

Disposition of Fluorine on New Firefighter Turnout Gear

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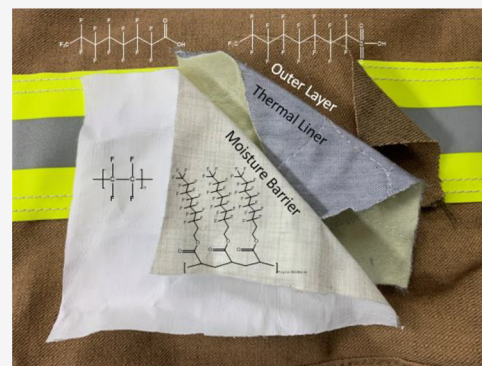
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Supporting Information

ABSTRACT: Firefighter turnout gear is essential for reducing occupational exposure to hazardous chemicals during training and fire events. Per- and polyfluoroalkyl substances (PFASs) are observed in firefighter serum, and possible occupational sources include the air and dust of fires, aqueous film-forming foam, and turnout gear. Limited data exist for nonvolatile and volatile PFASs on firefighter turnout gear and the disposition of fluorine on the individual layers of turnout gear. Further implications for exposure to fluorine on turnout gear are not well understood. Three unused turnout garments purchased in 2019 and one purchased in 2008, were analyzed for 50 nonvolatile and 15 volatile PFASs by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS) and gas chromatography–mass spectrometry (GC–MS), respectively. Particle-induced gamma ray emission (PIGE), a surface technique, and instrumental neutron activation analysis (INAA), a bulk technique, were used to measure total fluorine. Bulk characterization of the layers by pyrolysis-GC/MS (py-GC/MS) was used to differentiate fluoropolymer (e.g., PTFE) films from textile layers finished with side-chain polymers. The outer layer, moisture barrier, and thermal layers of the turnout gear all yielded measured concentrations of volatile PFASs that exceeded nonvolatile PFAS concentrations, but the summed molar concentrations made up only a small fraction of total fluorine (0.0016–6.7%). Moisture barrier layers comprised a PTFE film, as determined by py-GC–MS, and gave the highest individual nonvolatile (0.159 mg F/kg) and volatile PFAS (20.7 mg F/kg) as well as total fluorine (122,000 mg F/kg) concentrations. Outer and thermal layers comprised aromatic polyamide-based fibers (aramid) treated with side-chain fluoropolymers and had lower levels of individual nonvolatile and volatile PFASs. Equal concentrations of total fluorine by both PIGE and INAA on the outer and thermal layers is consistent with treatment with a side-chain fluoropolymer coating. New turnout gear should be examined as a potential source of firefighter occupational exposure to nonvolatile and volatile PFASs in future assessments.

KEYWORDS: firefighter turnout gear, side-chain fluoropolymer, PFAS, total fluorine, PTFE, meta- and para-aramid, pyrolysis-GC/MS



INTRODUCTION

Occupational exposure to harmful chemicals in the firefighting industry is an increasing concern among firefighters. Chemicals of concern include polycyclic aromatic hydrocarbons,¹ metals,¹ formaldehyde,² 1,3-butadiene,³ and per- and polyfluoroalkyl substances (PFASs).^{4–7} Elevated concentrations of PFASs are found in dust from fire stations^{8,9} and are detected in firefighter serum.^{6,10–13} Laitinen et al. suggested that used personal protective equipment (e.g., turnout gear) contaminated by aqueous film-forming foam as a possible source of firefighter exposure to PFASs,⁴ but exposure to PFASs imbedded in the turnout gear during manufacturing has not been examined. Another concern is the end-of-life treatment of turnout garments, as Chen et al. have extensively studied the disposal phase of PFAS-treated carpets and have suggested that PFASs could leach into the environment directly through air emissions or leachates in unlined landfills.¹⁴ Alternatively,

leaching of PFASs into the environment could occur indirectly by wastewater treatment plants in line landfills.¹⁴

Turnout gear is personal protective equipment worn by firefighters to minimize occupational exposure to hazardous conditions (heat, chemicals, radiation, etc.) during fire and training events. Turnout gear are complex, multilayer garments designed for performance under extreme thermal conditions. The outer (OU) layer provides resistance to heat, oil, and water and serves as an exoskeleton for the underlying layers. The moisture barrier (MB) layer is typically manufactured with the fluoropolymer polytetrafluoroethylene (PTFE) in order to

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obtain a desired water repellency. The thermal (TL) layer wicks moisture and is the closest to the skin.

New (unused) turnout gear has measurable PFASs. For example, Rewerts et al. found 6:2–10:2 fluorotelomer alcohols (FTOHs) on a single newly manufactured firefighter jacket,¹⁵ while Shinde and Ormond reported the tentative identification of 10:2 FTOH in the OU and MB layers of one turnout gear garment.¹⁶ Peaslee et al.¹⁷ reported nonvolatile PFASs for individual layers in new firefighter turnout gear after base-assisted extraction. To date, there are no systematic measurements of volatile PFASs, nor have the layers of turnout gear been characterized for their bulk chemical composition (e.g., fluoropolymer films).

Peaslee et al.¹⁷ also reported total fluorine by particle-induced gamma ray emission (PIGE), but the PIGE signals were off scale and thus total fluorine could not be quantified on the MB layer. Therefore, methods with a greater linear range, such as instrumental neutron activation analysis (INAA),^{32,33} are needed to quantify very high levels of total fluorine. To date, INAA is used to quantify trace-elements in textile dyes.^{18,19} The combination of PIGE and INAA can more completely describe the nature and location (e.g., disposition) of fluorine on turnout gear layers, since PIGE quantifies fluorine in the top 150–220 μm of textiles²⁰ and INAA interrogates the entire depth of the material.

We also propose a method to characterize the presence of fluoropolymer films in textiles. To the best of our knowledge, no attempts have been made to analytically distinguish between textile layers comprising fluoropolymer films (e.g., polytetrafluoroethylene or PTFE) from textile layers treated by industrial processes such as the application of side-chain fluoropolymers using a water-based fluoropolymer emulsion process.²¹ Pyrolysis-gas chromatography–mass spectrometry (py-GC/MS) is a conventional technique for the bulk characterization of polymers (e.g., synthetic) and natural fibers.^{22,23} Volatile compounds are generated by pyrolysis and analyzed by mass spectrometry, resulting in reproducible fingerprints^{24,25} that are visually compared to fingerprints in the literature or databases (e.g. NIST database) to infer the chemical nature of the polymer.²⁶ Matches are ranked by the similarity of mass spectral data (e.g., similarity indices or spectral contrast angles).²⁷ While pyrolysis products are tentatively assigned by this process, the overall polymer family cannot be identified. Newer algorithms rely on automatic comparison of py-GC/MS data with predefined peak lists generated from standards that are archetypical of a known polymer class.²⁸ Similarity indices are obtained from correlation coefficients.²⁷ To gain deeper insight into the chemistry of the textile sublayers, fluoropolymer (e.g., PTFE) films were differentiated from textile layers treated with side-chain fluoropolymers²¹ using py-GC/MS. Data analysis consisted of a set of mass spectra from the py-GC/MS profiles from samples and/or standards, which eliminates the need for a predefined list of characteristic peaks and correlation coefficients.

It is important to understand the disposition (e.g., location and arrangement) of fluorine when considering the firefighter exposure to PFASs, since the bioavailability and toxicity of fluoropolymers, side-chain fluoropolymers, and individual PFASs depend on their material properties and chemical structure. Although fluoropolymers were categorized as “polymers of low concern”,²⁹ Lohmann et al.³⁰ indicated that it is premature to discount the potential for fluoropolymers

(e.g., PTFE) to penetrate cell membranes based solely on their size. Side-chain fluoropolymers degrade slowly under environmental conditions, releasing individual PFASs.^{31–33} However, laundering,³⁴ weathering,³⁵ and the heat of fires may accelerate side-chain fluoropolymer degradation and, thus, exposure to individual PFASs. As for individual PFASs, they are bioavailable through water and diet, and US health advisory levels are available for PFOS and PFOA and many states have health advisory levels for other nonvolatile PFASs.³⁶

The objective of this study was to characterize the chemical composition, including individual PFASs, total fluorine, and polymers of the individual layers of three newly manufactured unused turnout garments purchased in 2019 and one unused garment purchased in 2008. For individual PFASs, 50 target nonvolatile and 15 target volatile PFASs were determined by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS) and gas chromatography–mass spectrometry (GC–MS), respectively. Total fluorine was measured by PIGE and INAA and used together with the bulk characterization of individual sublayers by py-GC/MS. A solution relying on the systematic evaluation of spectral contrast-angles³⁷ is also proposed for polymer identification by py-GC/MS.

EXPERIMENTAL METHODS

Standards and Reagents. Chemical and reagent source, purity, and acronyms for the 50 target nonvolatile PFASs, including perfluorocarboxylates (C4–C14 and C16); perfluorosulfonates (C3–10); Cl-PFOS; cyclic sulfonates (PF₆EtCH₂S); substituted sulfonamides (MeFOSA and EtFOSA); sulfonamide acetic acids (FOSAA, MeFOSAA, and EtFOSAA); x:2 telomer sulfonates (C4, 6, 8, and 10); saturated telomer acids x:2 (C6, 8, and 10); unsaturated telomer acids x:2 (C6 and 8); hexafluoropropylene oxide dimer acid (HFPO-DA); dodecafluoro-3H-4,8-dioxanone (ADONA); 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate and 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (9Cl-PF₃ONS and 11Cl-PF₃OUdS); bis(1H,1H,2H,2H-perfluorooctyl)phosphate and bis(1H,1H,2H,2H-perfluorodecyl)phosphate (6:2diPAP and 8:2diPAP); and bis-[2-(N-ethyleperfluorooctane-1-sulfonamido)ethyl] phosphate (diSamPAP) were purchased from Wellington Laboratories (Guelph, ON, Canada) and are listed in the Supporting Information (SI) (Table S1). In addition, 31 mass-labeled surrogate standards and two mass-labeled internal (instrumental) standards of PFOA and PFOS were used for quantification (Table S1).

Chemical source, purity, and acronyms for the 15 target volatile PFASs, including 4:2–10:2 fluorotelomer alcohols (FTOHs), N-methyl and -ethyl perfluorooctanesulfonamides (MeFOSA and EtFOSA, respectively), N-methyl and -ethyl perfluorooctane sulfonamido ethanolols (MeFOSE and EtFOSE, respectively), 8:2–10:2 fluorotelomer acrylates (FTAcS) purchased from Wellington Laboratories (Guelph, ON, Canada), and 12:2 FTOH, 4:2–6:2 FTAcS, and 6:2–8:2 fluorotelomer methylacrylates (FTMAcS) purchased from SynQuest Laboratories (Alachua, FL) are listed in the SI (Table S2). Ten mass-labeled internal standards (4:2, 6:2, 8:2, 10:2 FTOH, Et- and MeFOSA, and Me- and EtFOSE purchased from Wellington Laboratories (Guelph, ON, Canada), and 6:2 FTAc and 6:2 FTMAc purchased from Sapphire North America (Ann Arbor, MI)) were used to quantify the target analytes. A total of 24 additional suspect

Table 1. Firefighter Turnout Gear Suite Number (Year of Manufacture), Including Thermal Liner (TL), Moisture Barrier (MB), and Outer (OU) Layers, Total Nonvolatile and Volatile PFASs, Total Fluorine by either ¹PIGE or ²INAA, and Bulk Polymer Characterization of Sublayers by Py-GC/MS

	layer	nonvolatile PFAS (mg F/kg)	volatile PFAS (mg F/kg)	total fluorine (mg F/kg)	individual sublayers characterized by py-GC/MS
FF1 (2019)	TL ^a	0.00433	0.00827	18 ¹	unknown aramid ^g unknown aramid ^g unknown aramid ^g
	MB ^a	0.119	20.7	122,000 ²	PTFE meta-aramid
	OU ^{a,b}	0.0838 ± 0.117	0.899 ± 0.0911	4950 ²	unknown aramid ^g para-aramid
FF2 (2019)	TL ^{a,c}	0.0220	0.606	1430 ²	unknown aramid ^g unknown aramid ^g unknown aramid ^g
	MB ^{a,c}	0.159	18.8	120,000 ²	PTFE meta-aramid
	OU ^{b,d}	0.0247	0.340	2650 ²	unknown aramid ^g para-aramid
FF3 (2008)	TL ^e	0.0453	0.825	13 ²	unknown aramid ^g unknown aramid ^g unknown aramid ^g
	MB ^e	0.0569	4.33	116,000 ²	PTFE meta-aramid
	OU ^{e,b}	0.0218	3.26	2360 ²	para-aramid
FF4 (2019)	TL ^a	0.0248	0.233	17 ¹	unknown aramid ^g unknown aramid ^g unknown aramid ^g
	MB ^{a,c}	0.0438	0.671	43,700 ²	PTFE meta-aramid
	OU ^{b,f}	0.00993	10.9	5480 ²	unknown aramid ^g para-aramid

^aMeta-aramid. ^bPara-aramid. ^cPTFE. ^dPolybenzimidazole. ^eNo information available. ^fHigh-density carbon shell. ^gUnknown aramid fiber.

compounds were analyzed including 14:2 FTOH, C3–C7 methyl perfluoroalkane sulfonamido ethanol (MeFASes), C2–C7 ethyl perfluoroalkane sulfonamido ethanol (EtFASes), 4:2–10:2 fluorotelomer iodides (FTIs), C4, C6, C8, and C10 perfluoroalkyl iodides (PFIs), and 6:2–12:2 fluorotelomer olefins (FTOs) (Table S3). Pyrolysis-GC/MS utilized a PTFE standard (Scientific polymer Products Inc., Ontario, NY) and purchased samples of poly(*N,N*-(1,3-phenylene)isophthalamide) (Nomex, meta-aramid) and para phenylene terephthalamide (Kevlar, para-aramid) from Sigma-Aldrich, St Louis, MO.

Firefighter Turnout Gear. Four unused firefighter turnout pants were donated by the International Association of Fire Fighters (IAFF) and each was made by a different manufacturer (labeled in this study as FF1–FF4). Some information on the fabric composition was publicly available (Table 1). Manufacturing dates of the turnout pants were 2008 (one garment) and 2019 (three garments) (Table 1). Each garment was separated into OU, MB, and TL layers and then cut into 2 × 2 cm² and 1.5 × 1.5 cm² pieces using methanol-rinsed scissors for LC-qTOF and GC–MS analysis, respectively.

Extraction and Analysis of Nonvolatiles by LC-qTOF. Masses of each sample had a target weight of 0.30 (±0.01) g; 0.9 ng of each mass-labeled surrogate was spiked into all 15 mL polypropylene tubes prior to extraction and samples were subject to methanol extraction as adapted from Robel et al.³⁸ Adaptations included the addition of an extracted internal standard and a concentration step. After the final 10 mL of

extract is reached, 30 μL of ethylene glycol is added to each centrifuge tube and samples were concentrated under nitrogen to a final volume of 150 μL. Analysis consisted of a 50 μL aliquot of each extract into 150 μL conical vials and 0.30 ng of each mass-labeled internal standard was used to calculate recovery of the extracted mass-labeled surrogate. The separation and detection of nonvolatile PFASs were performed by liquid chromatography (Agilent 1260 HPLC) with a SCIEX 5500 qTOF interface with an electrospray ionization source that was operated in a negative-ion mode as previously described.³⁹ The gradient for both mobile phases is described in detail by Backe et al.,⁴⁰ while target PFAS identification and quantification are described by Schwichtenberg et al.³⁹ See the SI for additional details on whole method accuracy, precision, and LOD/LOQ (Tables S4 and S5). To compute total fluorine from individual PFAS concentrations, values that were <LOD or <LOQ were replaced with either 0 (for a minimum estimate) and for the maximum estimate, values <LOD were replaced with the measured LOD (Tables S4 and S6) and values <LOQ were replaced with the measured LOQ (Tables S4 and S6).

Extraction and Analysis of Volatiles by GC–MS. Masses of samples ranged from 0.035 to 0.070 g and were subjected to a methanol extraction, as modified from Rewerts et al.¹⁵ Samples were placed in 1.5 mL GC vials with methanol, spiked with internal standards, sonicated for 30 min at 25 °C, and then directly analyzed without any further cleanup. Analyses were performed by concurrent, solvent recondensation, large-volume splitless injection coupled with mass

spectrometry. Extracts (10 μL) were injected in splitless mode with an inlet temperature of 280 $^{\circ}\text{C}$. Separations were performed using an Agilent deactivated, fused silica tubing capillary column (5 m \times 0.53 mm i.d.) connected to a Restek Rxi-624Sil MS capillary column (30 m \times 0.25 mm i.d., 1.40 μm film thickness). Further description of GC parameters is provided in the SI along with additional details on whole method accuracy, precision, and LOD/LOQ (Table S6).

Total Fluorine Analysis by PIGE. Sample preparation for textiles was performed for PIGE as described in Ritter et al.⁴¹ Briefly, using methanol-rinsed scissors, 2 \times 2 cm^2 areas were cut from each layer of the firefighter turnout gear. Samples were mounted using clear adhesive tape onto a stainless-steel target frame with a 1 cm diameter hole for the ex vacuo ion beam analysis. Only one side from each layer was interrogated. For example, in the OU and TL layers, the exterior-facing sides were subject to the ion beam, whereas the inner-facing side of the MB was exposed to the ion beam. Total fluorine in ppm was determined from an external calibration curve using sodium fluoride standards prepared in cellulose nitrate mixtures. The concentration was converted into nmol F/ cm^2 based on the density of each sample. For each measurement, the total fluorine concentration measured by gamma rays was normalized to Ar gamma rays in the atmosphere.⁴² The calculated accuracy and precision does not apply to the MB layers due to the presence of PTFE in the layers, which resulted in total fluorine concentrations exceeding the calibration curve for PIGE analysis (>100,000 mg F/kg). Further discussion on the difficulty to measure total F in MB layers and conversion to nmol F/ cm^2 are provided in the SI.

Total Fluorine Analysis by INAA. To further characterize total fluorine content, this study utilized the thermal neutron reaction $^{19}\text{F}(\text{n},\gamma)^{20}\text{F}$ where the resultant product decays with a half-life of 11.03 s and emits a characteristic gamma ray at 1633.6 keV. Firefighter turnout gear samples were encapsulated in high density polyethylene (HDPE) NAA grade 2 dram vials (LA Plastics, Yorba Linda, CA) and weighed to the nearest 0.1 mg, with sample masses ranging from ca. 150–2000 mg, depending on anticipated F concentrations. Three replicates of CaF_2 (99.5%, Alfa Aesar, Haverhill, MA) were similarly encapsulated, with masses of ca. 25 mg each. Samples and standards were irradiated for 40 s at a thermal neutron flux of $10^{13} \text{ n} \cdot (\text{cm}^{-2} \cdot \text{s}^{-1})$, using the pneumatic tube facility at Oregon State University and then counted for 60 s using a 26% relative efficiency high purity germanium detector (ORTEC, Oak Ridge, TN) at a distance of 5 cm from the detector face. Sample quantification in ppm was based on the responses of the CaF_2 standards, using the weighted mean to convert activity to mass, and was converted to nmol F/ cm^2 . Additional details on whole method accuracy, precision, and LOD/LOQ are provided the SI.

Bulk Characterization by Py-GC/MS. The three layers of each firefighter turnout gear were manually separated into their individual respective sublayers (e.g., black film and white fabric and brown/black threads, Table S7). Separation of the three layers resulted in a total of 27 sublayers. The py-GC/MS workflow is depicted in Figure S1. Pyrolysis-GC/MS experiments were conducted using an EGA/PY-3030 pyrolyzer (Frontier Lab., Japan) and an Agilent 7890B GC with an Agilent HP-5 capillary column (30 m \times 0.25 mm, 0.15 μm film thickness). Pyrolysis-GC/MS profiles composed of 3480 scans were exported as netCDF files using the proprietary program msAxel (JEOL, Japan), which was also used for the control of

the instrument. The netCDF files were imported to the freeware Kendo (AIST, Japan) written with Visual Studio (Microsoft, USA) for the processing and visualization of mass spectral data.^{43,44} All the files were first thresholded at 1000 counts (average background signal from the detector before the py-GC/MS analysis) and “ CF_2 -filtered” scan-by-scan to extract any peak series spaced by 49.9968 (mass of a CF_2 moiety) \pm 0.003 Da, which was the tolerance chosen based on the dispersion of m/z values for the peak from hexamethylcyclotrisiloxane at m/z 207.0324 over 10 min of analysis.

The similarity of the extracted profiles compared with the py-GC/MS profile of a PTFE was evaluated by systematically computing a spectral contrast angle “theta”³⁷ between the mass spectra integrated over three scans for samples and the PTFE standard, which resulted in 1160 angles computed in total. The spectral contrast angle θ corresponds to the angle between the two mass spectra seen as vectors. The θ angle of two mass spectra with a similar peak list and similar relative abundance peak to peak tends to 0. Mass spectra with a θ angle $\leq 5^{\circ}$ were considered identical in the present study. The quantification of the degree of similarity/dissimilarity was then conducted using the spectral contrast angle method³⁷ for the summed mass spectra from three scans at a time for the FF sample and the PTFE standard (see the SI for more details). Consecutive sets of three scans and their summed mass spectra with a θ angle $< 5^{\circ}$ were further combined to get a reduced list of matching GC peaks between the FF sample and PTFE with no need for a predefined list of characteristic peaks. The same procedure was applied for the comparison of the remainder of py-GC/MS profiles after CF_2 -filtering with a meta-aramid standard.

RESULTS AND DISCUSSION

Target Nonvolatile PFASs. A total of 24 target individual nonvolatile PFASs from four classes were quantified on one or more firefighter turnout gear layers (Tables S8–S11). All three layers of the four turnout pants gave extensive perfluorocarboxylic acid (PFCA) homolog series, typically ranging from C4 up to C14, with C4–C10 as the most abundant (Table S8). The most frequently detected (100%) were PFBA (C4), PFHxA (C6), and PFHpA (C7) (Table S8 and Figure S2). While PFOS was detected in 11/12 layers, other perfluorosulfonic acids (PFSAs) (Table S9) and ECF- and fluorotelomer-derived PFASs were only infrequently detected (Tables S10 and S11). Exceptions included 6:2 FtS (5/12 layers), 6:2 diPAP (7/12 layers), and diSamPAP (4/12 layers) (Table S11). Total concentrations of nonvolatile PFASs were greatest in the MB, followed by TL and OU layers (Table 1). Concentrations for PFASs on textiles are reported in units of $\mu\text{g}/\text{m}^2$ ^{215,35,38,45} and ng/g ^{17,46,47} because a subset of prior literature reports these units for textiles. To convert from units of $\mu\text{g}/\text{m}^2$ to ng/g , the densities of each layer are provided in Table S8 along with an equation to convert between units (eq S4).

Peaslee et al. reported PFCA homolog series in firefighter turnout gear but at much higher concentrations (e.g., 805 ng/g PFOA).¹⁷ In contrast, the highest reported PFCA in the present study was for PFDoA in FF2-MB (61 ng/g ; Table S8) and was comparable to PFCA concentrations for other types of durable water-repellent clothing.³⁵ Durable water repellent clothing consists of outdoor jackets, skiwear, fisherman’s garments, military garments, and chemical production protective garments. The basic methanol extraction conditions employed by Peaslee et al. most likely have resulted in higher

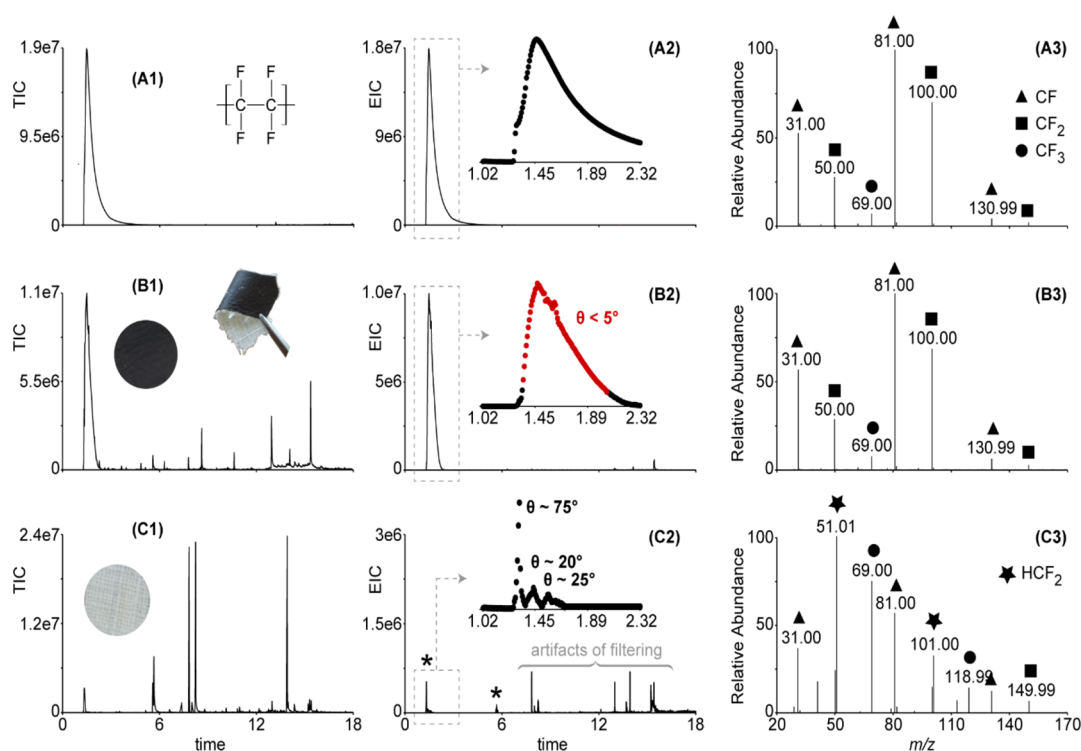


Figure 1. Py-GC/MS chromatograms (A1), after filtering for $-(CF)_2$ series (A2), and the sum the mass spectrum for the PTFE standard (A3); the black sublayer of the MB for FF1 (B1–B3); and the white sublayer of the MB for FF1 (C1–C3). Insets in A2 and B2 show magnification of the py-GC/MS profiles (1.02–2.32 min). Red dots indicate scans with a spectral contrast angle $\theta < 5^\circ$, which indicates a high similarity with the PTFE standard.

observed PFCA and PFSA concentrations. Methanol is recognized as not being exhaustive in the extraction of individual PFASs from side-chain fluoropolymers.^{33,48} Solvents such as tetrahydrofuran or methyl *tert*-butyl ether are more appropriate for exhaustive extraction of side-chain fluoropolymers. However, as a weaker extraction solvent, methanol may preferentially extract loosely bound, and potentially more bioavailable PFASs from the surfaces of polymers and materials coated in side-chain fluoropolymers.

Target Volatile PFASs. Nine target volatile PFASs including 6:2, 8:2, 10:2, and 12:2 FTOH, Me- and Et-FOSE, 8:2 and 10:2 FTAc, and 6:2 FTMac were quantified in at least one turnout gear layer (Tables S12 and S13). The total concentrations of volatile PFASs were higher than the nonvolatile PFASs in all layers (Table 1), and concentrations were the greatest in the MB, followed by OU and TL layers (Table 1). Longer-chain FTOHs including 8:2, 10:2, and 12:2 FTOH and Me- and Et-FOSE were only measured in FF3, which was an older suit from 2008 when C8 chemistry was still in use (Tables S12 and S13). Pants from 2019 (FF-1,2, and 4) only gave 6:2 FTOH (Table S12), which may reflect the change from C8 to C6-based PFAS chemistry.⁴⁹ In addition, 6:2 FTMac, which is a side-chain polymer intermediate,^{50,51} was found at the highest frequency (100%). The 8:2 and 10:2 FTAc were in FF4, which indicates the use of long-chain chemistry, despite FF-4 being manufactured in 2019 (Table S13). Deng et al. previously demonstrated the use of 6:2 FTMac to impart superhydrophobicity to fabric.⁵² van der Veen et al. also reported 6:2 FTMac and 6:2–10:2 FTOHs on other types of durable water-repellent clothing.³⁵

Of the 24 volatile suspects, only MeFBSE was detected in only FF1- and FF2-MB (Table S12). The identity of MeFBSE

was confirmed from injection of a mixture of standards provided by 3M. MeFBSE was first reported in a 1988 upholstery material¹⁵ but the identity was not confirmed. The chemical is structurally similar to a chemical released from a manufacturing plant in Alabama,⁵³ [(*N,N*-bis(2-hydroxyethyl)]perfluorobutanesulfonamide (FBSEE), which is an intermediate in PFAS production. There are currently no known toxicity data for MeFBSE, though 3M announced it would conduct toxicity analysis of FBSEE and FBSE.⁵⁴ The extracts were analyzed in full scan PCI mode to determine the presence of any secondary FTOHs (sFTOHs),³¹ but none were detected.

Total Fluorine. Both PIGE and INAA gave high total fluorine in all four MB layers (Table S14). However, PIGE values for the MBs were off scale ($>100,000$ mg F/kg), while INAA gave values ranging from 43,700 to 122,000 mg F/kg (Table 1). Total fluorine by PIGE for MBs was not reported by Peaslee et al. since the levels were too high¹⁷ and were attributed to the fluoropolymer (e.g., PTFE).

All four OU layers gave the next highest levels of total fluorine (Tables 1 and S14), but were a factor of 10 lower than those reported by Peaslee et al.¹⁷ However, total fluorine for the OU layers were similar to that of Schellenberger et al. who used a padding process to apply side-chain fluoropolymers to textiles.³⁴ Of three turnout gear layers, TL layers gave the lowest levels of total fluorine (Tables 1 and S14). The TL layers from FF1, FF3, and FF4 (Table 1) had $<LOD$ or lower (e.g., ≤ 32 mg F/kg) fluorine levels by either total fluorine technique (Table S14). The total fluorine of FF2-TL was in the same order of magnitude of the total fluorine in FF2-OU, which indicates that the TL layer of FF2 was likely treated with fluorine. Publicly available information indicated that FF2-TL

was treated with PTFE (Table 1). Visual inspection of FF2-TL sublayers following py-GC/MS analysis did not indicate a PTFE sublayer, but indicated the presence of a different type of fluorinated treatment. Low levels of total fluorine and individual nonvolatile and volatile PFASs on the TL layers in FF1, 3, and 4 are unlikely to be the result of deliberate treatment to impart water and oil repellency and may be the result of processing textile within a facility that regularly applies fluorinated coatings. Alternatively, migration of PFASs between layers is proposed by Peaslee et al.¹⁷ Overall, the summed molar concentrations of individual PFASs only made up a small fraction of total fluorine where minimum contributions ranged from 0.0016 to 6.3% (Table 1), whereas the maximum contributions ranged from 0.0018 to 6.4% (data not shown).

Bulk Characterization by Py-GC/MS. The py-GC/MS profile of a PTFE standard displayed an early broad chromatographic peak (Figure 1A1), which, when “CF₂-filtered”, gave a simpler total ion chromatogram with only the early eluting peak remaining (Figure 1A2). The filtered chromatographic peak gave an associated average mass spectrum displaying (CF₂)_nCF⁺• (31, 81, and 131 *m/z*), (CF₂)_n⁺• (50, 100, and 150 *m/z*), and (CF₂)_nCF₃⁺• (69, 119, and 169 *m/z*) ion series archetypical of perfluorinated chains (Figure 1A3).²² All four MBs were comprised of two layers, one of which gave a broad chromatographic peak as illustrated by the black sublayer of FF1-MB (Figure 1B1). When this sublayer was “CF₂-filtered”, a single chromatographic peak was obtained (Figure 1B2), which matched with the chromatogram of the PTFE standard (Figure 1A1,A2). Similarly, the comparison of the average mass spectrum of the black sublayer of FF1-MB (Figure 1B3) matched with that of the PTFE standard (Figure 1A3). Therefore, the py-GC/MS analysis confirmed the presence of the PTFE sublayer in the MB layers, as suggested by publicly available information (Table 1) and the high amount of total fluorine observed in this study (Tables 1 and S14) and in the previous study by Peaslee et al.¹⁷

While the black sublayer closely matched the PTFE profile, the white sublayer of the FF1-MB layer (Figure 1C1) did not give an early chromatographic peak (Figure 1C2) that was characteristic of the PTFE standard (Figure 1A1). The CF₂-filtered chromatogram only showed very small peaks (Figure 1C2 and inset) and the spectral contrast angle was greater than 20%. However, this sublayer showed a high similarity for six major GC peaks of the meta-aramid standard with spectral contrast angles $\theta < 5^\circ$ (Figure 2A1,A2) for their corresponding mass spectra. The meta-aramid standard did not show evidence of fluorine, which was consistent with the chemical structure of meta-aramid (Figure 2A2).

Analyses by py-GC–MS of TL and OU layers gave a poor match with PTFE and meta-aramid but gave high similarities with a para-aramid standard with seven major GC peaks and spectral contrast angles $\theta < 5^\circ$ (Figure 2B1,B2 and Figure S8) for four of the seven of the TL sublayers. The para-aramid standard did not show evidence of fluorine but was consistent with the chemical structure of para-aramid (Figure 2B2). Three of the seven TL and all OU sublayers did not have a good match with either meta- or para-aramid (Figure S10A,B) and was attributed to an unknown type of aramid (Table 1). In addition to confirmation of meta- and para-aramid profiles, extraction of $-(CF_2)_n-$ series from the py-GC/MS chromatograms of the OU (Figures S7 and S8) and TL sublayers

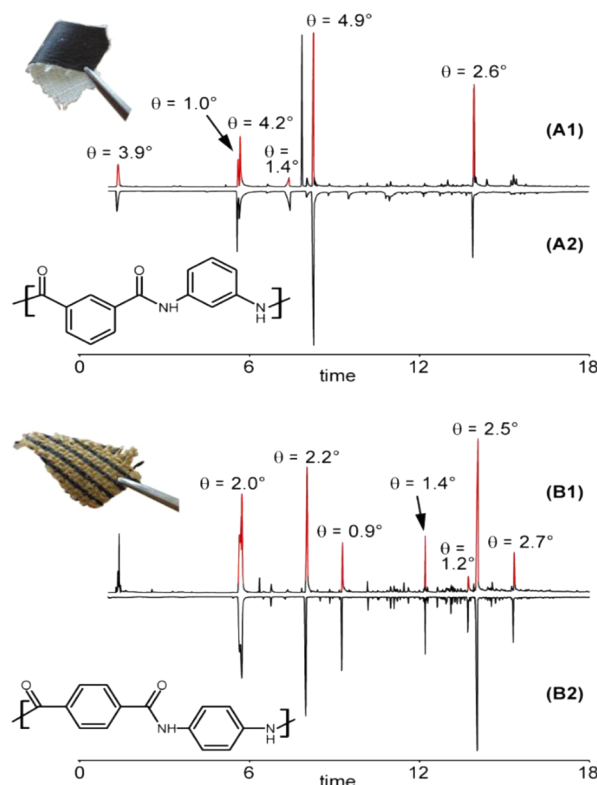


Figure 2. Py-GC/MS total ion chromatogram of the FF1-MB white fabric (black line) (A1) with the TIC profile of the meta-aramid standard (A2) and the FF1-OU black yarn (B1) with the TIC profile of the para-aramid standard (B2) with their respective spectral contrast angles, θ , which refers to the mass spectra rather than the chromatographic peaks.

(Figures S9 and S10) showed traces of non-PTFE compounds with $-(CF_2)_n-$ series in their EI mass spectra as indicated with * in Figure 1C2. These peaks were considered to be nonpolymeric PFASs (Figure S7 and S9B), which was consistent with nonvolatile and volatile PFAS results (Table 1). Additional details with py-GC/MS chromatograms and mass spectra are included in the SI (Figures S3–S5).

The analysis of samples by py-GC/MS with the computation of similarities vs the py-GC/MS profiles of standards at the GC and MS levels using spectral contrast angles provided rapid identification of fluoropolymers and nonfluorinated polymers. The method currently implemented in Kendo^{43,44} allows a specific moiety (e.g., CF₂) to be searched in order to extract simplified profiles out of complex raw data sets.⁴⁴ Multiple py-GC/MS profiles of standards were combined to compare the resulting profile with unknown samples for the simultaneous identification of different fluoropolymers.

Disposition of Fluorine. While others have speculated on the presence of fluoropolymer films or side-chain fluoropolymers,^{21,38,55,56} the present study offers multiple lines of converging chemical evidence along with direct measurements by py-GC/MS that identifies and differentiates fluoropolymer films and side-chain fluoropolymers. Using a hierarchy of chemical characterization tools, the disposition of fluorine on firefighter turnout gear was categorized into three main groups: fluoropolymer (e.g., PTFE) films, side-chain fluoropolymers, and individual residual PFASs. The highest contribution of total fluorine and individual volatile PFAS concentrations is attributed to the PTFE film on the MBs, as identified by py-

GC/MS (Table 1). Pure PTFE should give a theoretical total fluorine concentration of 760,000 mg F/kg (eq S1). However, the total F concentrations on the MBs (43,700–122,000 mg F/kg) are all significantly lower than the theoretical value. If one assumes that the meta-aramid sublayer of the MB has a total fluorine concentration (5000 mg F/kg) similar to the OU layers (see FF1 and 4; Table 1), only ~15% of the total weight of the MB is PTFE (eq S2). Selection of 5000 mg F/kg is consistent with Schellenberger et al. who used a padding process to apply side-chain fluoropolymers to aramid-based fibers and achieved a mean total fluorine concentration of 4500 mg F/kg.³⁴ Thus, the fluorine of the PTFE film is diluted by the meta-aramid sublayers. The observed total fluorine on the treated para- and meta-aramid sublayers (Table 1) is consistent with the expected weight % F (0.04–0.25 wt % F) coverage imparted by the padding process.⁵⁷

Side-chain fluoropolymers were likely added to the meta- and para-aramid sublayers in the MB, OU, and one TL sample (FF2). Because meta- and para-aramid are not inherently fluorinated, it is likely that the water-based “padding process” described in Holmquist et al.²¹ was used to impart a fluorinated coating. Schellenberger et al.³⁴ also used the padding process to apply side-chain fluoropolymers onto fibers with an estimated thickness of 0.3 μm . Fluorinated side chains are bonded via an ester linkage to a nonfluorinated polymeric backbone⁵⁸ and are typically based on FTOHs or polyfluoroalkyl sulfonamidoethanols.²¹ Quantification of n:2 FTOHs and N-methyl- and -ethyl-polyfluoroalkyl sulfonamidoethanols (Tables S12 and S13), which are used to make side-chain fluoropolymer monomers, which include the fluorotelomer acrylate and methacrylates (Table S13), are consistent with the chemistry associated with the padding process^{21,59} and the synthesis of fluorotelomer-based side-chain fluoropolymers.⁵⁹ Sulfonamido-based acrylates and methacrylates were not measured in the present study but could be investigated in future studies as confirmation. The volatile PFASs detected in firefighter turnout gear may be due to incomplete synthesis or lack of purification.^{30,59}

Individual PFASs (both nonvolatile and volatile) comprise a minor fraction of total fluorine, with some exceptions (the untreated TLs of FF1, 3, and 4). There are no apparent correlations between nonvolatile and total F, volatile and nonvolatile, or volatile and total F. However, there is a distinctly higher concentration of volatile PFASs associated with the MBs that contain PTFE. Thus, individual PFASs are not active ingredients in these textile treatment processes but are likely byproducts of incomplete reactions when synthesizing side-chain fluoropolymer monomers. Historically, side-chain fluoropolymer dispersions were allowed to be sold with up to 2% by weight of monomers per dry mass of polymer.⁶⁰ When side-chain fluoropolymer suspensions are applied and dried to textiles, loss of the residual PFASs and incomplete polymerizations typically result in residual monomers, smaller “polymers,” and oligomers.³⁰ Alternatively, cross-contamination during textile finishing processes could be the source of individual PFASs in textiles.²¹ Because these are new turnout gear garments, the individual PFASs cannot be attributed to degradation or environmental degradation reactions. Although PFOA have been substituted in polymer production for the ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA),³⁰ the substituted reagent is not detected in firefighter turnout pants herein (Table S11). Perfluoropolyether carboxylic acids (PFECAs) are another known

substitute for PFNA in polymer production³⁰ but were not included in this study. Moreover, ammonium 4,8-dioxo-3H-perfluorononanoate (ADONA) is used as a PFECA processing aid and was not detected in firefighter turnout gear either (Table S11). Although nontarget PFAS analysis was not performed, such analysis could reveal additional compounds of concern, such as flame retardants and plasticizers^{61,62} or newer polymerization aids. For example, Luo et al.⁶³ identified nonylphenol ethoxylates and octylphenol ethoxylates in cotton and polyester textiles.

If the layers of FF turnout gear are treated with side-chain fluorinated polymers based on ester linkages to a nonfluorinated polymeric backbone, then treatment with base-assisted extraction could result in elevated concentrations of individual PFASs reported in Peaslee et al.¹⁷ For this reason, the higher individual PFAS concentrations reported by Peaslee et al. may represent the long-term oxidation of the nonvolatile PFAS concentrations rather than immediately accessible concentrations on new turnout gear. Furthermore, within the European union, regulations of PFOS in textiles should not exceed concentrations above 1 $\mu\text{g}/\text{m}^2$ of the coated material.⁵⁷ The only sample which had measured concentrations of PFOS above 1 $\mu\text{g}/\text{m}^2$ is the MB of FF1 and 4, while the remaining samples range from 0.18 to 1 $\mu\text{g}/\text{m}^2$.

Implications. A formal exposure assessment was beyond the scope of this study because we currently lack relevant parameters (e.g., partition coefficients) that could be used to characterize thermodynamic driving force, which is necessary to predict the rate of migration and therefore the dose associated with wearing firefighter turnout gear. For this reason, it is not yet possible to determine if the turnout gear is a significant source of occupational exposure to PFASs for firefighters. However, migration of impregnated chemicals from fabrics to skin is well established,^{64–66} but not for PFASs, so further investigation of exposure is needed.

Dermal absorption of PFASs should be studied for not only PFCAs⁶⁷ but also other PFASs and especially volatile PFASs, particularly because concentrations of volatile PFASs were significantly higher than nonvolatile PFASs on the firefighter turnout gear. However, data gaps on dermal loading and absorptive flux must be filled before dermal exposure to PFASs from turnout gear can be reliably estimated. For a limited set of relatively lipid-soluble, semivolatile organic compounds, vapor uptake through skin may be comparable to, or exceed, inhalation exposure.^{68,69} However, the relative importance of vapor uptake and inhalation has not been determined for semivolatile PFASs. Clothing can be an important mediating factor in dermal exposure. Clean clothing, even if gas permeable, can be at least initially protective through sorption of organic vapors, but may promote dermal absorption once that clothing becomes contaminated,^{70,71} due to the enhanced mass transfer of the contaminant mass held close to the skin, suppression of volatilization, and warming of the skin. Fabric layers of turnout gear that are treated with side-chain fluoropolymers and individual PFASs may present the opportunity for elevated dermal exposure. Incidental ingestion of dust is another exposure route that should be considered for firefighters from turnout gear and dust in firehouses.⁷²

Release of PFASs in durable water-repellant clothing due to heat, UV, and moisture needs to be assessed. van der Veen et al.³⁵ measured textile degradation under UV light in textiles, but the effect of heat and moisture is currently unknown. The impact of burning/high temperatures on firefighter turnout

gear has previously been performed,⁷³ but not yet in the context of PFASs. The effect of laundering on side-chain fluoropolymers and individual PFASs found in firefighter turnout gear should be analyzed as well. Mayer et al. in 2019 showed the impacts of laundering on removal of external contaminants such as flame retardants and PAHs from firefighter turnout gear.⁷⁴ Side-chain fluoropolymers associated with individual fibers are released during washing, as demonstrated in the case of outdoor jackets.³⁴ However, no information is available on the fate of PFASs, side-chain fluoropolymers, and PTFE associated with firefighter turnout gear as a result of laundering; therefore, further research is warranted. Firefighter turnout gear is recommended to be replaced after being worn for a period of 10 years.⁷⁵ Thus, firefighter turnout gear has potential to release and to act as a long-term source of individual PFASs to the environment upon disposal to landfills.³⁴ Degradation of fluoropolymer films and side-chain fluoropolymers under landfill conditions has not been investigated either and is another research gap to be fulfilled.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c06322>.

Analytical method description; results of analytical performance for LC, GC, PIGE, and INAA; list of target nonvolatile and volatile PFAS analytes; list of suspect volatile PFAS analytes; whole method precision; nonvolatile PFAS surrogate standard recovery on blank, matrix blank, samples, and matrix spike; sublayers from FF layers and the amount analyzed by py-GC/MS; target PFCA, suflonate (PFS), miscellaneous electro-fluorination (ECF) PFAS, and miscellaneous telomer PFAS concentrations; target and suspect FTOHs, Me- and Et-FOSA, MeFASE, EtFASEs, FTAcS, and FTMAcS concentrations; total fluorine concentrations by PIGE and INAA; workflow schematic for comparison by spectral contrast angles of pyGC/MS analysis; frequency of detection for nonvolatile and volatile PFASs in all firefighter turnout gear pants; similarity between the py-GC/MS profiles of a sample and a standard by spectral contrast angle; $-(CF_2)_n-$ extracted profile; mass spectrum; remainders of $-(CF_2)_n-$ extracted profiles; theoretical PTFE film concentration calculation; fraction of the PTFE film on the MB layer; total weight percent of F on non-PTFE layers; and conversion from $\mu\text{g}/\text{m}^2$ to ng/g (PDF)

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Notes

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