A New Solid Phase Extraction Method for Short- and Long-Chain Perfluorinated Acids and Fluorotelomers in Water and Biota

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Introduction

There is growing interest in the environmental fate of perfluorinated acids, such as perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$), due to their widespread occurrence, persistence, and bioaccumulation. PFOS and PFOA have been found in fish and marine mammals from remote marine locations [1-4]. The environmental chemistry of perfluorinated compounds is relatively complex due to the existence of multitude of precursors and transformation products in the environment and biota. Perfluoroalkylsulfonamidoalcohols and fluorotelomer alcohols (FTOHs, $C_xF_{2x+1}CH_2CH_2OH$) are some of the precursor compounds used in several products. Reports of measurement of FTOHs and polyfluorinated sulfonamides in water and biota are scarce. Analysis of FTOHs and perfluorinated acids in ambient waters requires sensitive methods, due to the occurrence of these compounds at parts-per-trillion (ng/L) or lower levels. A reliable and sensitive analytical method for ultra-trace level analysis of perfluorinated acids, particularly PFOS and PFOA, in open ocean waters, has been reported recently [5]. In the present study, we have developed methods for the analysis of FTOHs, telomer acids, short-, and long-chain perfluorinated carboxylic acids, and perfluorooctanesulfonamide, in water and biological samples. The method is robust and can be applied in the analysis of a wide variety of poly- and per-fluorinated acids, and fluorotelomer compounds, in water and biota.

Materials and Methods

Twenty-two poly- and per-fluorinated compounds were examined in this study. The analytical procedure for the extraction of water samples was similar to that described earlier [5]. The modifications were aimed at accommodating more target analytes including telomer alcohols, telomer acids, and sulfonamides. Extraction using Oasis®HLB and Oasis®WAX cartridges was examined. The cartridges were conditioned prior to the passage of samples. HLB cartridges were preconditioned by passage of 5 mL of methanol, followed by 5 mL of water, at 2 drops/sec. WAX cartridges were preconditioned by passage of 4 mL of 0.1%NH_4OH in methanol, and then by 4 mL of methanol and 4 mL of water. Water samples (100-200 mL) spiked with various levels of target analytes (1-10 pg/mL final water concentration) were passed through the pre-conditioned cartridges at a rate of 1 drop/ sec. The cartridges were then washed and the target analytes eluted. Analysis of fluorochemicals was performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), composed of a HP1100 liquid chromatograph (Agilent Technologies, Palo Alto, CA) interfaced with a Micromass® (Beverly, MA) Quattro Ultima Pt mass spectrometer operated in the electrospray negative ionization mode. The limit of detection (LOD) of target chemicals was evaluated for each sample, based on the maximum blank concentration, the concentration factors, the sample volume, and a signal-to-noise ratio of 3. The LODs of target chemicals were in the range of 0.01-1 ng/L, when 100 mL of water sample was used in the analysis; LODs for biological samples were between 0.03 and 3 ng/g, wet wt, when 1 g of tissue was used for extraction.

Results and Discussion

Recoveries of fluorochemicals spiked onto HLB and WAX cartridges were compared (Fig. 1). Recoveries of target fluorinated compounds spiked into HLB cartridges were generally >80%, except for short-chain carboxylic acids such as, PFHxA, PFPeA, and PFBA, whose recoveries were less than 30%. So, weak anion exchange and reversed-phase sorbent, WAX cartridges, were used for comparison. The average recoveries of poly- and per-

fluorinated acids, including short-chain carboxylates, through WAX cartridges were between 85 and 107% (n=5), except for two FTOHs, 10:1 FTOH and 7:1 FTOH, for which the recoveries were 59 and 54%, respectively. Nevertheless, the recoveries of short-chain perfluorocarboxylates, PFBA, PFPeA, and PFHxA, through WAX cartridges were higher than were the recoveries through HLB cartridges (Fig. 1). Neutral polyfluorinated compounds such as PFOSA, n-ethyl FOSA, and fluorotelomer alcohols were separated from other fluorinated compounds by the WAX method. The WAX procedure was optimized by selecting appropriate pH (pH 4) and NH_4OH concentration (0.1%). In general, the WAX method provided better recoveries for poly- and per-fluorinated acids than did HLB.

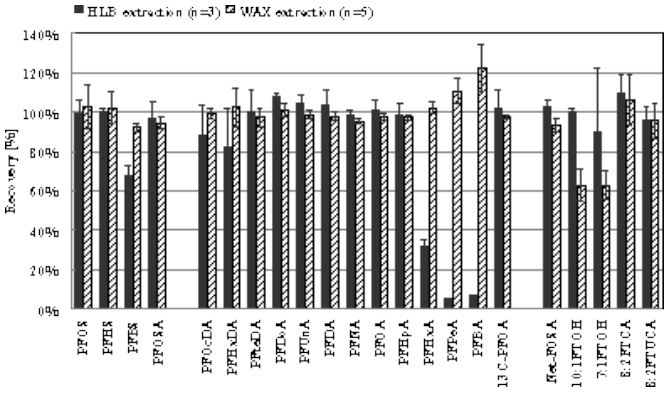

Figure 1. Recoveries of poly- and per-fluorinated acids, telomer alcohols, and telomer acids through Oasis®HLB and Oasis®WAX cartridges.

Analysis of biological matrices, particularly muscle tissues and other fibrousmatrices, for the determination of perfluorinated compounds is still challenging. In this study, we tested the alkaline digestion method for the analysis of FTOHs, fluorotelomer acids, and polyfluorosulfonamides, followed by WAX cartridges. Target fluorochemicals were spiked into 10 mL of 0.05N KOH in methanol and shaken at 250 rpm for 16 h. Then, 1 mL of the extract is diluted into 100 mL milli-Q water in a polypropylene container. The extract is then passed through the WAX cartridge and analyzed as described above. Recoveries of target compounds by the KOH digestion-WAX method were greater than those by the ion-pair extraction method (Fig. 2). Recoveries of FTOHs and telomer acids were low, 40-60%, although these values are greater than the values from the ion-pair extraction method. This suggests that the KOH digestion-WAX method can be used for the analysis of FTOHs in biological samples. However, appropriate internal standards, compounds that would behave similarly to FTOHs in the analytical method, are needed to check recoveries and to correct sample values, if necessary.

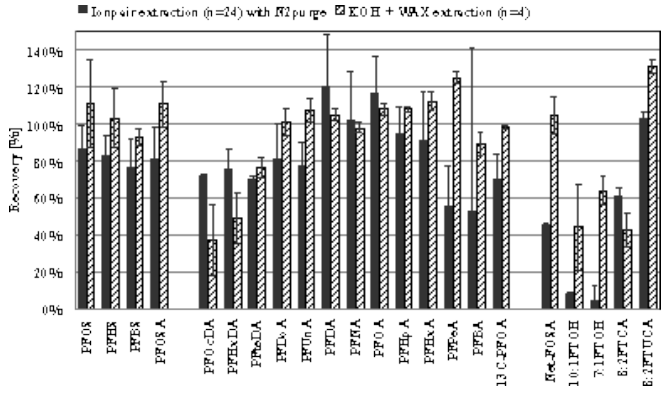

Figure 2. Recoveries of poly- and per-fluorinated acids, telomer alcohols, and telomer acids, analyzed by KOH digestion-WAX extraction and by the ion-pair extraction.

The method developed for biological samples, using KOH digestion followed by WAX extraction, was compared

with the ion-pair extraction method, in an analysis of human blood and beaver liver samples collected in Poland (Table 1). Concentrations of poly- and per-fluorinated acids were similar between the KOH-WAX and ion-pair extraction methods, for the blood samples. However, concentrations of PFOS, PFHS, and PFOSA in the liver samples analyzed by KOH-WAX method were 3- to 5- fold greater than the concentrations determined using the ion-pair extraction method. Concentrations of perfluorinated carboxylates in liver were similar between the KOH-WAX and ion-pair extraction methods. The greater concentrations of PFOS, PFHS, and PFOSA by the KOH -WAX method could be due to effective digestion and release of these compounds from the sample matrix.

Overall, the methods developed in this study for the measurement of poly- and per-fluorinated acids, FTOHs, fluorotelomer acids, and polyfluorosulfonamides are robust (suitable for both ionic and neutral compounds); they are capable of measuring the target compounds at several pg/L in water and at a few pg/g in biota. The method can be applied in the analysis of water, sediment, and biological matrices, so that we can better understand the fate of per- and poly-fluorinated compounds in the environment.

Table 1. Concentrations of poly- and per-fluorinated acids in human blood (ng/mL) and beaver liver (ng/g, wet wt) from Poland analyzed using ion-pair extraction and KOH digestion-WAX methods (NA= Not analyzed)

	Polish blood		Beaver liver	
	Ion-pair (n=2)	KOH-WAX (n=2)	Ion-pair (n=2)	KOH-WAX (n=2)
^{13}C-PFOA (%)	na	96	42	39
PFOS	84.2	87.5	38.7	133
PFHS	2.25	2.75	0.32	2.03
PFBS	<0.004	<0.08	<0.01	<0.03
PFOSA	2.63	3.47	0.12	0.82
PFOcDA	na	<0.04	<0.04	<0.16
PFHxDA	na	<0.04	<0.21	<0.16
PFTeDA	na	<0.04	0.05	<0.16
PFDoDA	0.10	<0.04	0.15	0.29
PFUnDA	1.13	1.57	0.53	1.21
PFDA	1.37	1.27	0.57	0.63
PFNA	3.82	4.46	1.34	1.12
PFOA	3.69	3.49	0.28	0.29
PFHpA	0.12	<0.04	0.02	<0.16
PFHxA	0.21	<0.04	0.03	<0.16
PFPeA	<0.05	<2	<0.21	<0.79
PFBA	<0.05	<2	<0.21	7.28
THPFOS	<0.01	<0.08	<0.04	<0.03
N-EtFOSA	na	<0.08	0.03	<0.03
10:1FTOH	na	<0.08	<0.04	<0.03
7:1FTOH	na	<0.04	<0.04	<0.16
8:2FTCA	na	<2	<0.21	<0.79
8:2FTUCA	na	<0.08	<0.01	<0.03

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