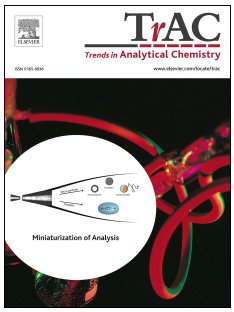
Accepted Manuscript



High-Resolution Mass Spectrometry (HRMS) Methods for Nontarget Discovery and Characterization of Poly- and Per-fluoroalkyl Substances (PFASs) in Environmental and Human Samples

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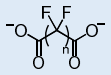
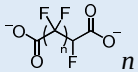
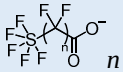
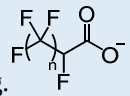
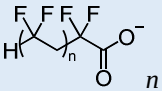
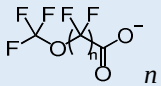
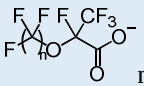
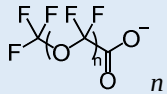
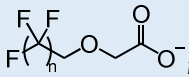
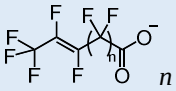
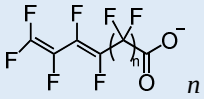
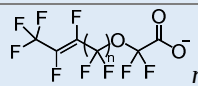
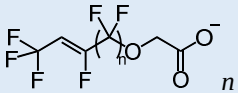
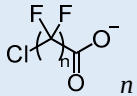
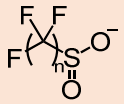
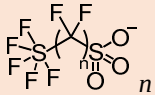
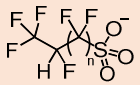
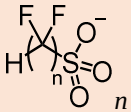
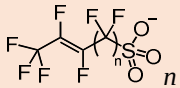
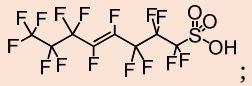
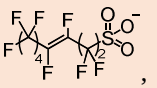
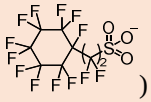
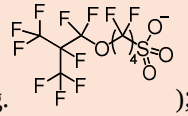
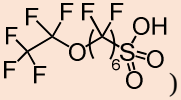
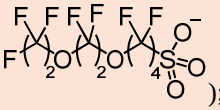
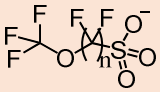
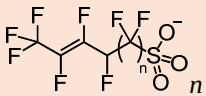
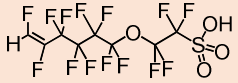
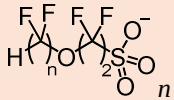
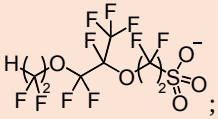
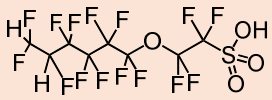
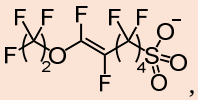
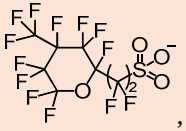
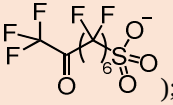
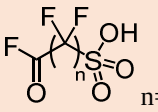
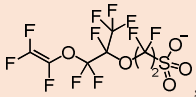
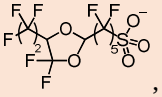
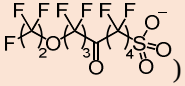
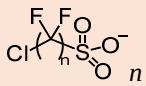
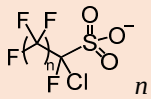
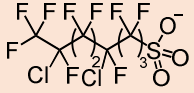
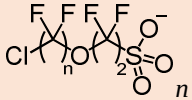
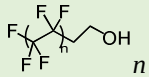
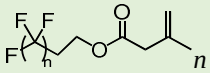
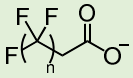
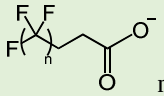
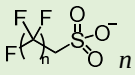
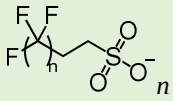
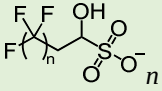
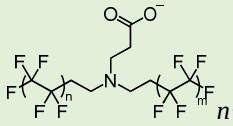
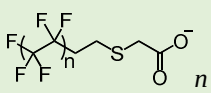
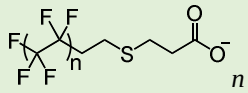
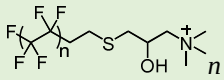
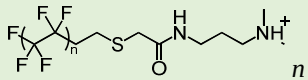
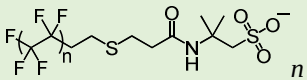
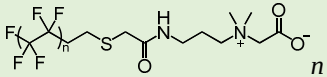
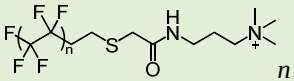
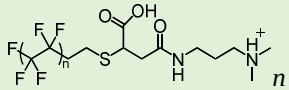
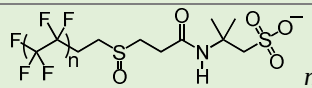
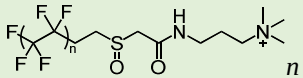
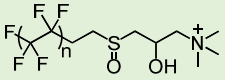
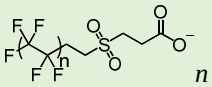
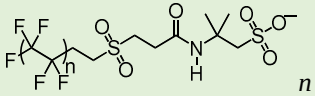
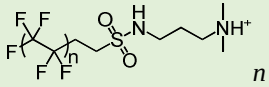
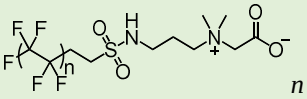
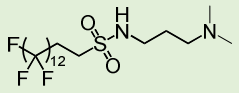
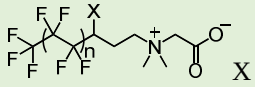
Table 1. Review of PFASs discovered by nontarget HRMS to date (October 31, 2018). A detailed version of this table is available on the NORMAN Suspect List Exchange (https://www.norman-network.com/?q=node/236) for purposes of suspect screening.

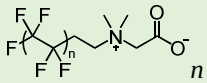
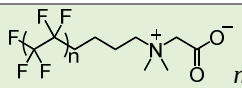
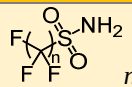
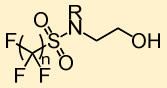
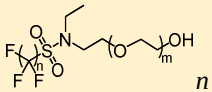
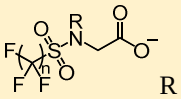
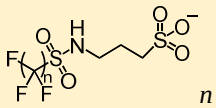
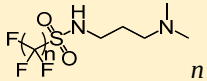
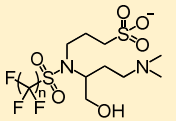
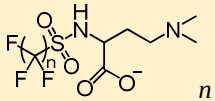
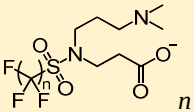
Sub-Category	Structure	Number of Classes & Analytes	Range of C & F numbers in each class	References
Modifications of perfluoroalkyl carboxylic acids (PFCAs): ≥14 classes & 99 homologues				
perfluoroalkyl dioic acids	 *n* = 7-15	1 & 9	C_9F_{14}-$C_{17}F_{30}$	[39, 41]
H-substituted perfluoroalkyl dioic acids	 *n* = 8-12	1 & 5	$C_{11}F_{17}$-$C_{15}F_{25}$	[41]
pentafluorosulfide-PFCAs	 *n* = 6-8	1 & 3	C_7F_{17}–C_9F_{21}	[31]
H-substituted-PFCAs	$(C_nF_{2n}H)CO_2^-$, *n* = 3-16 e.g.  n=2-15; $C_{2n}F_{2n}H_{2n}O_2^-$, *n* = 2-10 e.g.  *n* = 1-9	≥2 & ≥23	C_4F_4-$C_{17}F_{32}$/ $C_{20}F_{20}$	[31, 34, 36, 37, 39]
ether-PFCAs	 *n* = 1 & 8-15;  n=1-5;  *n* = 2-5	3 & 18	C_3F_5–$C_{15}F_{29}$	[35, 37, 41]

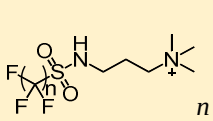
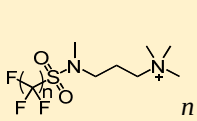
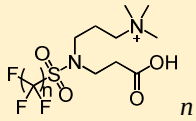
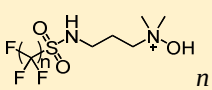
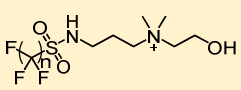
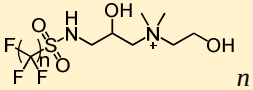
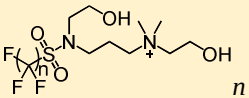
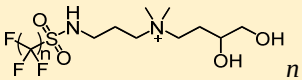
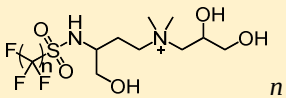
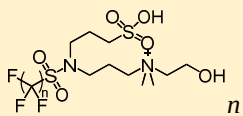
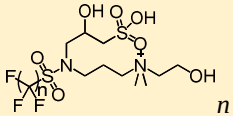
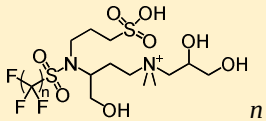
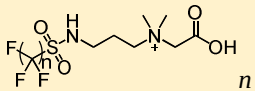
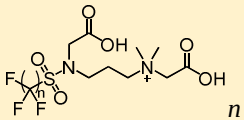
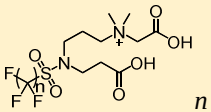
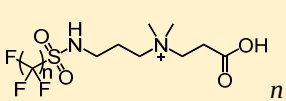
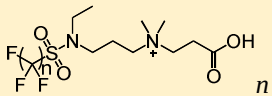
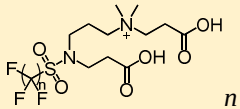
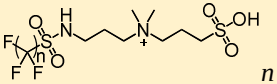
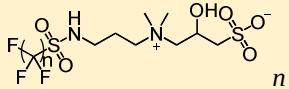
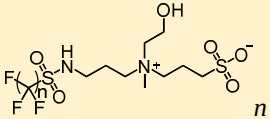
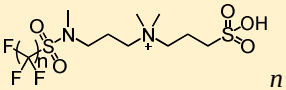
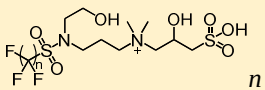
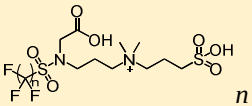
H-substituted-ether-PFCAs	 *n* = 6-11	1 & 6	C_9F_{13}-$C_{14}F_{23}$	[39]
Unsaturated-PFCAs	 *n* = 5-10;  *n* = 0-3	2 & 10	C_5F_5-$C_{14}F_{27}$	[39]
unsaturated-ether-PFCAs	 *n* = 0-4	1 & 5	C_5F_7-C_9F_{15}	[31, 39]
H-substituted-unsaturated-ether-PFCAs	 *n* = 2, 4-10	1 & 8	C_6F_6-$C_{14}F_{22}$	[39]
Cl-substituted-PFCAs	 *n* = 3-14	≥1 & 12	C_4F_6-$C_{15}F_{28}$	[34, 39, 42]
Modifications of perfluoroalkyl sufonic acids (PFSAs)L ≥28 classes & ≥124 homologs				
Perfluoroalkyl sulfinate	 *n* = 4-8	1 & 5	C_4F_9-C_8F_{17}	[31, 40]
pentafluorosulfide-PFSAs	 *n* = 3-9	1 & 7	C_3F_{11}-C_9F_{23}	[31]
H-substituted-PFSAs	 *n* = 0-8 (multiple isomers possible);  *n* = 4, 6;	≥2 & 11	C_2F_4-$C_{10}F_{20}$	[31, 36, 37]

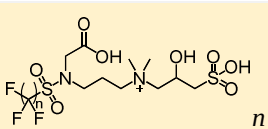
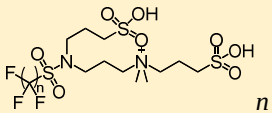
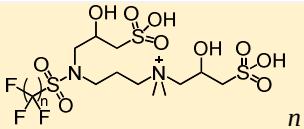
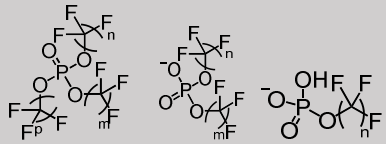
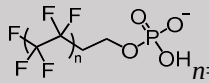
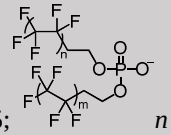
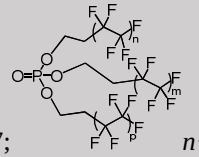
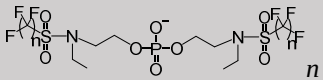
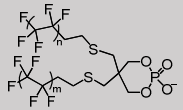
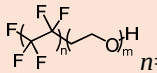
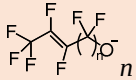
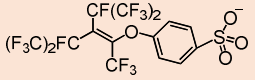
unsaturated/cyclic-PFSAs	 *n* = 1-10 (multiple isomers possible);  ; $C_nF_{2n-1}SO_3^-$ *n*=7-14 (multiple isomers e.g.  , )	≥4 & ≥18	C_4F_7-$C_{14}F_{27}$	[31, 40, 42, 43]
ether-PFSAs	$C_nF_{2n+1}SO_4^-$ *n*=4-12 (multiple isomers e.g. ); $C_nF_{2n+1}SO_4^-$ *n*=6-9 (multiple isomers e.g. ) $C_nF_{2n+1}SO_5^-$ *n*=6-12 (multiple isomers e.g. );  *n* = 2-9	≥4 & ≥28	C_3F_7-$C_{12}F_{25}$	[31, 42-44]
H-substituted-unsaturated-PFSAs	 *n* = 1-6 (multiple isomers possible); 	≥2 & ≥7	C_5F_8-$C_{10}F_{18}$	[31, 38]
H-substituted-ether-PFSAs	 *n* = 5, 6, 8;  ; 	≥3 & ≥5	C_8F_{16}-$C_{10}F_{20}$	[35, 38]
unsaturated-ether-PFSAs, or cyclic-ether-PFSAs, or carbonyl/ketone-PFSAs, or ketone-ether-PFSAs	$C_nF_{2n-1}SO_4^-$ *n*=6-13 (multiple isomers e.g.  ,  , );	≥7 & ≥26	C_3F_7-$C_{13}F_{25}$	[31, 40, 42-44]

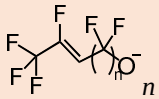
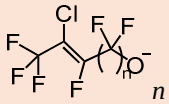
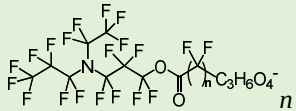
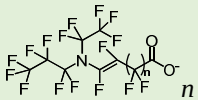
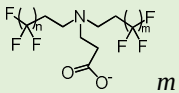
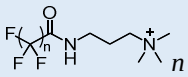
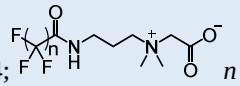
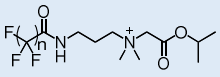
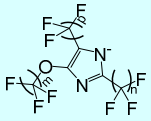
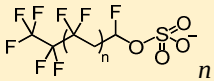
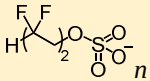
	 n=3-12; $C_nF_{2n-1}SO_5^-$ *n*=6-13 (multiple isomers e.g.  ,  , )			
Cl-substituted-PFSAs	 *n* = 7, 8;  *n* = 2-7; 	3 & 9	C_3F_6-C_8F_{16}	[31, 39, 40, 44]
Cl-substituted-ether-PFSAs	 *n* = 5-12	1 & 8	C_7F_{14}-$C_{14}F_{28}$	[38, 41-43]
Fluorotelomers (FTs): 27 classes & 115 homologues				
n:2 FT alcohols (FTOHs)	 *n* = 2-8	1 & 7	C_6F_9-$C_{18}F_{33}$	[48]
n:2 fluoroacrylates	 *n* = 5-14	1 & 10	$C_{12}F_{11}$-$C_{17}F_{21}$	[48]
n:1 or n:2 FT carboxylic acids	 *n* = 8-10;  n=3, 5	2 & 5	C_7F_7-$C_{12}F_{21}$	[31, 41]
n:1 or n:2 FT sulfonic acids	 *n* = 5,7;  *n* = 6, 8, 10,12,14;  *n* = 4, 6, 8;	3 & 10	C_6F_{11}- $C_{16}F_{29}$	[31, 40, 41]

n:2/m:2 FT amines	 *n*+*m* = 8-12	1 & 5	$C_{23}F_{34}$-$C_{31}F_{50}$	[48]
n:2 FT thioethers	 *n* = 2-5;  *n* = 2-6;  *n* = 2-5;  *n* = 2-6;  *n* = 1-7;  *n* = 2-7;  *n* = 3-5;  *n* =3-5	8 & 37	C_8F_9-$C_{25}F_{29}$	[29-31, 40, 48]
n:2 FT sulfoxides	 *n* = 2-5;  *n* = 3;  *n* = 3, 4	3 & 7	$C_{14}F_{13}$-$C_{16}F_{17}$	[30, 40]
n:2 FT sulfones	 *n* = 2-4;  *n* = 2-4	2 & 6	C_9F_9-$C_{17}F_{17}$	[31]
n:2 FT sulfonamides	 *n* = 3-6;  *n* = 2-8; 	3 & 12	$C_{13}F_9$- $C_{25}F_{33}$	[29-31]
FT betaines	 X = H, *n* = 2-6; X = F, *n* = 2-7;	4 & 17	$C_{12}F_9$-$C_{22}F_{32}$	[29-31]

	 *n* = 3-5;  *n* = 2-4			
Perfluoroalkane Sulfonamido Substances (PFSMs): 39 classes & 221 homologues				
perfluoroalkyl sulfonamides	 *n* = 2-8	1 & 7	C_2F_5-C_8F_{17}	[31, 36, 40]
alcohol-PFSMs	 R=H, *n* = 2-10; X=CH_3, *n* = 4;  *n* = 5-7, *m* = 0-8; *n* = 8, *m* = 0-14	3 & 52	C_4F_5-$C_{40}F_{17}$	[32, 36, 40, 48]
carboxylic acid-PFSMs	 R = H, *n* = 4-6; R = CH_3, *n* = 3-6,8; R = C_2H_5, *n* = 2-10	3 & 17	C_6F_5-$C_{14}F_{21}$	[31, 32, 36]
sulfonic acid-PFSMs	 *n* = 3-6	1 & 4	C_6F_7-C_9F_{13}	[31]
amine-PFSMs	 *n* = 3-8;  *n* = 5, 6;  *n* = 4-6;  *n* = 3-8;	4 & 17	C_8F_7-$C_{16}F_{17}$	[29, 30, 40]

ammonio-PFSMs	 *n* = 3-8;  *n* = 2-8;  *n* = 3-6;  *n* = 4-9;  *n* = 2-8;  *n* = 4-6;  *n* = 2-8;  *n* = 4-6;  *n* = 3-6;  *n* = 2-8;  *n* = 4-6;  *n* = 2-6;  *n* = 3-6,14,16;  *n* = 3-6;  *n* = 4-6;  *n* = 3-6;  *n* = 5, 6;  *n* = 3-6;  *n* = 3-8;  *n* = 3-9;  *n* = 4-6;  *n* = 3-6;  *n* = 3-6;  *n* = 3-6;	27 & ≥124	C_9F_7-$C_{25}F_{33}$	[29-32, 36, 40]

	 *n* = 3-6;  *n* = 3-8;  *n* = 2-6			
Perfluoroalkyl and polyfluoroalkyl phosphates (PFAPs): 8 classes & 35 homologues				
perfluoroalkyl-substituted-PFAPs	 *n*+*m* = 12,14,16,18,20, *p* = unknown		3 & 5	$\geq CF_7$-$\geq C_{21}F_{45}$	[48]
n:2 FTOH-substituted phosphate (i.e. PAPs)	 *n*=2-5;  *n*+*m*=6-17;  *n*+*m*=6-9, *p* = unknown		3 & 20	C_6F_9- $\geq C_{44}F_{79}$	[41, 48]
N-PFOSE di-substituted-PFAPs	 *n* = 8		1 & 1	$C_{24}F_{34}$	[48]
x:2/y:2 FTOH di-substituted thioether PFAPs	 *n*+*m* = 6-14		1 & 9	$C_{21}F_{26}$-$C_{37}F_{58}$	[48]
Perfluoroalkyl alcohols: ≥6 classes & ≥105 homologues				
Perfluoroalkyl alcohol	 *n* = 3, 4		1 & 2	C_3F_7–C_4F_9	[39]
Perfluoroalkyl polyethoxylate alcohol	 *n*=3-7, *m*=5-20		1 & 80	$C_{16}F_{13}$–$C_{54}F_{29}$	[48]
unsaturated perfluoroalkyl alcohols:	 *n* = 0-5, 8-13; 		≥2 & ≥13	C_4F_7–$C_{16}F_{31}$	[39, 41]

H-substituted-unsaturated-perfluoroalkyl alcohols:	 *n* = 4-8	1 & 5	C_7F_{12}–$C_{11}F_{20}$	[34]
Cl-substituted-unsaturated-perfluoroalkyl alcohols:	 *n* = 3-7	≥1 & ≥5	C_6F_{10}–$C_{10}F_{18}$	[34, 39]
Perfluoroalkyl and polyfluoroalkyl amines: ≥3 classes & ≥17 homologues				
Perfluoroalkyl amines	 *n* = 1-6;  *n* = 2-7	≥2 & ≥12	$C_{10}F_{18}$-$C_{18}F_{30}$	[42]
Polyfluoroalkyl amines	 *m* + *n* = 16, 18, 20, 22, 24	1 & ≥5	$C_{23}F_{34}$-$C_{31}F_{50}$	[48]
Perfluoroalkylamides: 3 classes & 22 homologues				
/	 *n* = 3-12,14;  *n* = 6-12,14;  *n* = 8,10,12	3 & 22	C_9F_7-$C_{22}F_{29}$/ $C_{23}F_{25}$	[30]
Perfluoroalkyl *N*-heterocycles: 1 class & 9 homologues				
/	 *m* + *n*+ *p* = 6-14 (e.g.1, 1 and 4 for m, n and p, respectively)	1 & 9	C_9F_{15}-$C_{17}F_{31}$	[42]
Polyfluoroalkyl sulfates: ≥2 classes & ≥8 homologues				
	 *n* = 1-6;  *n* = 2-3	≥2 & ≥8	C_4F_4-$C_{15}F_{18}$	[34, 36, 37]
Polymers				
Perfluoropolyethers	*with repeating units such as CF_2, CF_2O, C_2F_4O, C_2H_4O, $C_2H_2F_2$, etc*	/	/	[48]

	$(OH)_2OPO(C_2H_4O)_n(C_2H_2F_2O)_o(C_2F_4O)_p(CF_2O)_qPO(OH)_2$			
TOTAL	/	≥131 & ≥755	C_2F_4-$C_{44}F_{79}$	/