer-controlled with Analyst 1.5.1.

### 2.2. Chemicals and reagents

PFSAs and PFCAs was purchased from Wellington Laboratories (Guelph, Canada) in 2 mg/L solution mixtures, which contained perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), sodium perfluorooctanesulfonate (PFOS).

The mixture of mass-labeled PFSA and mass-labeled PFCA (2 mg/L) was also purchased from Wellington Laboratories, which contained $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-MPFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUdA.

HPLC-grade methanol was purchased from Merck (Merck, Germany). Pure water was produced by Milli-Q Reference system (Millipore, USA). Ammonium acetate was HPLC-grade (Aladdin, USA). Other chemicals were analytical reagent grade.

### 2.3. Sample collection

The water sample was collected in May 2015 from twenty sample spots of Taihu Lake, China. The sampling locations were distributed throughout the Taihu Lake which flow through the city of Wuxi (location 1, 2, 15, 16), Suzhou (location 7, 11, 12, 13, 14, 18, 19, 20), Changzhou (location 17) and Yixing (location 5) in Jiangsu province and Huzhou (location 6, 8, 9, 10) in Zhejiang province (Fig. 1). Water samples were collected at a depth of 0.5 m below the surface of the Taihu Lake, using a glass bottle which was precleaned with methanol to avoid the contamination. Meteorological conditions were noted for all the sample locations, such as temperature and pH of water, speed and direction of wind. All the water samples were stored at 4 °C until analysis.

### 2.4. Sample preparation

#### 2.4.1. Extraction

Water sample from Taihu Lake was mixed before pretreatment and 500 mL of source water was transferred into another glass bottle. 50 μL of the internal standard solution (100 μg/L) was added into the 500 mL water to gain the concentration of 10 ng/L for each sample. The OASIS HLB SPE tube (Waters, 500 mg, 6 mL) was conditioned with 5 mL of methanol and 5 mL of water successively. The 500 mL of supernatant water was then extracted through the SPE tube (500 mg, 6 mL, Waters) at a rate of 1 mL/min using the large volume sampler (CNW, China) which siphoned water sample from the glass bottle to SPE tube automatically. After drying of the SPE tubes with the vacuum, the analytes were eluted with 4 mL of methanol which was collected in a bottle tube.

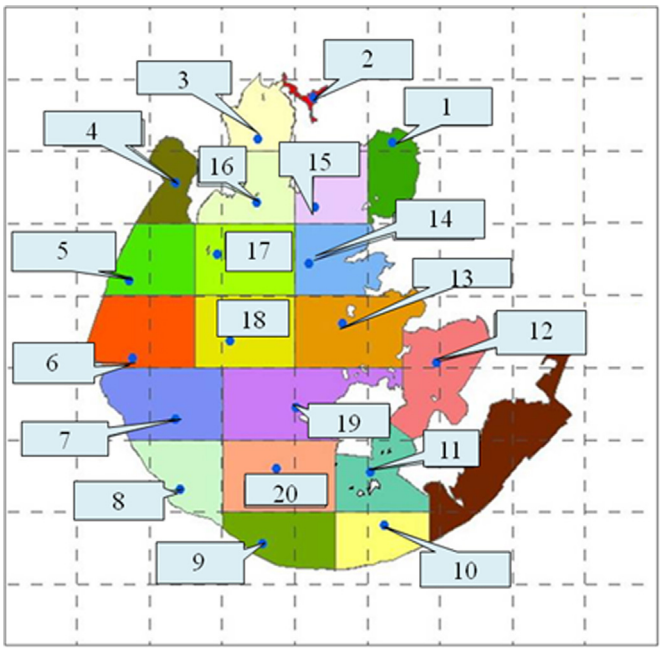


**Fig. 1.** Sample locations of Taihu Lake.

#### 2.4.2. Concentration

The eluant was dried with vacuum concentrator CentriVap (Labconco, USA) and was reconstituted with 250 μL methanol/water (25:75). The sample was centrifuged and the supernatant was transferred into a 250 μL vial glass insert (Agilent, USA) which was placed in the glass sample vial and stored at 4 °C before analyzed by UHPLC–MS/MS.

#### 2.4.3. LC/MS/MS system

All samples were analyzed by UHPLC–MS/MS system with a TurboIonSpray source. A short chromatographic column and the elution program of mobile phase were tested for obtain a proper chromatographic separation. For target quantitative analyses, data acquisition was performed in multiple reaction monitoring (MRM) mode. Generally, two MRM transitions between the precursor ion and the two most abundant product ions were selected for each analyte, one for quantification and the second one for confirmation. The MS conditions were optimized to provide the highest signal intensity. MS/MS parameters were optimized with direct infusion of each individual analyte into the mass spectrometry at 1000 ng/mL in the initial LC mobile phase at a flow rate of 5 μL/min.

#### 2.4.4. Quality assurance and quality control

Analytes were identified by the retention time (RT) comparing to the RT of the standard solution and the internal standard solution. Quantification was performed by the internal standard calibration curves.

Limit of detection (LOD) and limit of quantity (LOQ) were calculated as the amount of analyte giving a peak with a signal-to-noise ratio of 3 and 10, respectively. Recovery and reproducibility were evaluated from replicate analysis in 500 mL of Mill-Q water which contains three spiked levels for 5 ng/L, 10 ng/L and 20 ng/L (n = 6) while the spiked concentration of the internal standard in water sample was 10 ng/L.

Working standard solutions containing all PFCs were prepared by diluting stock solutions in methanol/water solutions to serial concentrations as 1, 6, 10, 16, 20, 30, 40, 50 μg/L for each analyte while the internal standard concentration was 20 μg/L. The matrix matched calibration solution was not needed because the