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Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota

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Abstract

Fluorotelomer alcohols and fluorotelomer acids have been proposed as a source of the perfluorinated carboxylic acids found in remote marine locations. To examine the sources and fate of perfluorinated acids in the environment, a method to determine a wide range of poly- and perfluorinated acids in environmental and biological matrices is needed. In this study, a method has been developed to measure a suite of neutral and acidic fluorochemicals including, fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids, in water and biological samples. The method involves solid-phase extraction with weak anion exchange (WAX) cartridges, followed by sequential elution with sodium acetate buffer, methanol, and 0.1% NH_4OH in methanol. For biological samples, prior to solid-phase extraction, tissues are digested in 0.5N potassium hydroxide/methanol, diluted in water, and passed through the WAX cartridge. Neutral compounds and telomer alcohols are separated from other poly- and perfluorinated acids. The method is robust (i.e., capable of measuring neutral and acidic compounds), and can be applied for the analysis of a range of poly- and perfluorinated acids, including telomer alcohols, telomer acids, perfluoroalkylcarboxylates, and perfluoroalkylsulfonates in water and biota. With the use of high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), a method detection limit in the range of several tens to hundreds of parts-per-quadrillion (pg/L) in water and at a few tens to hundreds of parts-per-trillion (pg/g) levels in biological matrices can be achieved.

Keywords: Perfluorinated chemicals; PFOS; Fluorotelomer alcohols; HPLC-MS/MS

1. 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 are metabolites of several polyfluorinated precursor compounds that are produced and used commercially [1–4]. PFOS and PFOA have been found in fish and marine mammals from remote marine locations [5–8]. PFOS and PFOA, because of their strong acidity, are expected to be present in ionized form, with little propensity for volatilization, under normal environmental conditions. Nevertheless, the occurrence of PFOS and PFOA in remote marine environment has led to several hypotheses. Among these hypotheses is, atmospheric transport of relatively more volatile precursor compounds, such as polyfluoroalkylated sulfonamides, sulfonamidoalcohols, and fluorotelomer alcohols, to remote marine locations, where the precursors break down, by biological or non-biological degradation processes, to PFOS and PFOA [3].

Polyfluoroalkylated sulfonamidoalcohols (FOSE; e.g., $C_8F_{17}–SO_2–N(C_2H_4OH)CH_3$), such as *N*-ethyl or *N*-

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methyl perfluorooctanesulfonamidoethanol (*N*-EtFOSE/*N*-MeFOSE), produced by electrochemical fluorination, are used in a variety of products for surface treatments. Such compounds have been shown to be metabolized to PFOS in mammals and fish [9,10]. These polyfluorinated sulfonamides have been reported to occur in indoor and outdoor air [11,12]. In 2000, the annual production of PFOS-related chemicals in the US was estimated to be 3 million kg [13]. The major producer of polyfluorinated sulfonamidoalcohols in the US, 3M, announced a phasing-out of these products beginning in 2001.

Fluorotelomer alcohols (FTOHs, $C_xF_{2x+1}CH_2CH_2OH$), produced via the telomerization process, are major raw materials used in various fluoropolymers and fluorosurfactants. These compounds have been shown to degrade to PFOA or other perfluorocarboxylates via atmospheric oxidation reactions or microbial degradation processes [3,14]. FTOHs are linear, long-chain, polyfluorinated alcohols and are used as intermediates in the synthesis of inks, paints and coatings, polymers, adhesives, waxes, polishes, and caulks (www.dupont.com/zonyl/flash.htm). The global production of FTOHs was estimated to be 5–6.5 million kg/year, of which 40% occurred in North America (US EPA Docket AR-226-1141). FTOHs have been measured in air over North America [12,15]. Similarly, fluorotelomer sulfonates have been measured in groundwater [16]. However, reports of measurement of FTOHs and polyfluorinated sulfonamides in water and biota are scarce. In order for the sources and fate of poly- and perfluorinated acids in the environment to be understood, analysis of FTOHs and polyfluorinated sulfonamides in water and biota is needed. 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 [17]. 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 perfluorinated acids, and fluorotelomer compounds, in water and biota.

2. Experimental

2.1. Materials and chemicals

Twenty-two poly- and perfluorinated compounds were examined in this study (Table 1). Purities of all of the analytical standards were ≥95%. Potassium salts of PFHS and PFBS, PFOSA, and *n*-ethyl FOSA were a gift from the 3M Company (St. Paul, MN). Potassium salt of PFOS was from Tokyo Chemical Industries (Portland, OR). Tetrahydroperfluorooctanesulfonic acid (THPFOS) was purchased from ICN (Costa Mesa, CA). PFBA, PFNA, and 7:1 FTOH were from Avocado Research Chemicals Ltd. (Lancashire, UK). PFPeA, PFHpA, PFDA, PFUnDA, and PFDoDA were from Fluorochem Ltd. (Derbyshire, UK). PFHxA was from Wako Pure Chemical Industries (Tokyo, Japan). PFOA was from Strem Chemicals Inc. (Newburyport, MA). PFTeDA, PFHxDA, PFOcDA, and 10:1 FTOH were from SynQuest Lab Inc. (Alachua, FL). 8:2 FTCA and 8:2

Table 1
List of target compounds analyzed, and the MS/MS parameters used

Acronym	Name	Formula	MS/MS mass transition	Cone voltage (V)	Collision energy (eV)
PFOS	Perfluorooctanesulfonate, potassium salt	$C_8F_{17}SO_3K$	498.6 → 79.7	90	35
PFHS	Perfluorohexanesulfonate, potassium salt	$C_6F_{13}SO_3K$	398.7 → 79.7	70	30
PFBS	Perfluorobutanesulfonate, potassium salt	$C_4F_9SO_3K$	298.7 → 79.7	35	25
PFOSA	Perfluorooctanesulfonamide	$C_8F_{17}SO_2NH_2$	497.7 → 77.7	55	25
PFOcDA	Perfluorooctadecanoic acid	$C_{17}F_{35}COOH$	912.9 → 869	50	15
PFHxDA	Perfluorohexadecanoic acid	$C_{15}F_{31}COOH$	812.9 → 769.3	40	15
PFTeDA	Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	712.9 → 669	40	12
PFDoDA	Perfluorododecanoic acid	$C_{11}F_{23}COOH$	612.7 → 568.8	35	10
PFUnDA	Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	563 → 519	35	10
PFDA	Perfluorodecanoic acid	$C_9F_{19}COOH$	512.8 → 468.8	35	10
PFNA	Perfluorononanoic acid	$C_8F_{17}COOH$	462.7 → 418.8	35	10
PFOA	Perfluorooctanoic acid	$C_7F_{15}COOH$	413 → 368.7	35	10
PFHpA	Perfluoroheptanoic acid	$C_6F_{13}COOH$	362.8 → 318.8	35	8
PFHxA	Perfluorohexanoic acid	$C_5F_{11}COOH$	312.8 → 268.8	35	7
PFPeA	Perfluoropentanoic acid	C_4F_9COOH	262.8 → 218.7	35	7
PFBA	Perfluorobutyric acid	C_3F_7COOH	212.8 → 168.8	35	7
THPFOS	1H,1H,2H,2H- perfluorooctanesulfonic acid	$C_8F_{13}H_4SOO^-$	426.7 → 406.7	55	20
N-ethyl FOSA	*N*-ethyl perfluorooctanesulfonamide	$C_8F_{17}SO_2NHCH_2CH_3$	525.9 → 168.9	60	25
10:1 FTOH	1H,1H-perfluoro-1-undecanol	$CF_3(CF_2)_9CH_2OH$	549 → 369	35	18
7:1 FTOH	Pentadecafluoro-1-octanol (PDFO)	$CF_3(CF_2)_6CH_2OH$	398.9 → 218.9	35	15
8:2 FTCA	8:2 fluorotelomer acid	$CF_3(CF_2)_7\ CH_2COOH$	477 → 393	35	20
8:2 FTUCA	8:2 fluorotelomer unsaturated acid	$CF_3(CF_2)_6\ CF{=}CHCOOH$	457 → 393	35	10

FTUCA were from Asahi Glass Co. Ltd. (Tokyo, Japan). Oasis®HLB (6 cc, 200 mg, 30 μm; hereafter referred as HLB for hydrophilic–lipophilic balance) and Oasis®Wax (6 cc, 150 mg, 30 μm; hereafter referred as WAX for weak anion exchange) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA). Potassium hydroxide (85%), ammonia solution (25%), ammonium acetate (97%), sodium acetate (98.5%), acetic acid (99.9%), and methanol (99.8% purity) were from Wako Pure Chemical Industries (Tokyo, Japan). Milli-Q water was used throughout the study. 1,2^{13}C-labeled PFOA was obtained from Perkin-Elmer (Boston, MA), and was used as an internal standard (Lot #3507-195; CUS51073000MG).

2.2. Extraction and purification

The analytical procedure for the extraction of water samples was similar to that described earlier [17]. 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/s. 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/s. The cartridges were then washed and the target analytes eluted. The particles that appeared in the final solution were removed by filtration using nylon syringe filters (Iwaki, Fukushima, Japan).

2.3. Instrumental analysis and quantification

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. A 10 μL aliquot of the sample extract was injected into a guard column (Zorbax XDB-C8, 2.1 mm i.d. × 12.5 mm, 5 μm; Agilent Technologies) connected sequentially to a Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate aqueous solution (solvent A) and methanol (solvent B) as mobile phases, starting at 10% methanol and increasing linearly. At a flow rate of 300 μL/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min, and was kept at that level until 12 min before reversion to original conditions, at the 20 min time point. The capillary was held at 1 kV. Cone- and desolvation-gas flows were kept at 60 and 740 L/h, respectively. Source and desolvation temperatures were kept at 120 and 400 °C, respectively. MS/MS was operated under multiple reaction monitoring (MRM) mode, and the parameters were optimized for transmission of the $[M-K]^-$ or $[M-H]^-$ ions, as shown in Table 1. Six calibration curve points prepared at 2,10, 50, 200, 1000, and 20,000 ppt (ng/L) standard, injected at 10 μL, were prepared routinely, to check for linearity. Quantification was based on the response of the external standards that bracketed the concentrations found in samples. 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 weight, when 1 g of tissue was used for extraction.

3. Results and discussion

3.1. SPE method development

Earlier studies have reported the application of solid-phase extraction, using Sep-Pak®C18 or Oasis®HLB cartridges, in the analysis of perfluorinated acids in water [17–21]. In the present study, 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%. Moreover, separation of neutral polyfluorinated compounds and FTOHs from other poly- and perfluorinated acids was not feasible with the HLB procedure. In order to improve the recoveries of short-chain perfluorinated acids and to separate FTOHs from other fluorinated compounds, we employed a weak anion exchange and reversed-phase sorbent, WAX. The WAX cartridges were conditioned by passage of 4 mL of 0.1% NH_4OH in methanol, 4 mL of methanol and 4 mL of milli-Q water, in sequence, prior to loading of the samples. One nanogram of a mixture of all of the target poly- and per-fluorochemicals was spiked onto WAX cartridges directly. The cartridges were then eluted with 4 mL of 25 mM sodium acetate buffer (pH 4). This fraction, F1, was discarded. The cartridges were then eluted with 4 mL of methanol (F2). F3 was collected by elution of 4 mL of 0.1% NH_4OH in methanol. All of these fractions were injected into HPLC-MS/MS.

The average recoveries of poly- and perfluorinated 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). The recoveries of

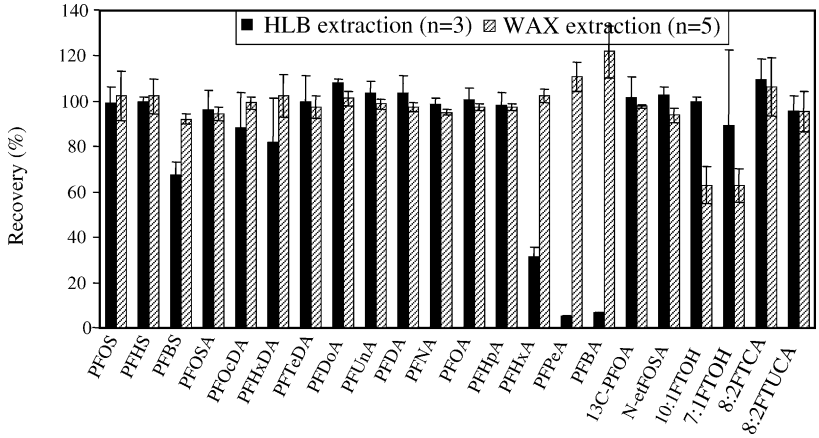

Fig. 1. Recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids through Oasis® HLB and Oasis® WAX cartridges.

FTOHs were relatively lower in WAX than in HLB cartridges, although the coefficient of variation between analyses was less than 10%. Recoveries of fluorotelomer acids through WAX cartridges were between 93 and 107%. The WAX cartridges provided not only better recoveries for most of the analytes, but also less variability (coefficient variation less than 10% for all of the target compounds) between analyses.

Neutral polyfluorinated compounds such as PFOSA, *n*-ethyl FOSA, and fluorotelomer alcohols were separated from other fluorinated compounds by the WAX method. PFOSA, *n*-ethyl FOSA, and FTOHs eluted in the methanol fraction, whereas the rest of the target analytes eluted in the fraction containing 0.1% NH_4OH/methanol. This separation should permit simultaneous analysis of telomer alcohols and neutral polyfluorinated acids by both gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS) techniques, since these compounds are amenable to both of these techniques. GC–MS with chemical ionization has been used in the analysis of FTOHs and polyfluorinated sulfonamides [12,15].

Acetate buffer (25 mM) is passed through the WAX cartridges after loading of samples, to remove interfering biomolecules (e.g., lipid or proteins) in the samples and to improve adsorption of target anions to the cartridge. The effect of pH of sodium acetate buffer on the recoveries of target fluorinated compounds was examined (Fig. 2). Recoveries of target fluorinated compounds did not vary considerably between pH values of 4 and 5. A pH of 4 was selected for further analysis. After passing the acetate buffer, the cartridges were dried so as to remove water, which would otherwise elute in the methanol fraction and would affect concentration of the extracts.

The effect of NH_4OH concentration on the recoveries of poly- and perfluorinated acids was examined over a range from 0.1 to 20% (Fig. 3). Recoveries of most of the target analytes were considerably reduced when the higher concentration, 20% NH_4OH in methanol, was used for elution. Lack of extraction of analytes from the sorbent, or breakdown/conversion of sulfonates and long-chain carboxylates to unsaturated acids under strongly alkaline conditions may explain lower recoveries of target analytes at 20% NH_4OH. However, variation of the NH_4OH concentration at less than 2% did not affect the recoveries; all of the tested concentrations of NH_4OH, from 0.1 to 2% in methanol yielded recoveries greater than 70% for most of the target analytes. We selected 0.1% NH_4OH for further studies, because a low concentration of NH_4OH introduces less water into the extracts. This enables concentration of the final extracts to lower volumes, when needed.

Next, the volume of 0.1% NH_4OH/methanol (F3) needed to elute all of the target compounds present in the samples was examined (Fig. 4). Most of the target compounds, in particu-

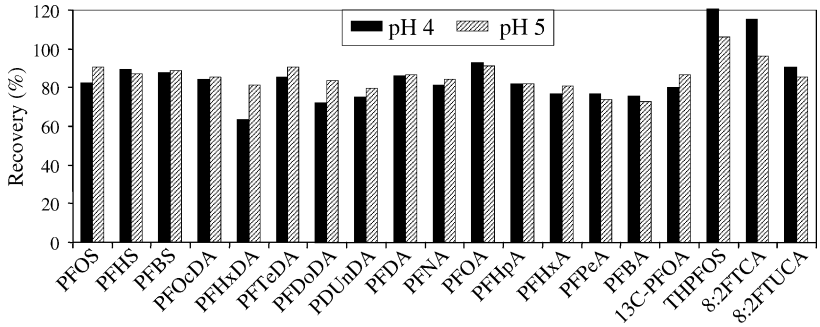

Fig. 2. Effect of pH of acetate buffer on the recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids through Oasis® WAX cartridge.

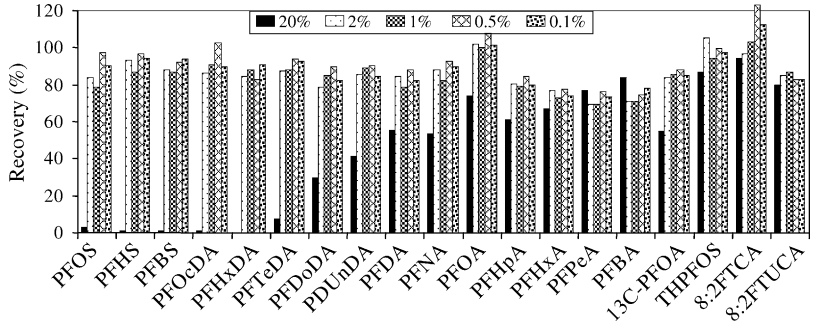

Fig. 3. Recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids through WAX cartridges as a factor of the concentration of NH_4OH in methanol.

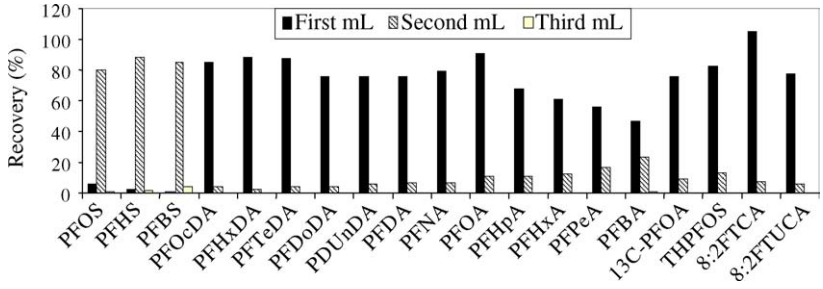

Fig. 4. Recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids through WAX cartridges as a factor of elution volume of NH_4OH in methanol.

lar, long-chain carboxylates and telomer acids, eluted within the first 1 mL of the 0.1% NH_4OH/methanol. The remainder of the compounds eluted within the second 1 mL of the 0.1% NH_4OH/methanol. Although most of the compounds eluted within the first 2 mL of 0.1% NH_4OH/methanol, we selected 4 mL, as a precaution, for further analysis. PFOSA, *n*-ethyl FOSA, and FTOHs elute with methanol in F2. The first 2 mL of methanol was adequate to elute these compounds, but to ensure safety, 4 mL was used in further analysis.

3.2. Procedural recoveries

Once the SPE conditions had been optimized, we spiked 100 mL of Milli-Q water samples with 1 ng each of the target fluorinated compounds in a polypropylene container, and mixed thoroughly. The samples were passed through the WAX or HLB cartridges. Procedural blanks were analyzed along with samples. In general, the WAX method provided better recoveries for poly- and perfluorinated acids than did HLB. The recoveries with both methods were relatively low for long-chain perfluorinated carboxylates (50–90%), PFOSA, *n*-ethyl FOSA, and FTOHs (35–55%) (Fig. 5). These sub-optimal recoveries were not cartridge specific, but rather were due to sorption of target compounds to the polypropylene containers, and evaporative loss of FTOHs during concentration of extracts under the nitrogen stream. Sorption of target analytes to polypropylene containers was assessed by extraction of the containers with methanol (after loading of cartridges with water spiked with target chemicals) and injection into LC–MS/MS. Residual long-chain perflu-

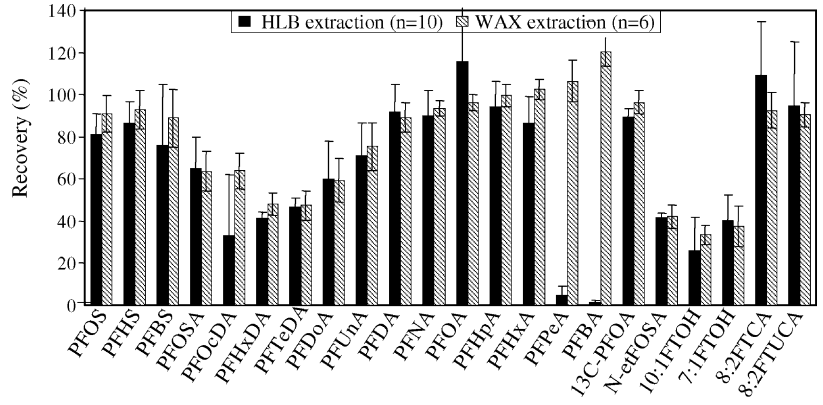

Fig. 5. Recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids spiked into water and extracted, using HLB and WAX cartridges.

orinated carboxylates were found in methanol (~10–30%). Due to the high volatility of FTOHs [22], concentration of the extracts under a nitrogen stream may lead to loss of FTOHs. Since the final volume of the extract eluted through the WAX cartridge is 4 mL, the extract can in our method be directly injected into LC–MS/MS without further concentration.

3.3. KOH digestion–WAX extraction for biological samples

An earlier study has reported the analysis of perfluorinated acids in biological samples using alkaline digestion [23]. In the present study, we tested the alkaline digestion method for the analysis of FTOHs, fluorotelomer acids, and polyfluorosulfonamides, followed by SPE using 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 (Fig. 6). Recoveries of target analytes extracted by KOH digestion–WAX extraction were compared with recoveries of the ion-pair extraction method described for biological samples [18]. Recoveries of target compounds by the KOH digestion–WAX method were greater than those by the ion-pair extraction method. 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.

Recoveries of ^{13}C-PFOA were tested along with several other poly- and perfluorinated acids for assessment of this compound's suitability as an internal standard. Because the recovery of ^{13}C-PFOA was similar to that for unlabeled PFOA, this labeled compound appears to be suitable for the analysis of perfluorocarboxylates of chain lengths between C6 and C10. However, ^{13}C-PFOA may not suitable as an internal standard for shorter- (C4 and C5) or longer-chain carboxylates (C12–C18), PFOS, and FTOHs and fluorotelomer acids, because the recoveries of ^{13}C-PFOA were not found to be related to recoveries of these compounds. Furthermore, ^{13}C-PFOA contained some impurities, such as PFBA (1%), PFPeA (0.8%), PFHpA (0.01%), and traces of 8:2 FTUCA. Use of at least this batch of ^{13}C-PFOA for trace-level analysis of the compounds listed above can produce erroneous data.

3.4. Procedural blanks and detection limits

One of the major problems associated with trace-level analysis of perfluorinated acids such as PFOS and PFOA is background contamination in the analytical blanks [17,24]. One known source of procedural contamination is fluoropolymers, such as polytetrafluoroethylene and perfluoroalkoxy compounds, which are present in a variety of laboratory products. Therefore, field and procedural blanks are duly needed to establish quantitation limits of perfluorinated acids in environmental and biological matrices. We tested several procedural blanks in this study, to check for procedural contamination by target perfluorinated compounds (Table 2). Various known sources of instrumental and procedural contamination, as described in an earlier study [17], had been eliminated. Few target compounds were detected in procedural blanks at a few pg/L in the final extract (Table 2). However, PFOA, PFDA, and PFUnDA were still found at relatively high concentrations. Depending on the volume of water or the weight of biological sample extracted, the LOD of a target fluorochemical can be on the order of a few pg/L for water samples, and a few pg/g for biological samples. Instrumental detection limits for target analytes are listed in Table 2. The Instrumental detection limit is based on the lowest acceptable calibration standard. A datum on a curve was deemed

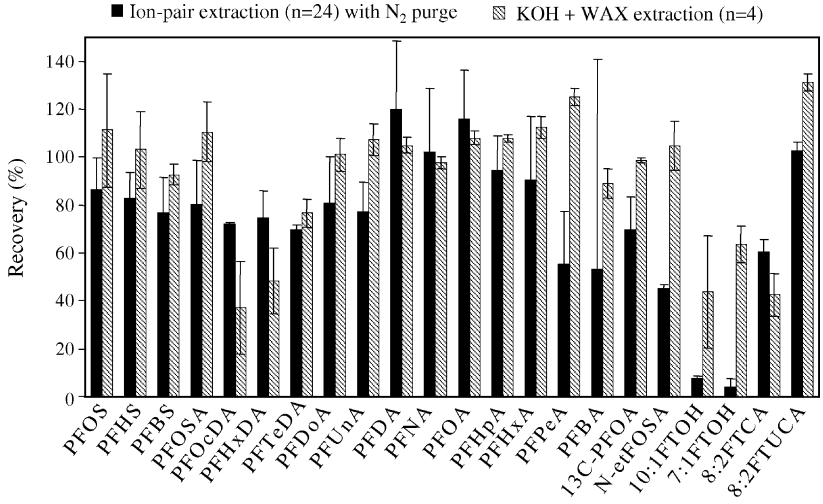

Fig. 6. Recoveries of poly- and perfluorinated acids, telomer alcohols, and telomer acids, analyzed by KOH digestion–WAX extraction and by the ion-pair extraction method.

Table 2
Levels of poly- and perfluorinated acids in procedural blanks, and instrumental detection limits

Acronym	Amount (pg) in the final 4 mL extract[a]	Instrumental detection limit (pg)[b]
PFOS	4.3–14.2	0.1
PFHS	ND	0.02
PFBS	ND	0.02
PFOSA	3.4–9.7	0.02
PFOcDA	4.2–9.2	0.1
PFHxDA	ND-12.3	0.1
PFTeDA	ND-3.4	0.1
PFDoDA	4–5.6	0.1
PFUnDA	4.2–17.3	0.1
PFDA	3–13.9	0.1
PFNA	0.5–9.8	0.1
PFOA	1.2–13	0.1
PFHpA	ND-4.8	0.1
PFHxA	ND-9.2	0.1
PFPeA	ND	0.5
PFBA	ND	0.5
THPFOS	ND-0.6	0.02
N-Ethyl FOSA	ND-3.9	0.02
10:1 FTOH	ND	0.02
7:1 FTOH	ND	0.1
8:2 FTCA	ND	0.5
8:2 FTUCA	ND	0.01

ND, not detected.
[a] 10 μL was injected from the final 4 mL extract. Thus, 4.3 pg in final 4 mL would correspond to ∼1 pg/mL; 10 μL injection would result in a detection limit of 0.01 pg in the sample extract.
[b] Instrumental detection limit was based on the lowest acceptable calibration standard.

Table 3
Comparison of concentrations (ng/L) of poly- and perfluorinated acids in water samples from Tokyo Bay and from Tomakomai Bay, analyzed using Oasis® HLB and Oasis® WAX cartridges

	Tokyo Bay, Station 6, July 2004		Tomakomai Bay, Station 14, December 2003	
	HLB (n = 2)	WAX (n = 2)	HLB (n = 2)	WAX (n = 2)
^{13}C-PFOA (%)	97	92	109	93
PFOS	13.7	13.5	2880	2550
PFHS	2.17	1.99	96	92
PFBS	0.21	0.51	<0.32	0.28
PFOSA	0.41	0.31	380	351
PFOcDA	<0.5	<0.2	<1.5	<0.45
PFHxDA	<0.5	<0.2	<1.5	<0.45
PFTeDA	<0.5	<0.2	<1.5	<0.45
PFDoDA	<0.5	<0.2	<1.5	0.54
PFUnDA	0.78	0.60	57.8	57
PFDA	<0.5	0.42	12.1	11.5
PFNA	7.42	7.55	343	288
PFOA	34.8	35.1	63.7	62.4
PFHpA	1.64	1.99	9.83	10.6
PFHxA	<0.5	1.25	<1.5	17.9
PFPeA	<2.5	32.3	<7	7.48
PFBA	<2.5	9.11	<7	2.20
THPFOS	<0.1	<0.04	47.7	51.1
N-Ethyl FOSA	<0.1	<0.04	<0.3	<0.09
8:2 FTOH	<10	<4	<30	<9
10:1 FTOH	<0.1	<0.04	<0.3	<0.09
7:1 FTOH	<0.5	<0.2	<1.5	<0.45
8:2 FTCA	<2.5	<1	<7	<2.25
8:2 FTUCA	<0.1	<0.04	<0.3	0.14

acceptable if it was back-calculated to be within 30% of the theoretical value, when evaluated against the 1/x weighted curve.

3.5. Analysis of water and biota samples

We tested the performance of the WAX method developed in this study by analyzing water samples collected from Tokyo Bay and Tomakomai Bay. Several samples from different locations were analyzed using the method developed in this study, but results for only two of the locations are presented here, as an example. Water samples from Tomakomai Bay were collected in December 2003, 3 months after a fire that had resulted in the release of aqueous film-forming foams (AFFF) containing perfluorinated acids [25]. Concentrations of fluorochemicals measured using the WAX and the HLB methods were compared (Table 3). Concentrations of perfluorinated acids determined in water samples using the WAX method were similar to those obtained using the HLB method. Nevertheless, the WAX method detected the presence of short-chain perfluorinated acids such as PFHxA, PFPeA, PFBA, and PFBS; these were not detected in the HLB method. By both of these methods, FTOHs and telomer acids were not found in water. Relatively high concentrations of several perfluorinated acids in run-off waters collected in Tomakomai Bay suggest the release of several poly- and perfluorinated acids from the use of AFFF. PFOS and PFNA were the major perfluorinated compounds found in water samples from Tomakomai Bay, whereas PFOA was the major perfluorinated acid found in Tokyo Bay water samples.

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 4). Similar to that for water, several biota samples from different locations were analyzed using the method developed in this study, but results for only blood and liver are presented here, as an example. Concentrations of poly- and perfluorinated 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 three- to five-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 (Fig. 7) for the measurement of poly- and perfluorinated acids, FTOHs, fluorotelomer acids, and polyfluorosulfonamides are robust; they are capable of measuring the target compounds at several

Table 4
Concentrations of poly- and perfluorinated acids in human blood (ng/mL) and beaver liver (ng/g, wet weight) samples from Poland analyzed using ion-pair extraction and KOH digestion–WAX methods

	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-Ethyl FOSA	na	<0.08	0.03	<0.03
10:1 FTOH	na	<0.08	<0.04	<0.03
7:1 FTOH	na	<0.04	<0.04	<0.16
8:2 FTCA	na	<2	<0.21	<0.79
8:2 FTUCA	na	<0.08	<0.01	<0.03

na, not analyzed.

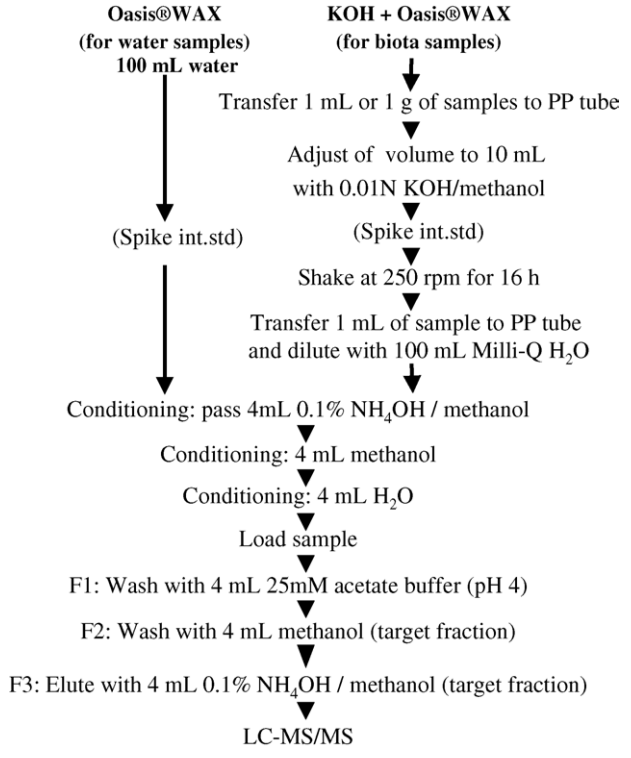

Fig. 7. Flow-chart of analytical method for poly- and perfluorinated acids, telomer alcohols, and telomer acids in water and biological samples using WAX cartridges.

pg/L in water and at a few pg/g in biota. The method can be applied in the analysis of water, and biological matrices, so that we can better understand the fate of per- and polyfluorinated compounds in the environment.

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