

**Supporting Information**

**Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams (AFFF) Used by  
the US Military**

*Benjamin J. Place<sup>1</sup> and Jennifer A. Field<sup>2\*</sup>*

<sup>1</sup> Department of Chemistry, Oregon State University, Corvallis, OR

<sup>2</sup> Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis,  
OR

\*Corresponding Author Information:

1007 ALS Building

Oregon State University

Corvallis, OR 97331

Email: Jennifer.Field@oregonstate.edu

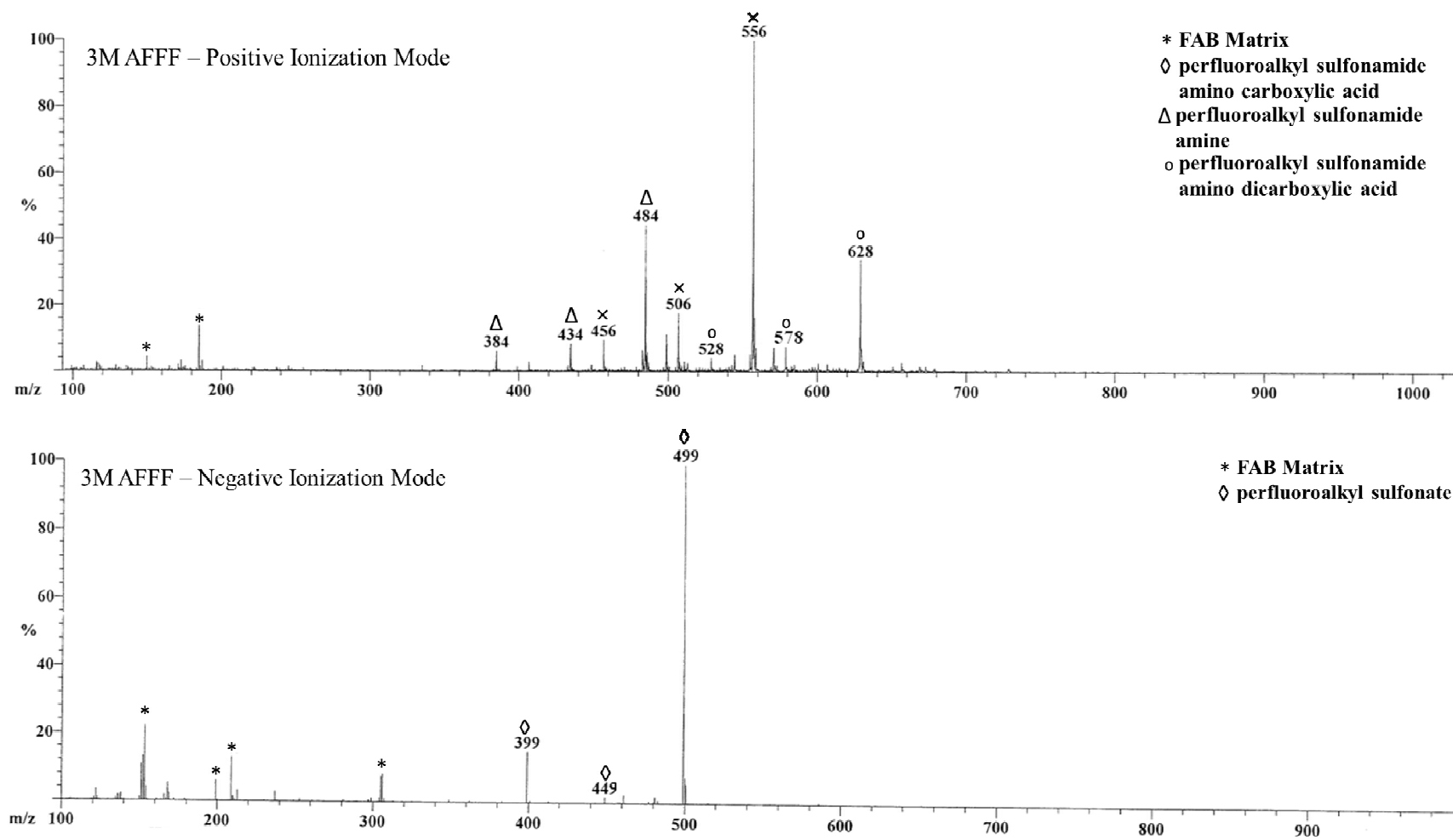
Phone: 541-737-2267

## **Materials and Methods**

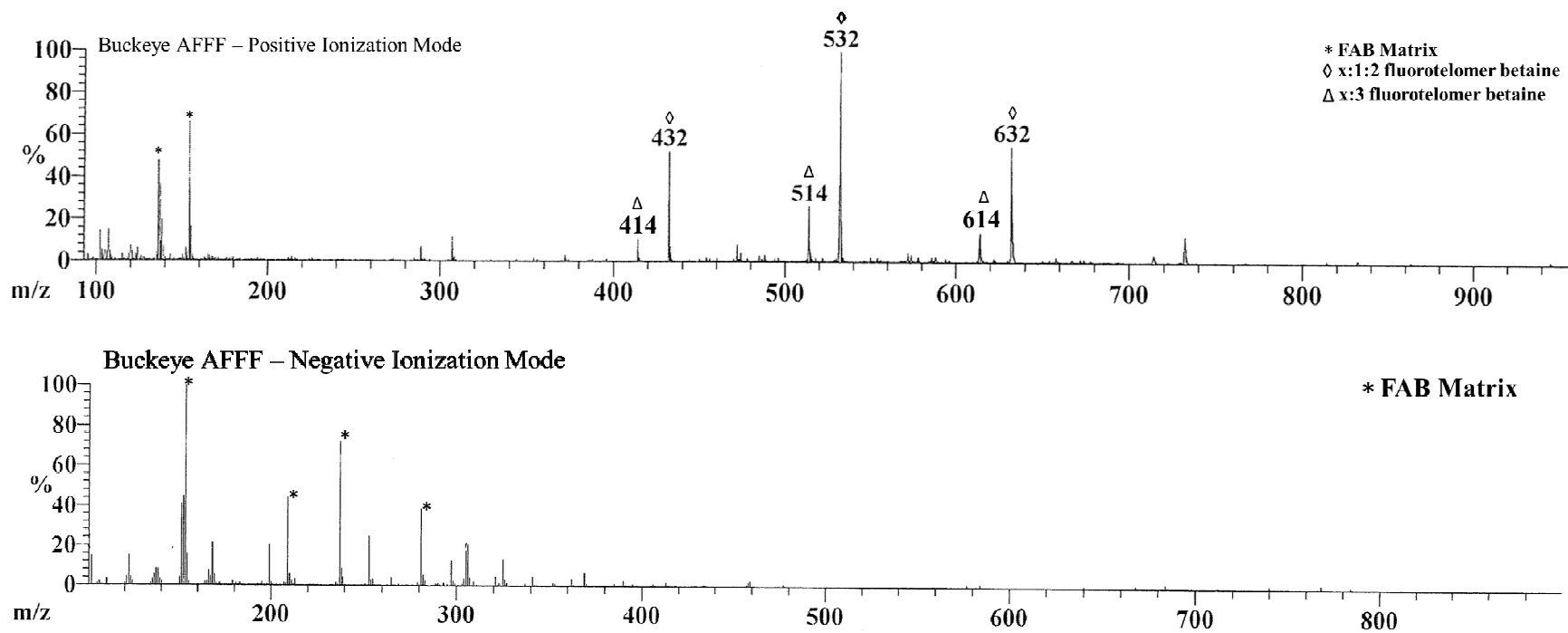
### *High Performance Liquid Chromatography Quadrupole-Time-of-Flight Mass Spectrometry*

Separations were performed on a Waters Acquity H-Class UPLC (Waters Corp., Milford, MA) using a Acquity BEH C18 column (2.1 mm ID x 100 mm, 1.7  $\mu$ m particle size). The mobile phase consisted of 0.5 mM ammonium acetate in water (A) and methanol (B) and the flow rate was maintained at 0.3 mL/min for the entirety of the separation. The gradient program began with a mobile phase of 20% B followed by a slope to 95% B in 10 min, held at 95% B for 5 min then a downward slope to 20% B over 0.5 min and held at 20% B for 2.5 min to re-equilibrate the column. The column was maintained at a constant temperature of 60 °C. The sample injection size was 20  $\mu$ L.

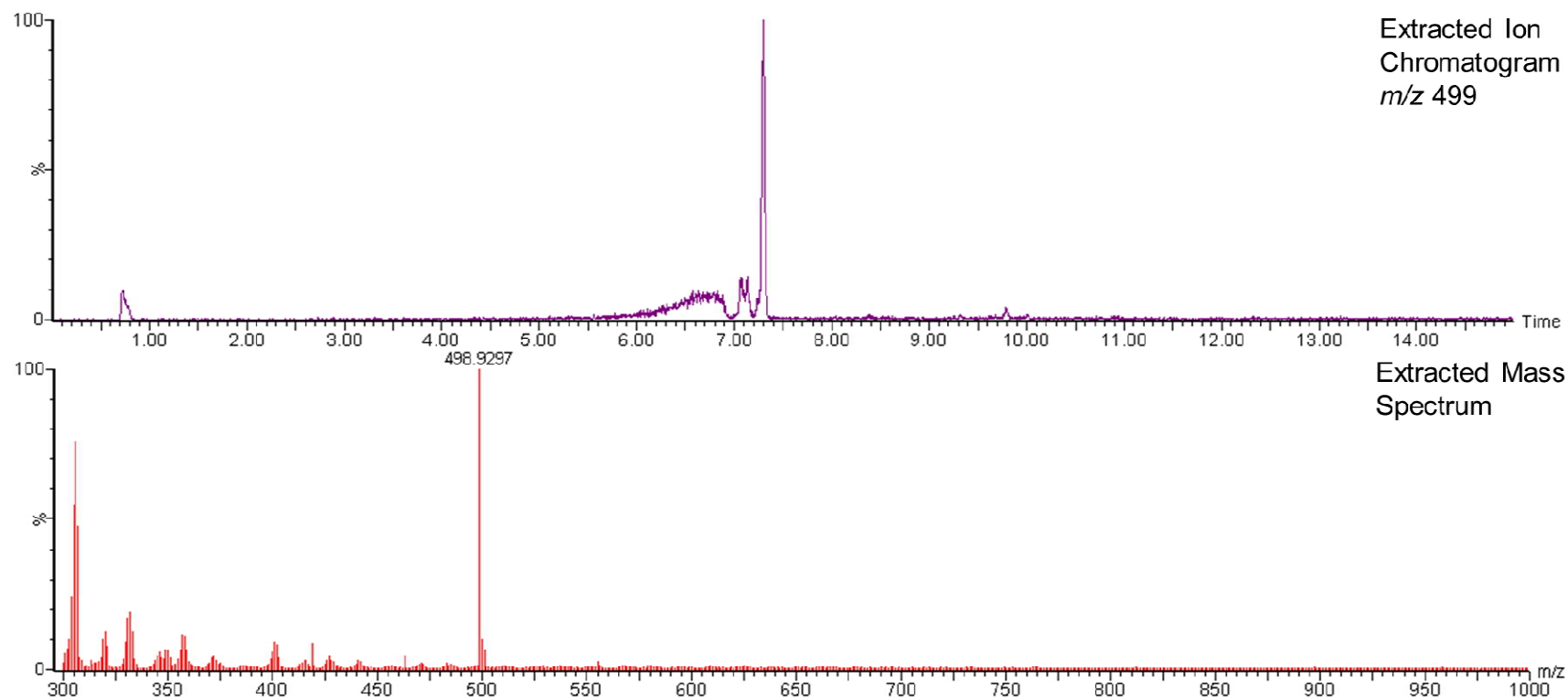
**Figure S1.** Example FAB-MS mass spectra of a 3M AFFF product.



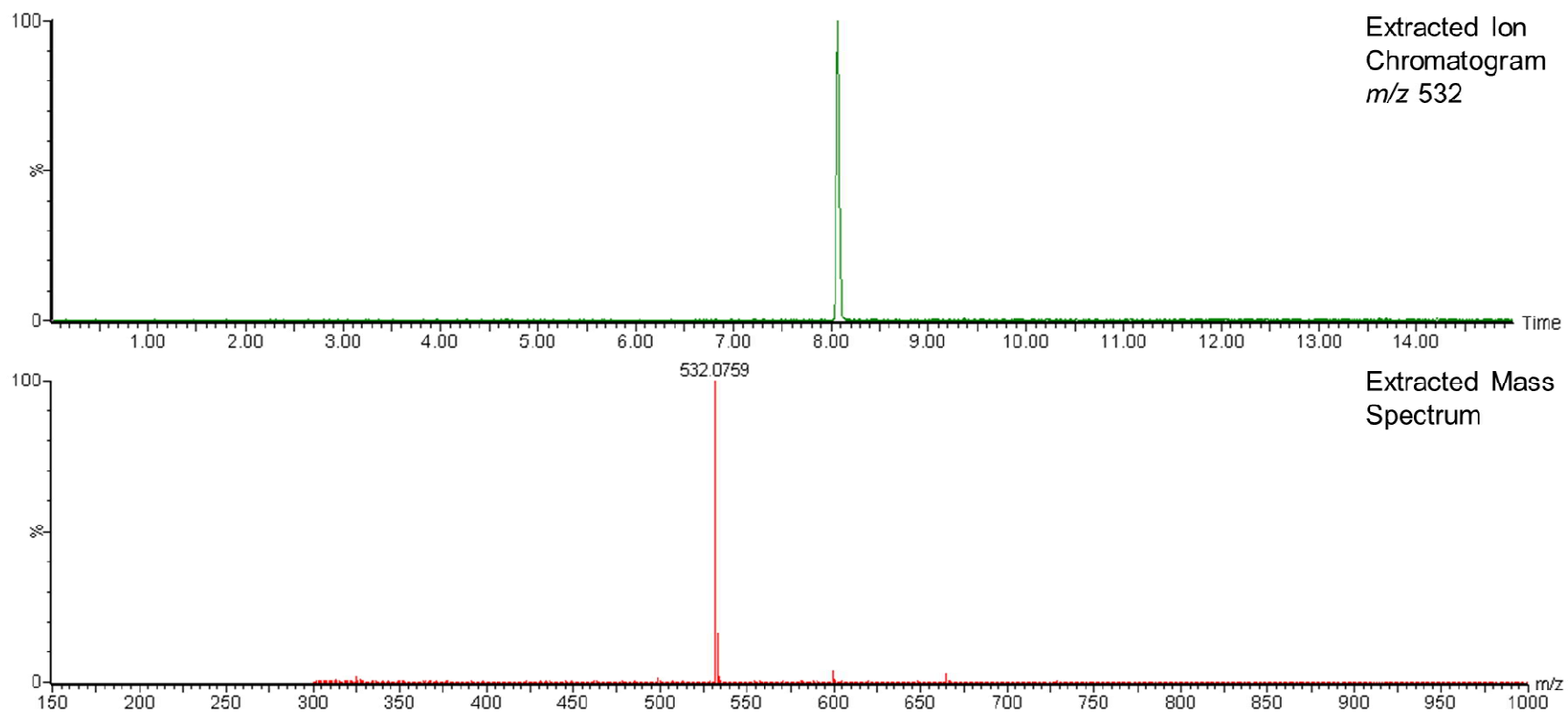
**Figure S2.** Example FAB-MS mass spectra of a Buckeye product.



**Figure S3.** Example QTOF-MS high resolution chromatogram and mass spectrum of a 3M AFFF product, specifically isolating peak  $m/z$  499. This high resolution mass ( $m/z$  498.9297) was determined to be perfluorooctane sulfonic acid.



**Figure S4.** Example QTOF-MS high resolution chromatogram and mass spectrum of a Buckeye AFFF product, specifically isolating peak  $m/z$  532. This high resolution mass ( $m/z$  532.0759) was determined to be 7:1:2 fluorotelomer betaine.



**Table S1.** High mass accuracy measurements for all identified AFFF fluorochemicals. ‡ High mass accuracy identification codes, Identification code ranking: 1 = Formula identified from accurate mass and isotopic match, 2 = Formula identified only from accurate mass, 3 = Formula alternatively identified (e.g. FAB-MS fluorochemical mass spacing from identified fluorochemical)

AFFF Product	Nominal Mass	Accurate Mass	Measured Mass	Error (ppm)	Isotopic Fit Conf %	Ion State	Ion Formula	ID Code‡	
3M	385	385.0632	385.0632	0	96.88	[M+H] <sup>+</sup>	C9H14N2O2S1F9	1	
	399	398.9361	398.9378	4.3	65.69	[M-H] <sup>-</sup>	C6O3S1F13	1	
	435	435.0600	435.0586	-3.2	99.12	[M+H] <sup>+</sup>	C10H14N2O2S1F11	1	
	449	448.9329	448.9328	-0.2	89.07	[M-H] <sup>-</sup>	C7O3S1F15	1	
	457	457.0844	457.0829	-3.3	94.3	[M+H] <sup>+</sup>	C12H18N2O4S1F9	1	
	485	485.0568	485.0567	-0.2	99.62	[M+H] <sup>+</sup>	C11H14N2O2S1F13	1	
	499	498.9297	498.9303	1.2	97.34	[M-H] <sup>-</sup>	C8O3S1F17	1	
	507	507.0812	507.0807	-1	3.33	[M+H] <sup>+</sup>	C13H18N2O4S1F11	2	
	557	557.0780	557.0768	-2.2	94.27	[M+H] <sup>+</sup>	C14H18N2O4S1F13	1	
	579	579.1023	579.1034	1.9	51.45	[M+H] <sup>+</sup>	C16H22N2O6S1F11	1	
	629	629.0991	629.0967	-3.8	61.06	[M+H] <sup>+</sup>	C17H22N2O6S1F13	1	
	National Foam	513	513.0881	513.0890	1.8	99.99	[M+H] <sup>+</sup>	C13H18N2O2S1F13	1
		571	571.0936	571.0930	-1.1	99.81	[M] <sup>+</sup>	C15H20N2O4S1F13	1
		613	613.0818	613.0818	0	49.55	[M+H] <sup>+</sup>	C15H18N2O2S1F17	1
671		671.0872	671.0861	-1.6	96.62	[M] <sup>+</sup>	C17H20N2O4S1F17	1	
771		771.0808	771.0818	1.3	91.47	[M] <sup>+</sup>	C19H20N2O4S1F21	1	
871		871.0745	871.0771	3	15.18	[M] <sup>+</sup>	C21H20N2O4F25S	2	
Ansul	586	586.0391	586.0394	0.5	84.23	[M-H] <sup>-</sup>	C15H17N1O4S2F13	1	
	602	602.0341	602.0332	-1.5	6.63	[M-H] <sup>-</sup>	C15H17N1O5S2F13	2	
	686	686.0328	686.0312	-2.3	13.65	[M-H] <sup>-</sup>	C17H17N1O4S2F17	2	
Angus	496	496.0980	496.0967	-2.6	14.49	[M] <sup>+</sup>	C14H19N1O1S1F13	2	
	586	586.0391	586.0381	-1	0.17	[M-H] <sup>-</sup>	C15H17N1O4S2F13	2	
	596	596.0916	nd	nd	nd	[M] <sup>+</sup>	C16H19N1O1S1F17	3	
Chemguard	602	602.0341	602.0332	-1.5	6.63	[M-H] <sup>-</sup>	C15H17N1O5S2F13	2	
	586	586.0391	586.0375	-2.7	9.64	[M-H] <sup>-</sup>	C15H17N1O4S2F13	2	
	581	581.1144	581.1125	-3.3	98.2	[M+H] <sup>+</sup>	C17H22N2O3S1F13	1	
	681	681.1080	681.1093	1.9	40.34	[M+H] <sup>+</sup>	C19H22N2O3S1F17	1	
Buckeye	781	781.1016	781.1032	2.0	3.99	[M+H] <sup>+</sup>	C21H22N2O3S1F21	2	
	414	414.0927	414.0909	-4.3	0.66	[M] <sup>+</sup>	C12H15N1O2F11	2	
	432	432.0833	432.0844	2.5	29.64	[M] <sup>+</sup>	C12H14N1O2F12	2	
	514	514.0863	514.0852	-2.1	7.41	[M] <sup>+</sup>	C14H15N1O2F15	2	
	532	532.0769	532.0756	-2.4	3.77	[M] <sup>+</sup>	C14H14N1O2F16	2	
	614	614.0799	614.0792	-1.1	0.42	[M] <sup>+</sup>	C16H15N1O2F19	2	
Fireade	632	632.0705	632.6900	-2.4	19.75	[M] <sup>+</sup>	C16H14N1O2F20	2	
	513	513.0881	513.0866	-2.9	9.36	[M+H] <sup>+</sup>	C13H18N2O2S1F13	2	
	571	571.0936	571.0931	-0.9	98.54	[M] <sup>+</sup>	C15H20N2O4S1F13	1	
	613	613.0818	613.0799	-3.1	0.01	[M+H] <sup>+</sup>	C15H18N2O2S1F17	2	
	671	671.0872	671.0879	1	99.75	[M] <sup>+</sup>	C17H20N2O4S1F17	1	
	771	771.0808	771.0811	0.4	44.04	[M] <sup>+</sup>	C19H20N2O4S1F21	1	
	871	871.0745	871.0724	-2.5	77.66	[M] <sup>+</sup>	C21H20N2O4F25S	1	

**Table S2.** Structural identification of all identified AFFF fluorochemicals. \* x:y:z fluorotelomer indicates an alkyl chain with x carbons completely fluorinated, y carbons partially fluorinated, and z carbons non-fluorinated. †Refer to the generic structures in **Figure 3** and **4**; numbers in parentheses indicate completely fluorinated chain length. ‘Pat.’ refers to patent used for structural determination, the numbers correspond to the reference.

AFFF Product	Nominal Mass	Generic Name	IUPAC Name	Generic Structure †	Pat.	
3M	385	perfluorobutane sulfonamide amine	N-(3-(dimethylamino)propyl)-perfluorobutane-1-sulfonamide	3D (4)	1	
	399	perfluorohexane sulfonic acid	1-perfluorohexane sulfonic acid	3A (6)	1, 2	
	435	perfluoropentane sulfonamide amine	N-(3-(dimethylamino)propyl)-perfluoropentane-1-sulfonamide	3D(5)	1	
	449	perfluoroheptane sulfonic acid	1-perfluoroheptane sulfonic acid	3A (7)	1, 2	
	457	perfluorobutane sulfonamide amino carboxylic acid	3-(N-(3-(dimethylamino)propyl)-perfluorobutylsulfonamido)propanoic acid	3B (4)	1	
	485	perfluorohexane sulfonamide amine	N-(3-(dimethylamino)propyl)-perfluorohexane-1-sulfonamide	3D(6)	1	
	499	perfluorooctane sulfonic acid	1-perfluorooctane sulfonic acid	3A (8)	1, 2	
	507	perfluoropentane sulfonamide amino carboxylic acid	3-(N-(3-(dimethylamino)propyl)-perfluoropentylsulfonamido)propanoic acid	3B (5)	1	
	557	perfluorohexane sulfonamide amino carboxylic acid	3-(N-(3-(dimethylamino)propyl)-perfluorohexylsulfonamido)propanoic acid	3B (6)	1	
	579	perfluoropentane sulfonamide ammonio dicarboxylic acid	N-(2-carboxyethyl)-3-(N-(2-carboxyethyl)-perfluoropentylsulfonamido)-N,N-dimethylpropan-1-aminium	3C (5)	1	
	629	perfluorohexane sulfonamide ammonio dicarboxylic acid	N-(2-carboxyethyl)-3-(N-(2-carboxyethyl)-perfluorohexylsulfonamido)-N,N-dimethylpropan-1-aminium	3C(6)	1	
	National Foam	513	6:2 fluorotelomer sulfonamide amine	N-[3-(dimethylamino) propyl]-1H,1H,2H,2H-perfluoro-1-octanesulfonamide	4B (6)	3
		571	4:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-hexanesulfonamido)propan-1-aminium	4A (4)	3
613		8:2 fluorotelomer sulfonamide amine	N-[3-(dimethylamino) propyl]-1H,1H,2H,2H-perfluoro-1-decanesulfonamide	4B (8)	3	
671		6:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	4A (6)	3	
771		8:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-decanesulfonamido)propan-1-aminium	4A (8)	3	
871		10:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-dodecanesulfonamido)propan-1-aminium	4A (10)	3	
Ansul	586	6:2 fluorotelomer thioether amido sulfonic acid	2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propanamido)propane-1-sulfonate	4C (6)	4, 5, 6	
	602	6:2 fluorotelomer thioether amido sulfonic acid (+ oxygen)	n/a	n/a		
	686	8:2 fluorotelomer thioether amido sulfonic acid	2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-decyl)thio)propanamido)propane-1-sulfonate	4C (8)	4, 5, 6	
Angus	496	6:2 fluorotelomer thio hydroxy ammonium	2-hydroxy-N,N,N-trimethyl-3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propan-1-aminium	4D (6)	4	
	586	6:2 fluorotelomer thioether amido sulfonic acid	2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propanamido)propane-1-sulfonate	4C (6)	4, 5, 6	
	596	8:2 fluorotelomer thio hydroxy ammonium	2-hydroxy-N,N,N-trimethyl-3-((1H,1H,2H,2H-perfluoro-1-decyl)thio)propan-1-aminium	4D (8)	4	
	602	6:2 fluorotelomer thioether amido sulfonic acid (+ oxygen)	n/a	n/a		
Chemguard	586	6:2 fluorotelomer thioether amido sulfonic acid	2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propanamido)propane-1-sulfonate	4C (6)	4, 5, 6	
	581	6:2 fluorotelomer thioether amido amino carboxylic acid	4-((3-(dimethylamino)propyl)amino)-4-oxo-2((1H,1H,2H,2H-perfluorooctyl)thio)butanoic acid	4E (6)	7	
	681	8:2 fluorotelomer thioether amino carboxylic acid	4-((3-(dimethylamino)propyl)amino)-4-oxo-2((1H,1H,2H,2H-perfluorodecyl)thio)butanoic acid	4E (8)	7	
	781	10:2 fluorotelomer thioether amino carboxylic acid	4-((3-(dimethylamino)propyl)amino)-4-oxo-2((1H,1H,2H,2H-perfluorododecyl)thio)butanoic acid	4E (10)	7	
Buckeye	414	5:3 fluorotelomer betaine	N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorooctan-1-aminium	4F (5)	4	
	432	5:1:2 fluorotelomer betaine*	N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorooctan-1-aminium	4E (5)	4	
	514	7:3 fluorotelomer betaine	N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorodecan-1-aminium	4F (7)	4	
	532	7:1:2 fluorotelomer betaine*	N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorodecan-1-aminium	4E (7)	4	
	614	9:3 fluorotelomer betaine	N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorododecan-1-aminium	4F (9)	4	
	632	9:1:2 fluorotelomer betaine*	N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorododecan-1-aminium	4G (9)	4	
Fireade	513	6:2 fluorotelomer sulfonamide amine	N-[3-(dimethylamino) propyl]-1H,1H,2H,2H-perfluoro-1-octanesulfonamide	4D (6)	3	
	571	4:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-hexanesulfonamido)propan-1-aminium	4A(4)	3	
	613	8:2 fluorotelomer sulfonamide amine	N-[3-(dimethylamino) propyl]-1H,1H,2H,2H-perfluoro-1-decanesulfonamide	4B (8)	3	
	671	6:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	4A (6)	3	
	771	8:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-decanesulfonamido)propan-1-aminium	4A (8)	3	
	871	10:2 fluorotelomer sulfonamide betaine	N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-dodecanesulfonamido)propan-1-aminium	4A (10)	3	



## References

1. Alm, R. R.; Stern, R. M. Aqueous film-forming foamable solution useful as fire extinguishing concentrate. U.S. Patent 5,085,786, Feb. 4, 1992.
2. Berger, T. W. Aqueous film-forming foam fire extinguisher. U.S. Patent 4,359,096, Nov. 16, 1982.
3. Norman, E. C.; Regina, A. C. Alcohol resistant aqueous film forming firefighting foam. U.S. Patent 5,207,932, May 4, 1993.
4. Clark, K. P.; Kleiner, E. K. Synergistic surfactant compositions and fire fighting concentrates thereof. U.S. Patent 5,616,273, Apr. 1, 1997.
5. Dear, R. E. A.; Kleiner, E. K. Fluorinated sulfonic acids and derivatives thereof. U.S. Patent 4,014,926, Mar. 29, 1977.
6. Falk, R. A. Aqueous wetting and film forming compositions. U.S. Patent 4,090,967, May 23, 1978.
7. Mueller, K.F. Perfluoroalkyl substituted anhydrides and polyacids, and derivatives thereof. U.S. Patent 4,153,590, May 8, 1979.