

## Supporting Information

### Additional Detailed Introduction:

Roth et al. (2020) investigated the occurrence of PFAS in the headspace above mildly agitated and dilute AFFF mixtures and found that 16 of the 30 measured PFAS were present: five FTOHs (0.5–38.1  $\mu\text{g}/\text{m}^3$ ), 10 PFCAs (0.4–13670  $\mu\text{g}/\text{m}^3$ ), and 1 FTS (72.1  $\mu\text{g}/\text{m}^3$ ). Measurements were made with TD samplers in combination with GC/MS and LC/MS/MS in combination with XAD resin/polyurethane foam (XAD/PUF) samplers. The 10 PFCAs detected ranged in carbon chain length from C<sub>5</sub> to C<sub>16</sub>. The dominant compounds were PFOA, PFHxA, and perfluorodecanoic acid (PFDA). The retention time and prominent fragment ions at m/z 69, 119, 131 and 169 matched well with the PFOA standard and fragmentation reported by Yamada et al. (2005). However, those ions are common to many compounds with a perfluoroalkyl chain.

In a subsequent comment on the Roth et al. (2020) publication, it was noted that PFOA appeared to thermally degrade to form perfluoro-1-heptene (PFHp-1) when PFOA was injected onto thermal desorption tubes and desorbed to a GC/MS, making it difficult to differentiate between PFHp-1 and other thermally labile PFAS such as PFOA (Titaley et al., 2020). Upon closer inspection of the experimental and published spectra of PFOA and PFHp-1, Roth et al. noted several inconsistencies between the expected and observed spectra, including the lack/presence of a m/z 44 (loss of CO<sub>2</sub>) and lack/presence of a m/z 45 (loss of COOH) present in the NIST published standard mass spectrum but not in other published GC/MS spectra. Thus, it is possible that the “PFOA-like peak” observed by GC/MS was aerosolized or volatilized PFOA (which was known to be present in the AFFF tested), but it is also possible that the single GC peak represents PFHp-1 and/or the sum of various thermally labile PFAS (Roth et al., 2020;

Titaley et al, 2020). This uncertainty about the volatility of the PFCAs motivates the current paper.

PFCAs are generally considered to be predominantly partitioned to the particulate phase in the atmosphere (ITRC, 2022). Since PFCAs are primarily ionic at environmentally relevant pH, in aqueous solution their volatility was initially expected to be low (ITRC, 2022). However multiple mechanisms for the PFCAs to enter the gas phase have been suggested: foam bubble bursting (Johansson et al., 2019); cosolvent effects on pKa (Bastow et al., 2022); and direct sublimation from the solid phase to the gas phase (Kaiser, 2010). However, Johansson et al. (2019) reported that PFCAs can be introduced into the atmosphere through bubble bursting. The formation of foams *in situ* in the presence of aqueous solutions of surfactants and gas flows has been previously reported, so a bubble bursting mechanism could conceivably be relevant to VI (Maire and Fatin-Rouge, 2017; Bertin et al., 2017). Additionally, Bastow et al. (2022) described how the equilibrium between ionized and neutral forms can be shifted toward the neutral PFAS, enhancing volatilization, when organic phases make up a significant component of the matrix (i.e., cosolvent effects). Gas phase PFHpA, PFHxA, and PFOA at concentrations below 2.5 ng/m<sup>3</sup> have been reported in indoor air at background sites (Shoeib et al., 2011). Additionally, Kaiser et al. (2010) measured sublimation (direct transition from solid phase to gas phase) of PFOA at 45°C. This work was done in both bench-scale measurements and at larger scale in a drying out sump in a manufacturing facility, in which, they measured 7 µg/m<sup>3</sup> PFOA in the air near an aqueous sump at pH 7, attributed primarily to sublimation from the walls of the sump. Detectable levels of PFOA were also observed in a weeklong bench scale studies being transported in gas phase nitrogen partitioned against a pH 7 PFOA solution in a round bottom flask.

In more recent research, the University of Nevada measured the Henry's law constants (HLCs) of 15 PFAS, but PFOA was not volatile enough to be measured until the pH was reduced substantially, suggesting PFOA is not volatile when dissolved in water at circumneutral pH, although cosolvent effects were not evaluated (Abusallout et al., 2022). Efforts by others to validate the COSMOtherm model for prediction of PFAS HLCs suggest that PFOA is relatively nonvolatile. However, this model and the experiments used to validate it considered the air/water interface an experimental artifact and worked to negate its effects (i.e., HLCs were obtained by dividing hexadecane:water partitioning coefficients by hexadecane:air coefficients, thus the air/water interface was avoided or not represented) (Endo et al., 2023). The air/water interface in soil systems is extensive and complex due to varying saturations in the capillary fringe and attributable to water table fluctuation (Sakaki et al., 2013). Together, these studies suggest that in the experiments conducted by Roth et al. (2020), where PFOA was measured in the gas phase, PFOA was aerosolized during the mild agitation of the AFFF or ejected as aerosols during popping of the AFFF bubbles immediately before the gas phase was collected, rather than present as a vapor. cosolvent effects may also explain the presence of gas phase PFOA.

#### Additional Methods Information

Initial calibration standards were prepared using purchased methanolic stock standards, where available, ranging from 2 to 100 µg/mL from Wellington Laboratories, Accustandard, and/or Cambridge Isotope Laboratories. The 12:2 FTOH material was purchased as a solid from Synquest Laboratories, and a stock standard prepared by weighing an amount into a class A volumetric flask, diluting to volume with methanol, and sonicating for 30 minutes. Table S6 lists the typical primary and secondary stock standards purchased for calibration used during the validation tests.

A multi-point initial calibration curve was generated by spiking CAMSCO PFAS/PFCA multi-bed sorbent tubes with 2.0  $\mu\text{L}$  of a 0.5  $\mu\text{g}/\text{mL}$  methanolic solution of 2-perfluorohexyl[1,1- $^2\text{H}_2$ ]-[1,2- $^{13}\text{C}_2$ ]ethanol as the internal standard (IS) and 2-Perfluorooctyl[1,2- $^{13}\text{C}_2$ ]ethanol as the field surrogate. Following the IS and surrogate addition, methanolic working standards containing the list of target PFAS were spiked onto tubes using aliquots from the working methanolic standards ranging from 1.0 to 4.0  $\mu\text{L}$  to generate a six-point calibration curve spanning from 0.1 ng to 10 ng with an internal standard and field surrogate concentration of 1.0 ng. Standards were spiked onto the sorbent tubes using an unheated injection port with a flow of ultra-pure nitrogen at a rate of 80 mL/min for 3 to 5 min to flush methanol from the sorbent tube prior to analysis.

The initial calibration linearity was evaluated following the procedure outlined in EPA Method TO-17, calculating the Relative Response Factor (RRF) at each calibration level, and determining the average RRF and the Relative Standard Deviation (RSD) across all the levels and evaluating against the TO-17 acceptance criterion of <30% RSD. Representative stock standards used during the laboratory validation studies can be found in Supporting Information Table S6.

Accuracy of the initial calibration curve was determined by spiking a methanolic working standard prepared from a second source. This initial calibration verification (ICV) standard was prepared in the same manner as a calibration standard with the addition of the internal standard and field surrogate. Independent sources of stock standards were not available for 5:2s FTOH, 7:2s FTOH, and 12:2 FTOH. For these targets, a second standard was independently prepared by a different chemist and/or using a second ampule purchased from the same vendor.

To comply with regulatory and TO-17 method requirements, Method Detection Limit (MDL) studies were conducted following CFR Appendix B Part 136 Revision 2. A minimum of seven spiked sorbent tubes and seven blank sorbent tubes were analyzed in three separate analytical batches over three days with a minimum of two spikes and two blanks analyzed on each day. The spikes were prepared by spiking methanolic working standards at 0.1 ng for each target compound following the procedures used for calibration standards. Blanks were prepared by spiking conditioned sorbent tubes with IS and surrogate only. The method MDL for each target compound was determined by evaluating both blank and spike samples.

#### Approach to Tentatively Identify Compounds without Calibration Standards

Calibration standards were not available for the 9:2s, 11:2s, and 13:2s fluorotelomer alcohols. In the absence of calibration standards and full scan EI spectra in the literature, the laboratory developed an approach to tentatively identify these compounds based on data generated for a calibrated list of fluorotelomer alcohols. The retention time for the uncalibrated secondary alcohols was based on the observation that 5:2s FTOH and 7:2s FTOH eluted at a similar retention time as 4:2 and 6:2 FTOH, respectively, on the TD-GC/MS system using the Agilent DB-624 UI 60 m x 0.25 mm ID x 1.4  $\mu\text{m}$  column and associated GC temperature program (Figure S2). Assuming similar behavior with increasing chain length and utilizing a consistent GC temperature ramp rate across the elution of the target compounds, retention time windows for 9:2s, 11:2s, and 13:2s FTOH were set up consistent with the corresponding calibrated 8:2, 10:2, and 12:2 FTOHs, respectively.

Reviewing the MRM transitions used for quantitation of the calibrated secondary FTOHs, the precursor mass ion for 7:2s FTOH exhibited a predictable increase of  $m/z$  100 ( $\text{C}_2\text{F}_4$ ) relative to 5:2s FTOH, reflecting the additional two perfluorinated carbons in the 7:2s FTOH structure.

The MRM transitions added to the instrument acquisition program and expected time segment assume a precursor mass ion that increases by  $m/z$  100 for each  $C_2F_4$  increase in the structure. To estimate a Relative Response Factor (RRF) for the tentatively identified compounds, the RRFs were evaluated for the representative 5:2s and 7:2s FTOH MRM transition. The RRF for 7:2s FTOH was consistently approximately twice that of 5:2s FTOH; however, extrapolating this relationship to the uncalibrated longer chain secondary FTOHs based on two points was not warranted, thus we used the RRF of 7:2s FTOH to estimate the uncalibrated secondary alcohols.

**Table S1. PFAS Compounds Assessed**

CAS	Short Name	Compound Class	Compound	Standard Commercially Available?	Initial Analytical Method Completed Prior to US EPA, 2023 and Schumacher et al., 2023
2043-47-2	4:2 FTOH	FTOH	2-Perfluorobutyl ethanol	Yes, at least two sources	Yes
914637-05-1	5:2 sFTOH	sFTOH	1-Perfluoropentyl ethanol	Available from single source	Yes
647-42-7	6:2 FTOH	FTOH	2-Perfluorohexyl ethanol	Yes, at least two sources	Yes
24015-83-6	7:2 sFTOH	sFTOH	1-Perfluoroheptyl ethanol	Available from single source	Yes
678-39-7	8:2 FTOH	FTOH	2-Perfluorooctyl ethanol	Yes, at least two sources	Yes
--	9:2 sFTOH	sFTOH	1-Perfluorononyl ethanol	No standard found to date, none available in Yoo et al. (2010)	No
865-86-1	10:2 FTOH	FTOH	2-Perfluorodecyl ethanol	Yes, at least two sources	Yes
--	11:2 sFTOH	sFTOH	1-Perfluoroundecyl ethanol	No standard found to date; none available in Yoo et al. (2010)	No
39239-77-5	12:2 FTOH	FTOH	2-Perfluorododecyl ethanol	Available from single source	No
--	13:2 sFTOH	sFTOH	1-Perfluorotridecyl ethanol	No standard found to date; none available in Yoo et al. (2010)	No
335-67-1	PFOA	PFCA	Perfluorooctanoic acid	Yes, at least two sources	Yes
4151-50-2	N-EtFOSA	FOSA	n-Ethylperfluoro-1-octansulfonamide	Yes, at least two sources	Yes
31506-32-8	N-MeFOSA	FOSA	n-Methylperfluoro-1-octanesulfonamide	Yes, at least two sources	Yes
375-22-4	PFBA	PFCA	Perfluorobutanoic acid	Yes, at least two sources	Yes
375-85-9	PFHpA	PFCA	Perfluoroheptanoic acid	Yes, at least two	Yes

CAS	Short Name	Compound Class	Compound	Standard Commercially Available?	Initial Analytical Method Completed Prior to US EPA, 2023 and Schumacher et al., 2023
				sources	
307-24-4	PFHxA	PFCA	Perfluorohexanoic acid	Yes, at least two sources	Yes
2706-90-3	PFPeA	PFCA	Perfluoropentanoic acid	Yes, at least two sources	Yes

Note: FOSA = perfluorooctanesulfonamide; FTOH = fluorotelomer alcohols; sFTOH = secondary fluorotelomer alcohol; PFCA = perfluorocarboxylic acid



**Table S2. Initial TO-17 PFAS Method Parameters utilized for soil gas analysis in field studies reported by RTI (2022) and Schumacher et al. (2023).**

Gerstel Thermal Desorption (3.5+) Settings	
Transfer Temperature	300°C
Transfer Temperature Mode	Fixed
Desorption Mode:	Splitless
Sample Mode:	Remove Tube – no Standby Cooling
Standby Temperature:	50°C
Dry Purge:	Not used
Tube Desorption Temperature Program	
Initial Temperature	50°C
Delay Time	0.5 min
Initial Time	0.00 min
Ramp 1 – Rate 1	400°C/min
End Temperature	300°C
Hold time	5.0 min
CIS Focusing Trap	
Carrier Gas	Helium
Initial Temperature	-130°C
Equilibration Time	0.25min
Initial Time	0.00 min
Ramp 1: Rate:	12°C/min
End Temp:	275°C
Hold Time:	4.00min
Trap type:	Quartz wool deactivated (PN012437)
Agilent 8890 GC parameters	
Column	DB-624 Ultra Inert 60m x 0.25mm ID x 1.4 µm
Flow	1 mL/min
Control mode	Constant Flow
Initial Temperature	40°C Hold Time = 3 min
Ramp	15°C/min
Final Temperature	230°C Hold for 4.34 minutes
Front PTV Inlet	Helium
Mode	Solvent Vent
Purge Flow to Split Vent	5 to 10 mL/min at 0.01 min (Low split) 200 mL/min at 0.01 (High split)
Vent Flow	50 mL/min
Agilent 7000D Tandem Mass Spectrometer	
MSD Transfer Line	250°C
Quench Gas He	2.5 mL/min
Collision Gas N2	1.5 mL/min
Source Temperature	250°C

**Table S3. Initial TO-17 analytical performance using Table 1 method parameters used for soil gas analysis (RTI, 2022; Schumacher et al., 2023)**

High sensitivity method (low split) calibration range = 0.05 ng to 5.0 ng

Low sensitivity method (high split) calibration range = 1.0 to 60 PFCAs, 1.0 ng to 500 ng FTOH

Analyte	High Sensitivity Method		Low Sensitivity Method		%DE <sup>d</sup>
	Linearity (%RSD)	ICV (%R)	Linearity (%RSD)	ICV (%R)	
PFBA	10	112	17	116	100
PFPeA	13	126	14	134	100
PFHxA	13	115	17	122	100
PFHpA	11	103	5.4	119	100
PFOA	6.5	90	20	88	100
4:2 FTOH	6.7	94	8.8	78	100
5:2s FTOH	5.8	104	7.6	82	99.8
6:2 FTOH	21 <sup>a</sup>	73	14	81	99.6
7:2s FTOH	8.4	105	9.3	81	99.9
8:2 FTOH	21	72	10	76	99.5
10:2 FTOH	21	73	9.6	78	99.4
n-MeFOSA	27 <sup>b</sup>	43	32 <sup>c</sup>	89	100
n-EtFOSA	24 <sup>b</sup>	48	24 <sup>c</sup>	87	100

a. Low calibration level = 0.1 ng

b. Low calibration level = 0.6 ng (4-point calibration)

c. Low calibration level = 5.0 ng (4-point calibration); high calibration level = 60 ng

d. Desorption efficiency evaluated at 60 ng for PFCAs and n-MeFOSA and n-EtFOSA and at 500 ng for FTOHs.

**Table S4. Modified TO-17 PFAS Vapor Phase Compound Reporting Limits and QC Acceptance Criteria.**

Analytes	Reporting Limit (ng total per sample tube)	Acceptance Criteria		
		ICAL <sup>†</sup> (%RSD)	LCS (% R)	CCV (%D)
2-Perfluorobutyl ethanol (4:2 FTOH)	0.10	≤30	60-140	30
2-Perfluorohexyl ethanol (6:2 FTOH)	0.20	≤ 30	60-140	30
1-Perfluoroheptyl ethanol (7:2 FTOH)	0.10	≤ 30	60-140	30
2-Perfluorooctyl ethanol (8:2 FTOH)	0.10	≤ 30	60-140	30
2-Perfluorodecyl ethanol (10:2 FTOH)	0.10	≤ 30	60-140	30
Perfluorobutanoic acid (PFBA)	0.40	≤ 30	60-140	40
Perfluoropentanoic acid (PFPeA)	0.10	≤ 30	60-140	40
Perfluoroheptanoic acid (PFHpA)	0.10	≤ 30	60-140	40
Perfluorohexanoic acid (PFHxA)	0.10	≤ 30	60-140	40
Perfluorooctanoic acid (PFOA)	0.10	≤ 30	60-140	40
n-Methylperfluoro-1-octanesulfonamide (N-MeFOSA)*	1.0	≤ 40	50-150	50
n-Ethylperfluoro-1-octanesulfonamide (N-EtFOSA)*	1.0	≤ 40	50-150	50
<b>Internal Standards (IS)</b>				
<b>Analyte</b>	<b>CCV IS % Recovery</b>		<b>Sample IS % Recovery</b>	
2-Perfluorohexyl[1,1-2H2]-[1,2-13C2]ethanol	60 – 140		60 – 140	

\*Data were qualified as estimated due to the variability in observed recovery.

†ICAL = Initial Calibration, LCS = Laboratory Control Sample, CCV = Continuing Calibration Verification, %D = % Difference, %R = % Recovery, %RSD = % Relative Standard Deviation

**Table S5. Instrument parameters for method validation (Gerstel TD 3.5+ and Markes TD100-xr)**

<b>(Gerstel 3.5+) Thermal Desorption Settings</b>	
Transfer Temperature	300°C
Transfer Temperature Mode	Fixed
Desorption Mode:	Splitless
Sample Mode:	Remove Tube – no Standby Cooling
Standby Temperature:	50°C
Dry Purge:	Not used
<b>Tube Desorption Temperature Program</b>	
Initial Temperature	50°C
Delay Time	0.5 min
Initial Time	0.00 min
Ramp 1 – Rate 1	400°C/min
End Temperature	320°C
Hold time	10.0 min
<b>CIS Focusing Trap</b>	
Carrier Gas	Helium
Initial Temperature	-150°C
Equilibration Time	0.25 min
Initial Time	0.00 min
Ramp 1: Rate:	12°C/min
End Temp:	275°C
Hold Time:	4.00 min
Trap type:	Quartz wool deactivated
<b>Agilent 8890 GC parameters</b>	
Column	DB-624 Ultra Inert 60m x 0.25mm ID x 1.4 µm
Flow	1 mL/min
Control mode	Constant Flow
Initial Temperature	40°C Hold Time = 3 min
Ramp	15°C/min
Final Temperature	230°C Hold for 4.34 minutes
Front PTV Inlet Mode	Solvent vent
PTV Total Flow	On 6 mL/min
Purge Flow to Split Vent	5 mL/min at 0.01 min
Vent Flow	50 mL/min
<b>Agilent 7000D Tandem Mass Spectrometer</b>	
MSD Transfer Line	250°C
Quench Gas He	2.5 mL/min
Collision Gas N2	1.5 mL/min
Source Temperature	250°C

<b>Markes TD100-xr</b>	
Carrier gas	Helium
Flow path temperature	150°C
Dry purge time	3 min
Dry purge flow	40 mL/min
Desorb 1 time	10 min
Desorb 1 temperature	320°C
Desorb 1 trap flow	50 mL/min
Trap purge time	1 min
Trap purge flow	20 mL/min
Trap Low Temperature	20°C
Trap heat rate	MAX
Trap high temperature	290°C
Trap desorb time	3 min
Trap desorb split flow	5 mL/min
Focusing Trap	U-T12ME-2S
<b>Agilent 8890 GC parameters</b>	
Column	DB-624 Ultra Inert 60 m x 0.25 mm ID x 1.4 µm
Flow	1 mL/min
Control mode	Constant Flow
Initial Temperature	40°C Hold Time = 3 min
Ramp	15°C/min
Final Temperature	230°C Hold for 4.34 minutes
Back Inlet Mode	Splitless
Heater	On 150°C
Septum purge flow	On 0.5 mL/min
<b>Agilent 7000D Tandem Mass Spectrometer</b>	
MSD Transfer Line	250°C
Quench Gas He	2.5 mL/min
Collision Gas N2	1.5 mL/min
Source Temperature	250°C

**Table S6. Representative Stock standards utilized for Laboratory Validation Studies**

CAS	Compound	Vendors	Stock Solution Concentration in MeOH ( $\mu\text{g/mL}$ )	Chemical Purity
2043-47-2	2-Perfluorobutyl ethanol (4:2 FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
		Accustandard	$98.6 \pm 2.4$	$\geq 98\%$
914637-05-1	1-Perfluoropentyl ethanol (5:2s FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
647-42-7	2-Perfluorohexyl ethanol (6:2 FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
		Accustandard	$100.4 \pm 2.4$	99.0
24015-83-6	1-Perfluoroheptyl ethanol (7:2s FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
678-39-7	2-Perfluorooctyl ethanol (8:2 FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
		Accustandard	$101.1 \pm 2.4$	94.0
865-86-1	2-Perfluorodecyl ethanol (10:2 FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%
		Cambridge Isotope Laboratories, Inc.	$50.0 \pm 0.5$	98.4%
39239-77-5	2-Perfluorododecyl ethanol (12:2 FTOH)	Synquest Laboratories	Solid	82%
4151-50-2	n-Ethylperfluoro-1-octanesulfonamide (n-EtFOSA)	Cambridge Isotope Laboratories, Inc.	$100.0 \pm 1.2$	94%
		Accustandard	$101.8 \pm 2.4$	97.1%
31506-32-8	n-Methylperfluoro-1-octanesulfonamide (n-MeFOSA)	Cambridge Isotope Laboratories, Inc.	$100.0 \pm 0.3$	98%
		Accustandard	$101.1 \pm 2.4$	96.1
375-22-4	Perfluorobutanoic acid (PFBA)	Wellington Laboratories	$2.00 \pm 0.1$	>98%
		Accustandard	$101.9 \pm 2.4$	100%
375-85-9	Perfluoroheptanoic acid (PFHpA)	Wellington Laboratories	$2.00 \pm 0.1$	>98%
		Accustandard	$103.0 \pm 2.4$	97.0%
307-24-4	Perfluorohexanoic acid (PFHxA)	Wellington Laboratories	$2.00 \pm 0.1$	>98%
		Accustandard	$101.4 \pm 2.4$	100%
2706-90-3	Perfluoropentanoic acid (PFPeA)	Wellington Laboratories	$2.00 \pm 0.1$	>98%

CAS	Compound	Vendors	Stock Solution Concentration in MeOH ( $\mu\text{g/mL}$ )	Chemical Purity
		Accustandard	$100.6 \pm 2.4$	99.0%
335-67-1	Perfluorooctanoic acid (PFOA)	Wellington Laboratories	$2.00 \pm 0.1$	>98%
		Accustandard	$101.8 \pm 2.4$	100%
NA	2-Perfluorohexyl-[1,1- $^2\text{H}_2$ ]-[1,2- $^{13}\text{C}_2$ ]-ethanol	Wellington Laboratories	$50.0 \pm 2.5$	>98%
NA	2-Perfluorooctyl (1,2- $^{13}\text{C}_2$ ) ethanol ( $^{13}\text{C}_2$ -8:2 FTOH)	Wellington Laboratories	$50.0 \pm 2.5$	>98%

**Table S7. Experiment 3 Test Matrix**

Column	PFOA		PFHp-1	
	Direct Inject	Thermal Desorption	Direct Inject	Thermal Desorption
Agilent HP-5MS (SVOC) 30 m x 0.25 mm x 0.2 $\mu\text{m}$ <i>40°C for 3 min, 15°C/min to 230°C</i>	1.0 $\mu\text{L}$ aliquot; Injection port temp @ 280°C	1.0 $\mu\text{L}$ aliquot on sorbent tube; Desorb @ 320°C for 10 min	1.0 $\mu\text{L}$ aliquot; Injection port temp @ 280°C	1.0 $\mu\text{L}$ aliquot on sorbent tube; Desorb @ 320°C for 10 min
Agilent DB-624 UI (VOC) 60 m x 0.25 mm x 1.4 $\mu\text{m}$ <i>40°C for 3 min, 15°C/min to 230°C</i>	1.0 $\mu\text{L}$ aliquot; Injection port temp @ 280°C	1.0 $\mu\text{L}$ aliquot on sorbent tube; Desorb @ 320°C for 10 min	1.0 $\mu\text{L}$ aliquot; Injection port temp @ 280°C	1.0 $\mu\text{L}$ aliquot on sorbent tube; Desorb @ 320°C for 10 min

**Table S8. MRM transitions for PFAS Identification**

Compound	Precursor	Product
PFBA	150	100
	150	69
	100	69
PFPeA	200	131
	200	69
PFHxA	250	131
	180	131
	250	69
PFHpA	300	131
	231	181
	300	69
PFOA	350	131
	231	181
	350	69
4:2 FTOH	244	127
	95	69
	196	77
	263	195
5:2s FTOH	299	69
	219	69
	313	43
7:2s FTOH	399	69
	319	69
	355	86
	319	131
6:2 FTOH	344	127
	295	69
	295	231
	363	295
Isotopically labelled 6:2FTOH (2-Perfluorohexyl-[1,1- <sup>2</sup> H <sub>2</sub> ]-[1,2- <sup>13</sup> C <sub>2</sub> ]-ethanol)	348	129
	96	69
2-Perfluorooctyl (1,2- <sup>13</sup> C <sub>2</sub> ) ethanol (13C2-8:2 FTOH)	446	128
	407	69
	446	96
	465	396
8:2 FTOH	444	127
	395	95
	463	395
	395	131
10:2 FTOH	544	127
	505	119
	505	169
	563	495
12:2 FTOH	605	69
	595	69
	663	595
	644	127



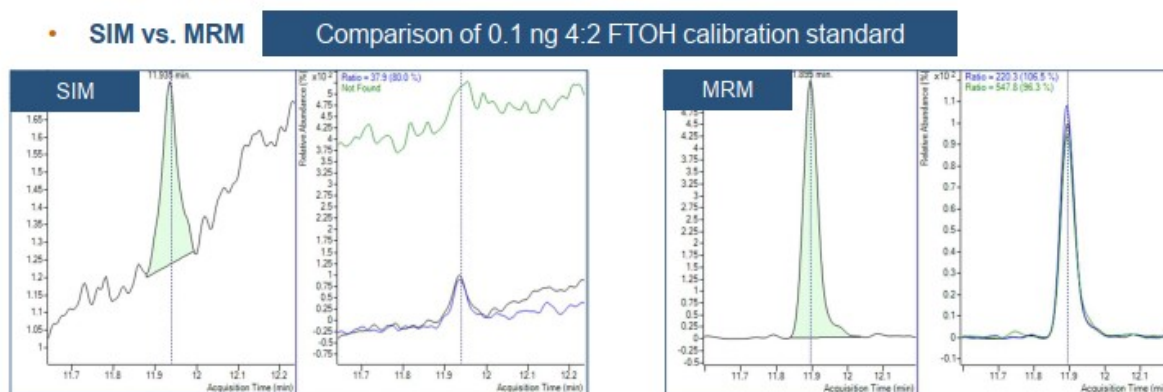
Compound	Precursor	Product
n-MeFOSA	448	69
	131	69
n-EtFOSA	448	69
	108	80
	219	69

**Table S9. IDOC Performance Comparison on Gerstel and Markes**

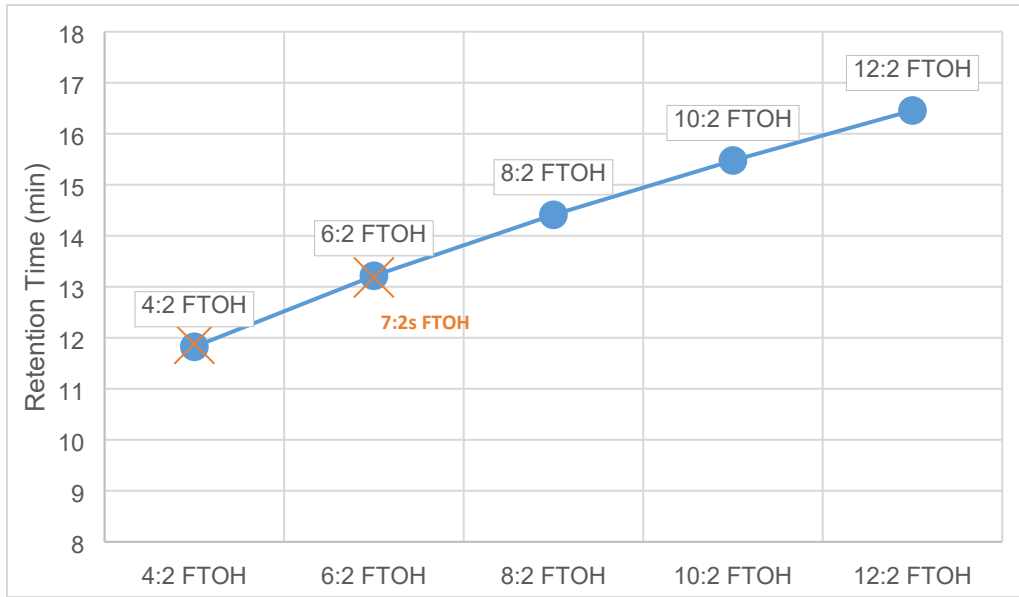
Analyte	Gerstel 3.5+		Markes TD100-xr	
	Average Recovery	Relative Standard Deviation	Average Recovery	Relative Standard Deviation
4:2 FTOH	97%	4.1%	96%	9.5%
5:2s FTOH*	112%	1.6%	93%	7.6%
6:2 FTOH	110%	3.3%	92%	5.9%
7:2s FTOH*	127%	10%	91%	7.5%
8:2 FTOH	109%	20%	100%	3.9%
10:2 FTOH	104%	17%	78%	8.8%
12:2 FTOH**	110%	13%	76%	9.3%
N-MeFOSA	103%	20%	95%	8.2%
N-EtFOSA	104%	19%	95%	9.7%

\*Second source stock standards not commercially available. Same lot number provided by vendor, prepared using different ampoules.

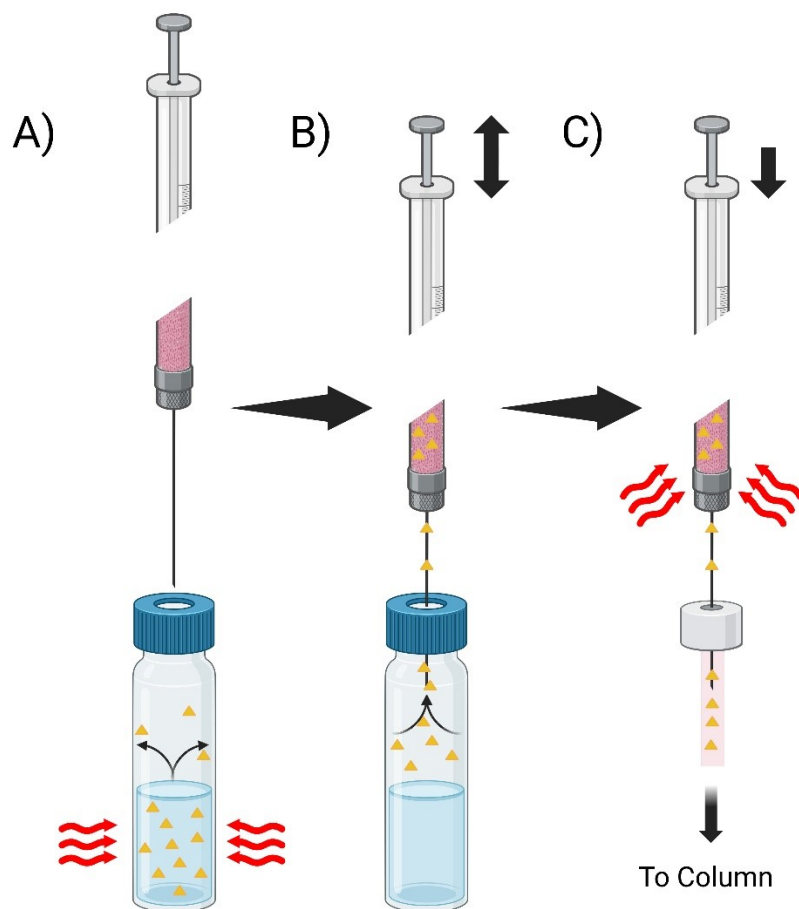
\*\*Second source not available; independently prepared from neat material.



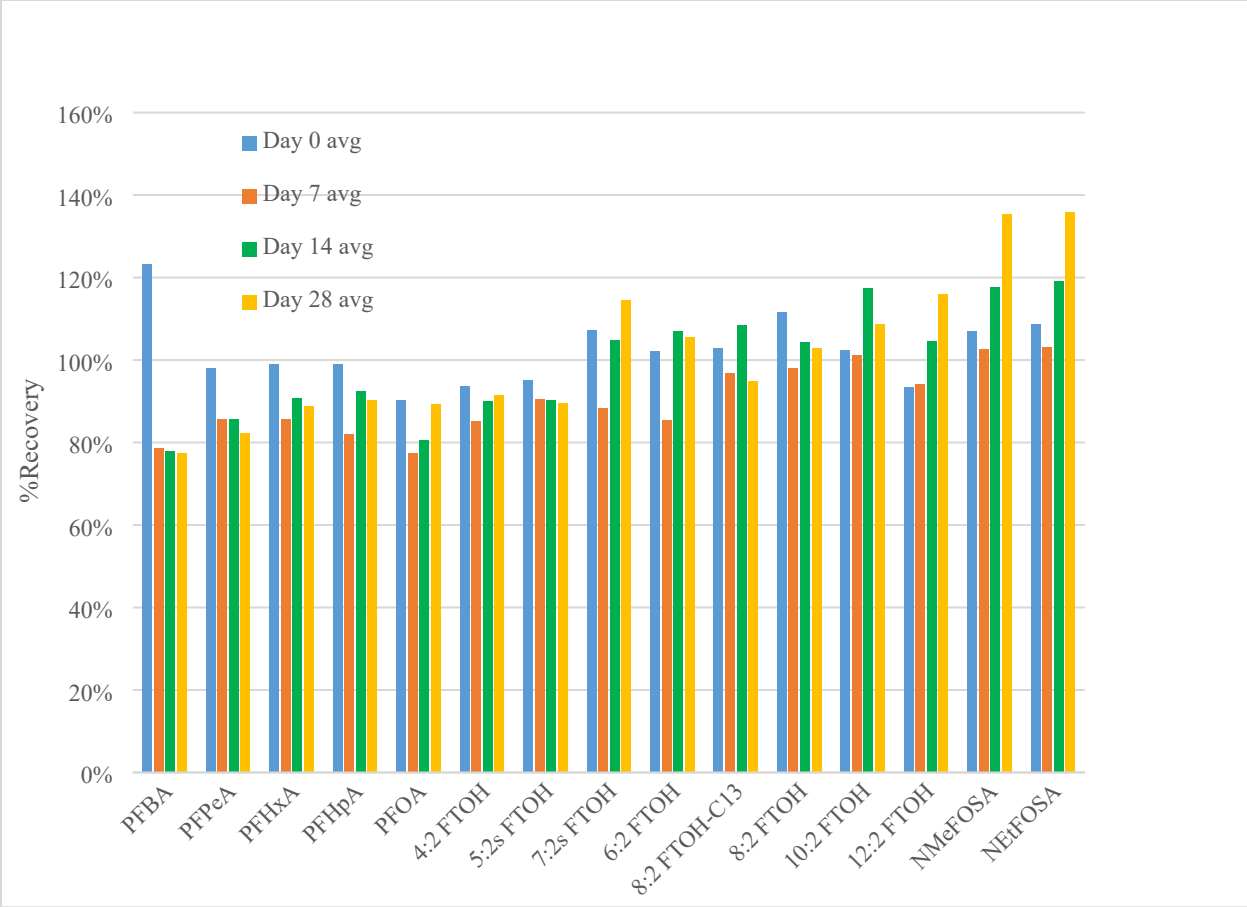
**Figure S1. Sensitivity Benefit of MRM (MS/MS) shown in right panels over Selected Ion Monitoring (SIM) with SQ MS shown in left two panels**



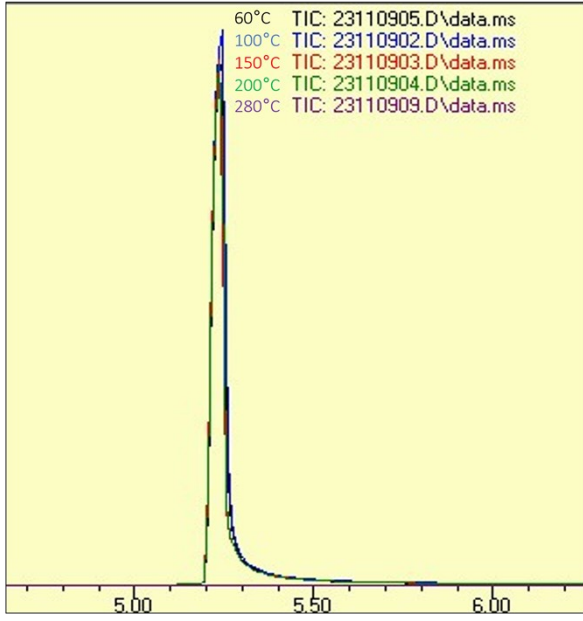
**Figure S2. Retention Time Relationship between Calibrated Secondary and Linear FTOH.**



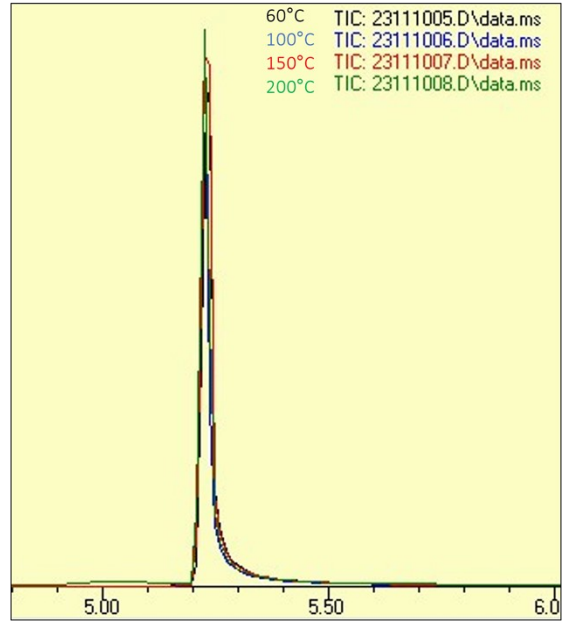
**Figure S3: Process of Typical ITEX-DHS Injection.** Note that in experiments conducted in this research, the sample was solid phase PFOA without a solvent. **A)** sample vial is heated and agitated to partition analytes into the headspace. **B)** headspace is drawn over the sorbent a specified number of times to sorb analytes. **C)** sorbent is flash heated to desorb analytes into a specified volume of headspace and the mixture injected directly into the GC inlet.



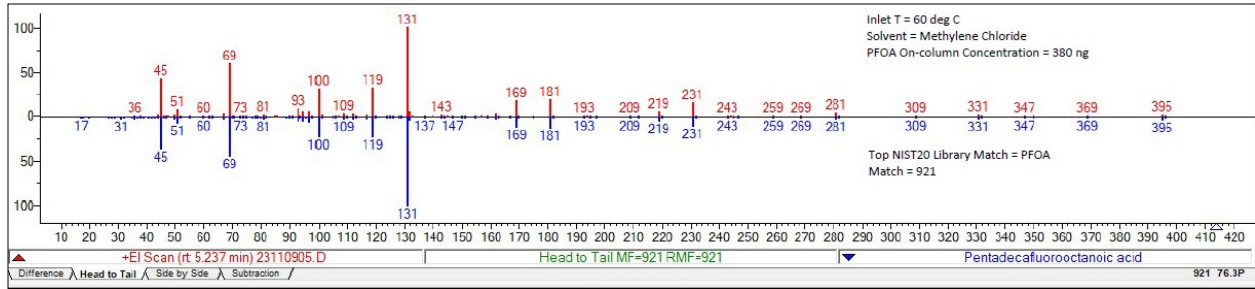
**Figure S4. Storage Stability Test Results – Each bar represents the average recovery of a set of three tubes; colors represent holding times as per key.**



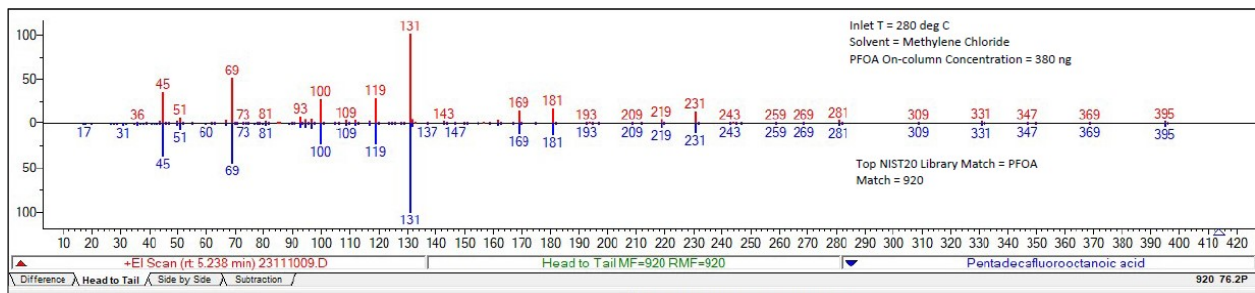
**Figure S5a. Experiment 1: Total Ion Chromatograms of Direct Injections of PFOA in Dichloromethane across GC Inlet Temperatures of 60°C to 280°C**



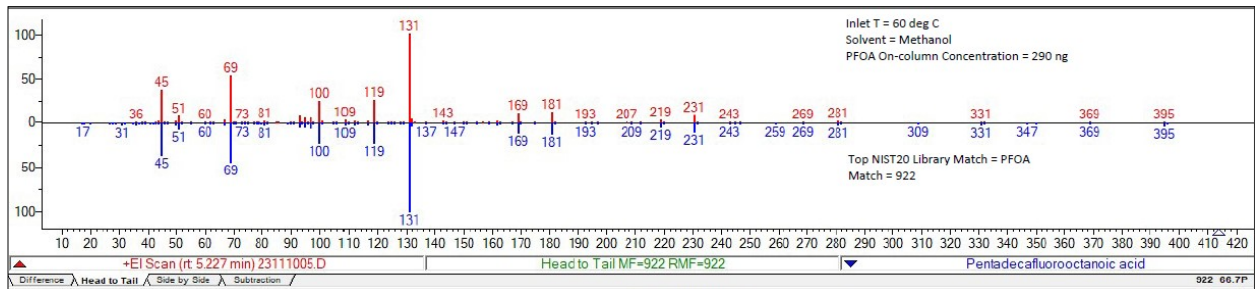
**Figure S5b. Experiment 1: Total Ion Chromatograms of Direct Injections of PFOA in Methanol across GC Inlet Temperatures of 60°C to 280°C**



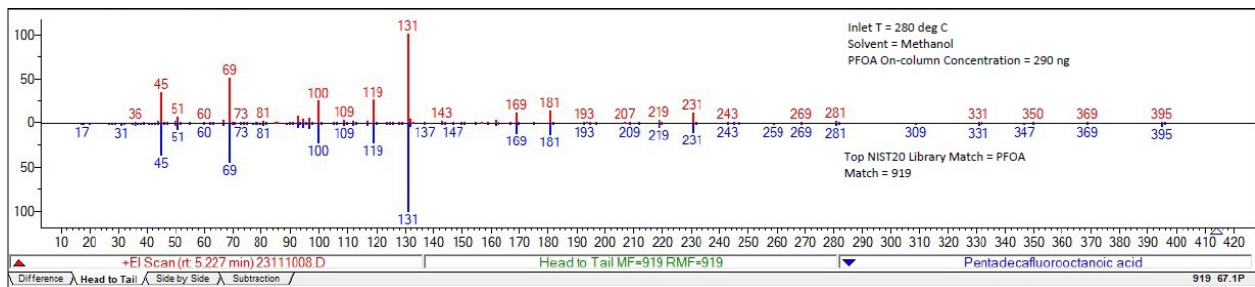
**Figure S6a. Experiment 1 PFOA Spectra 60°C Inlet Temperature (5700 µg/mL in Dichloromethane) – Red Is Experimental Data and Blue Is the NIST Library Match Spectra**



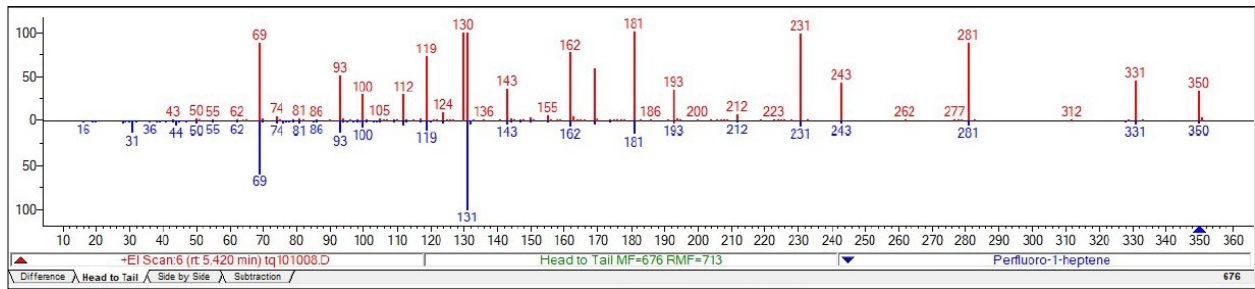
**Figure S6b. Experiment 1 PFOA Spectra 280°C Inlet Temperature (5700 µg/mL in Dichloromethane)**



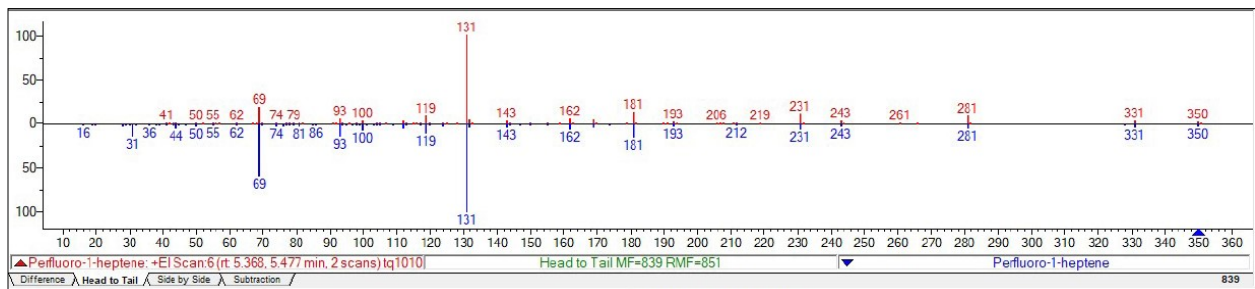
**Figure S6c. Experiment 1 PFOA Spectra 60°C Inlet Temperature (4300 µg/mL in Methanol)**



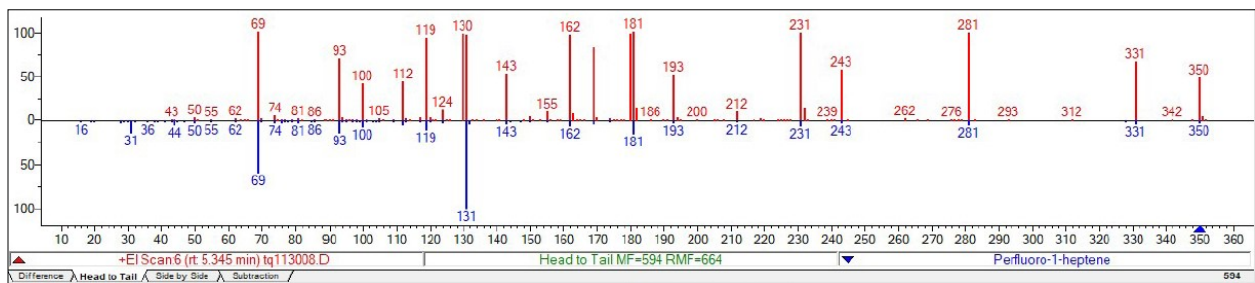
**Figure S6d. Experiment 1 PFOA Spectra 280°C Inlet Temperature (4300 µg/mL in Methanol)**



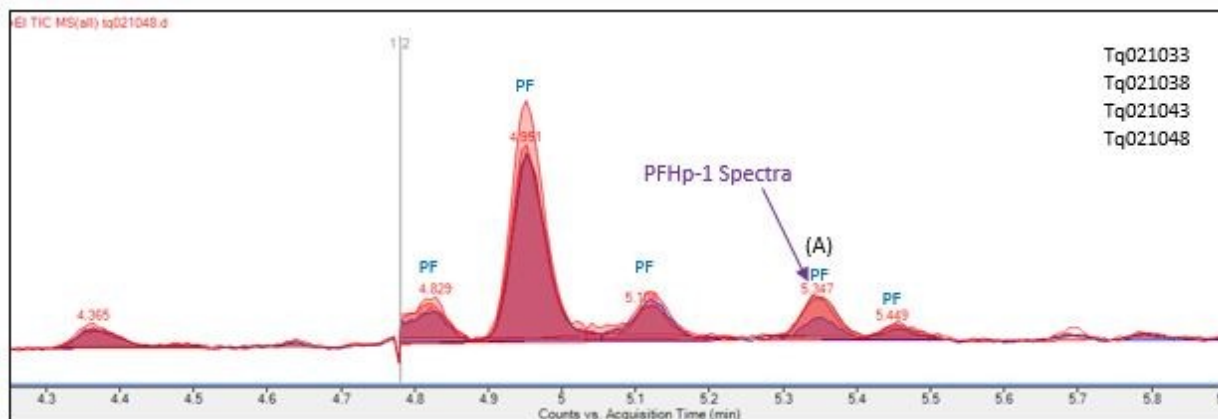
**Figure S7a. Experiment 2: Thermal Desorption Peak (A) Apex Mass Spectrum. Red Is Experimental Data and Blue Is the Library Match Spectra.**



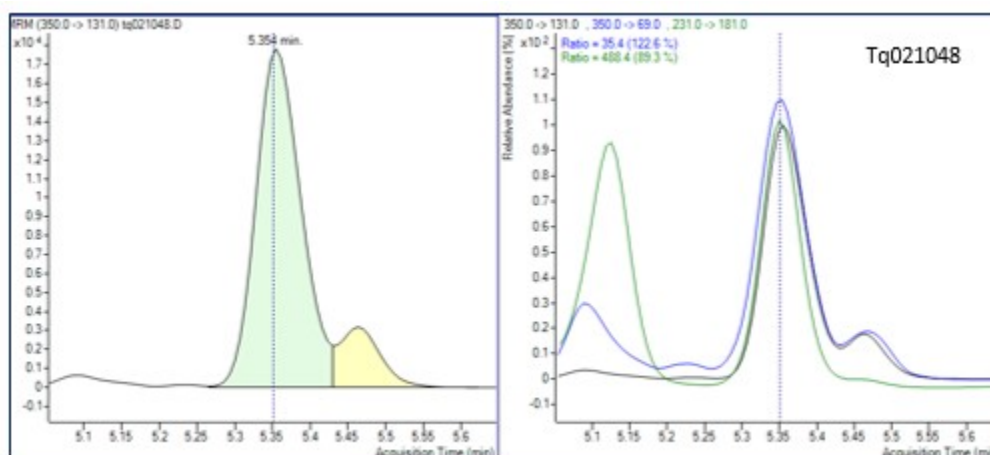
**Figure S7b. Experiment 2 Thermal Desorption Peak (A) Left and Right Shoulder of Peak Mass Spectra.**



**Figure S8. Experiment 2: Saturated Peak (A) Mass Spectra (Apex) With 250°C Tube/Trap Desorption Temperature**



**Figure S9. Total Ion Chromatogram Overlay of 4 Replicate 100 ng PFHp-1 spiked tubes analyzed by TD-GC/MS/MS**



**Figure S10. MRM data for representative 100 ng PFHp-1 Spiked Tube by TD-GC/MS/MS**

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