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Determination of perfluorooctanoic acid and perfluorooctane sulfonate by automated in-tube solid-phase microextraction coupled with liquid chromatography–mass spectrometry

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ABSTRACT

We have developed a simple, rapid, and sensitive method for the determination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by on-line in-tube solid-phase microextraction (SPME) coupled with liquid chromatography–mass spectrometry (LC–MS). PFOA and PFOS were separated within 10 min by high-performance liquid chromatography using an Inertsil ODS-3 column and 10 mM ammonium acetate/methanol (35/65, v/v) as a mobile phase at a flow rate of 0.25 mL min^{-1}. Electrospray ionization conditions in the negative ion mode were optimized for MS detection of PFOA and PFOS. The optimum in-tube SPME conditions were 20 draw/eject cycles with a sample size of 40 μL using a CP-Pora PLOT amine capillary column as the extraction device. The extracted compounds could be desorbed easily from the capillary by passage of the mobile phase, and no carryover was observed. Using the in-tube SPME LC–MS method, good linearity of the calibration curve (r = 0.9990 for PFOA, r = 0.9982 for PFOS) was obtained in the range of 0.05–5 ng mL^{-1} each compound. The detection limits (S/N = 3) for PFOA and PFOS were 1.5 and 3.2 pg mL^{-1}, respectively. The method described here showed about 100-fold higher sensitivity than the direct injection method. The within-day and between-day precisions (relative standard deviations) were below 3.7 and 6.0%, respectively. This method was applied successfully to the analysis of PFOA and PFOS in environmental water samples and to the elution test from a Teflon®-coated frying pan without interference peaks. The recoveries of PFOA and PFOS spiked into river samples were above 81%, and PFOA was detected at pg mL^{-1} levels in environmental water samples and eluate from the frying pan.

1. Introduction

Perfluorinated compounds (PFCs), especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Fig. 1), are heat stable, highly resistant to degradation and environmental breakdown, and repel both water and oil. Therefore, these compounds are widely used as surfactants in emulsion polymerization of fluoropolymers in industrial products such as non-stick pans, stain/water repellents for clothing/furniture to floor waxes and paper coatings (for instance Teflon®, Bortex®, Stainmaster®, and Scotchguard®) [1,2]. PFCs tend to persist in the environment and are now ubiquitous environmental contaminants, showing bioaccumulation in wildlife and humans. PFOA and PFOS showed a low order of toxicity in an acute toxicity study in rodents, but they exhibited versatile toxicities in primates [3]. Both compounds are carcinogenic in rodents, causing reproductive toxicity, neurotoxicity, and hepatotoxicity [1–5]. However, it is unclear whether PFC exposure affects humans, although experiments in rodents have demonstrated numerous negative effects. Recent epidemiology studies have demonstrated measurable levels of PFCs in the serum of fluorochemical production workers, and these chemicals have also been reported at very low levels in both environmental and blood samples from the general population [6,7]. The average levels for non-occupationally exposed humans are in the range of 3–5 ppb for PFOA and 20–35 ppb for PFOS [8,9]. Therefore, a sensitive, selective, and simple method to determine these compounds at trace levels in environmental and biological samples is required.

PFOA and PFOS became detect all over the world. In particular they have been detected in various environmental waters such as river water [10–20], lake water [19–21], seawater [22–24], ground water [25], tap water [15,19,20,26–28] and wastewater [10,13,29–32], packing materials [33,34], textiles [33–35], house dust [36], and air samples [37] at the concentration from the ppt to ppb level. Analyses of these compounds in environmental samples have been carried out mainly by capillary zone

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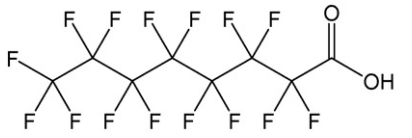
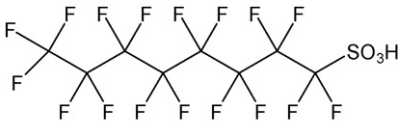


Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonate (PFOS)

Fig. 1. Structures of PFOA and PFOS.

electrophoresis (CZE) [20], gas chromatography–mass spectrometry (GC–MS) [33,37], liquid chromatography–mass spectrometry (LC–MS) [13,23,28,34], and liquid chromatography–tandem mass spectrometry (LC–MS–MS) [14–19,21,24,25,35]. CZE method with indirect UV detection is low sensitive with detection limits of 0.6–2.4 ppm [20]. Although GC–MS method is sensitive with detection limits of 1.6–13.9 ppb [33], it requires derivatization prior to analysis. On the other hand, LC–MS or LC–MS–MS methods are specific and sensitive, (detection limits of ppt level) and their use is becoming increasingly widespread. However, most of these methods require time-consuming sample preparation procedures, such as liquid–liquid extraction or solid-phase extraction, to remove coexisting substances in the samples and to pre-concentrate analytes prior to analysis.

In-tube solid-phase microextraction (SPME), using an open tubular fused-silica capillary with an inner surface coating as the SPME device is simple and can be coupled easily on-line with HPLC and LC–MS. In-tube SPME allows convenient automation of the extraction process, which not only reduces the analysis time, but also provides better precision and sensitivity than manual off-line techniques. We have already developed in-tube SPME methods for the determination of various compounds in environmental samples with LC–MS–MS [38–40]. The details of the in-tube SPME technique and applications have been summarized in several reviews [41–43]. Here, we report an automated on-line in-tube SPME LC–MS method for simultaneous determination of PFOA and PFOS in environmental samples.

2. Experimental

2.1. Materials

PFOA and PFOS (Fig. 1) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and Kanto Chemical (Tokyo, Japan), respectively. Each compound was dissolved in methanol to make a stock solution at a concentration of 1 mg mL^{-1}. The solutions were stored at 4 °C and diluted to the required concentrations with pure water prior to use. HPLC grade methanol and water used as mobile phases were purchased from Kanto Chemical. All other chemicals were of analytical grade.

2.2. Instrument and analytical conditions

The LC–MS system used was a Model 1100 series LC coupled with an atmospheric pressure electrospray ionization (ESI) MS (Agilent Technologies, Boeblingen, Germany). An Inertsil ODS-3 column (50 mm × 2.1 mm, particle size 5 μm; GL Science Inc., Tokyo, Japan) was used for LC separation under the following conditions: column temperature, 40 °C; mobile phase, 5 mM ammonium acetate/methanol (35/65, v/v) at a flow rate of 0.25 mL min^{-1}. ESI-MS conditions were as follows: nebulizer gas, N_2 (12 L min^{-1}) (35 psi); drying gas, N_2 (12 L min^{-1}, 350 °C); fragmenter voltage, 130 V; capillary voltage, 4000 V; ionization mode, negative ion mode; mass scan range, m/z 100–600; selected ion monitoring (SIM), m/z 413 (PFOA) and 499 (PFOS); and dwell-times for the ions in SIM, 289 ms. LC–MS data were processed with an HP ChemStation.

2.3. In-tube solid-phase microextraction

A GC capillary column (60 cm × 0.32 mm i.d.) was used as the in-tube SPME device, and placed between the injection loop and injection needle of the autosampler. The injection loop was retained in the system to avoid fouling of the metering pump. Capillary connections were facilitated using a 2.5-cm sleeve of 1/16-in. polyetheretherketone (PEEK) tubing at each end of the capillary. PEEK tubing with an international diameter of 330 μm was suitable to accommodate the capillary used. Standard 1/16-in. stainless steel nuts, ferrules, and connectors were used to complete the connections. CP-Sil 5CB (100% polydimethylsiloxane, film thickness 5 μm), CP-Sil 19CB (14% cyanopropyl phenyl methylsilicone, film thickness 1.2 μm), CP-Wax 52CB (polyethylene glycol, film thickness 1.2 μm), CP-Pora PLOT amine (basic modified styrene divinylbenzene polymer, film thickness 10 μm) (Varian Inc., Lake Forest, CA), Supel-Q PLOT (divinylbenzene polymer, film thickness 17 μm), and Carboxen 1006 PLOT (Carboxen molecularsives, film thickness 15 μm) (Supelco, Bellefonte, PA) were tested for comparison of extraction efficiency. The autosampler software was programmed to control SPME extraction, desorption, and injection. In addition, 2-mL autosampler vials with a septum, one containing 1.5 mL of methanol and another containing 1.5 mL of water, were set into the autosampler. The capillary column was washed and conditioned by two repeated draw/eject cycles (40 μL each) of these solvents, and then a 50 μL air plug was drawn prior to the extraction step. This air gap is necessary to avoid not only sample mixing but also desorption of analyte from capillary coating by mobile phase during the eject step. For sampling and extraction, 2-mL screw-cap autosampler vials equipped with sil-

Table 1
Program for in-tube SPME process.

Sequence	Event	Switching valve	Vial	Draw/ejection		
				Cycle[a]	Volume (μL)	Speed (μL min^{-1})
1	Conditioning of the capillary	Load	MeOH	D/E (2)	40	200
2	Drawing of air into the capillary	Load	Empty	D (1)	50	200
3	Conditioning of the capillary	Load	Water	D/E (2)	40	200
4	Extraction of analytes into the capillary	Load	Sample	D/E (20)	40	150
5	Needle washing	Load	MeOH	D/E (1)	2	200
6	Desorption of analytes from the capillary	Inject	–	–	–	–
7	HPLC separation of analytes and return to sequence 1	Load	–	–	–	–

[a] D: draw; E: ejection.