



WELLINGTON LABORATORIES



Greyhound
CHROMATOGRAPHY
AND ALLIED CHEMICALS

REFERENCE AND HANDLING GUIDE:
PERFLUOROALKYL COMPOUNDS

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The popularity of our Reference and Handling Guide for Halogenated Aromatic Compounds has prompted us to introduce an analogous guide for Fluorinated Compounds. Analysis of fluorinated compounds is still a new and challenging field which has grown enormously in recent years.



If you have any comments on our present reference guides and/or suggestions for future reference guides, or if you would like to receive a copy of our more concise **Quick Reference Guide for Perfluoroalkyl Compounds**, please contact us at:

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GUIDELINES FOR THE USE AND HANDLING OF WELLINGTON'S FLUORINATED PRODUCTS

HAZARDS

Our products are polyfluorinated alkyl compounds offered as solutions in organic solvents such as methanol, isopropanol and nonane.

Although the maximum concentration is 50 µg/ml, that is 0.005% (w/v), these compounds must be considered toxic and should be handled accordingly.

As with all of our products, due care should be exercised to prevent human contact and ingestion. The absence of a toxicity warning for any of our products must not be interpreted as an indication that there is no possible health hazard.



NOTE:
THESE MATERIALS SHOULD ONLY BE USED BY PERSONNEL TRAINED IN THE HANDLING OF HAZARDOUS CHEMICALS. ALL PROCEDURES SHOULD BE PERFORMED IN A FUME HOOD AND SUITABLE GLOVES, EYE PROTECTION AND CLOTHING SHOULD BE WORN AT ALL TIMES.

RECEIPT, INSPECTION, HANDLING AND STORAGE

Unless crystalline material is provided, all of our reference standard solutions are shipped in flame-sealed, pre-scored amber glass ampoules. Upon receipt, inspect the ampoules for breakage and leakage and then store them upright in a refrigerator until needed.

Prior to opening, allow the solution to drain into the bottom of the ampoule, lightly tapping the ampoule if necessary. Using the plastic ampoule collar provided, hold the ampoule upright and snap the top off, breaking away from the body. Transfer the solution to an amber glass container with a glass stopper for storage.

ADDITIONAL HANDLING SUGGESTIONS SPECIFIC TO THE COMPOUND WILL BE PROVIDED WITH THE CERTIFICATE OF ANALYSIS.

DISPOSAL

All waste materials generated during the use of these solutions should be treated as hazardous in accordance with national and regional regulations. A licensed disposal company should be employed.

ACCURACY

Each of our stock solutions is prepared from crystalline material that has been well characterized as to its structure and purity. The crystalline material is weighed using microbalances that are externally calibrated using NIST-traceable weights.

Solutions are prepared by completely dissolving the crystalline material in ultrapure, distilled-in-glass solvents. The volumetric flasks used for this purpose, and the pipets used for subsequent preparation of dilutions and mixtures, are all of class A tolerance and NIST-traceable.

The maximum percent relative combined uncertainty for solution preparation is calculated to be $\pm 5\%$.

INTERLABORATORY CERTIFICATION

Wellington has contributed standards to various independent interlaboratory testing studies. Since 2005, our standards have been tested in several international round-robins. Data from these studies are available upon request.

Wellington plans to continue participating in independent interlaboratory studies to confirm the accuracy of our reference standard solutions.

EXPIRY DATE/SHELF LIFE

In order to accurately determine the shelf life of our products, testing must reveal degradation or loss in concentration of the particular analyte. Most of these fluorinated compounds are presumed to be stable based on current scientific literature. However, many of these compounds have never been offered as solutions and therefore may have degradation pathways that have not been previously observed.

Consequently, we continue to monitor the stability of these compounds by:

- i) comparing freshly prepared solutions to older solutions by GC/MS and/or LC/MS.
- ii) monitoring the solutions during storage by GC/MS and/or LC/MS.

Thus, our stability studies are still ongoing. In the absence of a "true expiry date", we consider that our reference solutions retain their accuracy for a period of at least 2 years from delivery in the unopened ampoule.

Common Acronyms

PFCA	Perfluoroalkylcarboxylic acid
PFOA	Perfluorooctanecarboxylic acid
PFAS	Perfluoroalkylsulfonate
PFOS	Perfluorooctanesulfonate
PFASi	Perfluoroalkylsulfinate
FOSA	Perfluorooctanesulfonamide
FOSAA	Perfluorooctanesulfonamidoacetic acid
FOSE	Perfluorooctanesulfonamidoethanol
FTOH	Fluorinated telomer alcohol (-OH functional group)
FTA	Fluorinated telomer acid
FTUA	Fluorinated telomer unsaturated acid
FTS	Fluorinated telomer sulfonate
PFAPA	Perfluoroalkylphosphonic acid
PFPi	Perfluoroalkylphosphinate
PAP	Mono-substituted polyfluoroalkylphosphate ester
diPAP	Di-substituted polyfluoroalkylphosphate ester
PFAI	Perfluoroalkyl iodide
SFA	Semifluorinated alkane
FTI	Fluorinated telomer iodide
FTO	Fluorinated telomer olefin
FTAC	Fluorinated telomer acrylate

Conversion Factors and Units of Measure

Prefix	Symbol	Factor	Fraction	
centi	c	10^{-2}	= 1/100	part per hundred
milli	m	10^{-3}	= 1/1,000	part per thousand
micro	μ	10^{-6}	= 1/1,000,000	part per million (ppm)
nano	n	10^{-9}	= 1/1,000,000,000	part per billion (ppb)
pico	p	10^{-12}	= 1/1,000,000,000,000	part per trillion (ppt)
femto	f	10^{-15}	= 1/1,000,000,000,000,000	part per quadrillion (ppq)
atto	a	10^{-18}	= 1/1,000,000,000,000,000,000	part per quintillion
zepto	z	10^{-21}	= 1/1,000,000,000,000,000,000,000	part per sextillion
yocto	y	10^{-24}	= 1/1,000,000,000,000,000,000,000,000	part per septillion

Typical HPLC/UPLC Flow Rates

Column ID (mm)	Particle Size 5 μ m	Particle Size 3 μ m	Particle Size 2 μ m	Particle Size sub 2 μ m*
1.0	0.05 ml/min	0.07 ml/min	0.1 ml/min	0.15 ml/min
2.1	0.2	0.3	0.5	0.4 - 0.6
3.2	0.5	0.7	1.0	0.8
4.6	1.0	1.5	2.0	1.0

*Flow rate may be limited by column back pressure.

Common Buffers

Buffer Type	pKa	Buffer pH Range	Examples
Acetate	4.8	3.8 - 5.8	Ammonium Acetate Acetic Acid Sodium Acetate
Ammonia	9.2	8.2 - 10.2	Ammonium Hydroxide Ammonium Phosphate (mono- and di-basic) Ammonium Carbonate
Borate	9.2	8.2 - 10.0	Sodium Borate Boric Acid
Carbonate	10.2	9.2 - 11.2	Ammonium Carbonate Ammonium Bicarbonate
Citrate	3.1 4.7 5.4	2.1 - 4.1 3.7 - 5.7 4.4 - 6.4	Trisodium Citrate Diammonium Citrate Triammonium Citrate Citric Acid
Formate	3.8	2.8 - 4.8	Ammonium Formate Formic Acid
Phosphate	2.1 7.2 12.3	1.1 - 3.1 6.2 - 8.2 11.3 - 13.3	Potassium Phosphate Monobasic Potassium Phosphate Dibasic Potassium Phosphate Tribasic Phosphoric acid

Conversion Factors for Units of Pressure Measurement

	PSI	bar	torr	kPa	atm	inches Hg	kg/cm ²
PSI=	1	0.06895	51.713	6.8948	0.068	2.0359	0.0703
bar=	14.5038	1	751.88	100	0.9869	29.5300	1.0197
torr=	0.0193	0.00133	1	0.1330	0.00132	0.0394	0.00136
kPa=	0.1450	0.0100	7.52	1	0.00987	0.2962	0.0102
atm=	14.696	1.0133	760	101.32	1	29.921	1.0332
inches Hg=	0.49612	0.03376	25.400	3.376	0.0334	1	0.0345
kg/cm ² =	14.223	0.9806	735.5	98.06	0.967	28.958	1

General Structure of Various Fluorinated Compounds

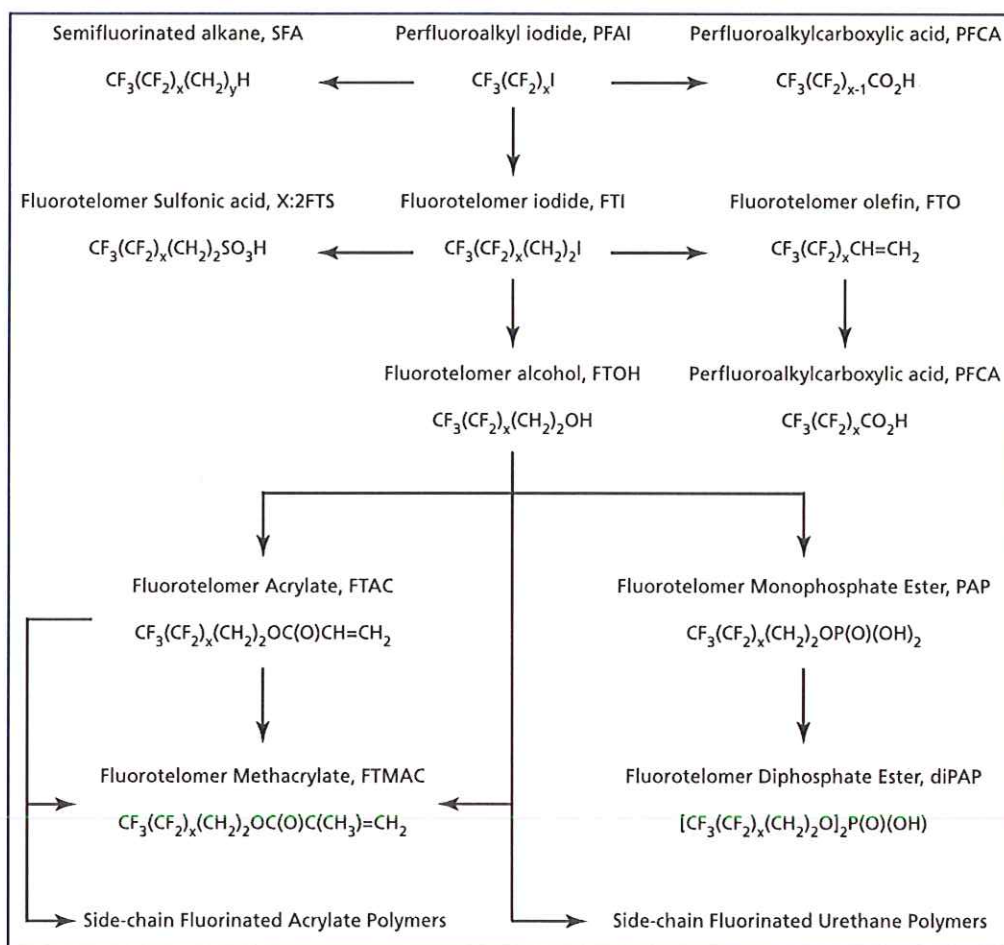
PFCA	$R_f\text{-CO}_2\text{H}$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 20	
PFAS	$R_f\text{-SO}_3^-$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 20	
PFASI	$R_f\text{-SO}_2^-$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 20	
FOSA	$R_f\text{-SO}_2\text{NH}_2$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 7$	
N-alkylFOSA	$R_f\text{-SO}_2\text{NRR}'$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 7$	R = Me or Et R' = H
FOSAA & N-alkylFOSAA	$R_f\text{-SO}_2\text{NRR}'$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 7$	R = $\text{CH}_2\text{CO}_2\text{H}$ R' = H or Me or Et
N-alkylFOSE	$R_f\text{-SO}_2\text{NRR}'$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 7$	R = $\text{CH}_2\text{CH}_2\text{OH}$ R' = Me or Et
FTOH	$R_f\text{-CH}_2\text{CH}_2\text{OH}$ $R_f\text{-CH(OH)CH}_3$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 15	
FTA	$R_f\text{-CH}_2\text{CO}_2\text{H}$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 15	
FTUA	$R_f\text{-CF=CHCO}_2\text{H}$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 15	
PFAPA	$R_f\text{-PO}_3\text{H}_2$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 15	
PFPi	$(R_f)_2\text{P(O)OH}$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 10	
PAP	$R_f\text{CH}_2\text{CH}_2\text{OP(O)(OH)}_2$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 10	
diPAP	$(R_f\text{CH}_2\text{CH}_2\text{O})_2\text{P(O)OH}$	$R_f = \text{CF}_3(\text{CF}_2)_n$	$n = 0$ to 10	

Commonly Used Units of Measure

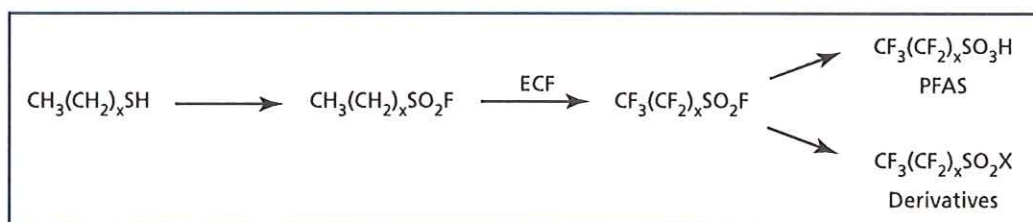
wt/wt basis				wt/vol basis			
ppm	mg/kg	$\mu\text{g/g}$	ng/mg	ppm	mg/l	$\mu\text{g/ml}$	ng/ μl
ppb	$\mu\text{g/kg}$	ng/g	pg/mg	ppb	$\mu\text{g/l}$	ng/ml	pg/ μl
ppt	ng/kg	pg/g	fg/mg	ppt	ng/l	pg/ml	fg/ μl
ppq	pg/kg	fg/g	ag/mg	ppq	pg/l	fg/ml	ag/ μl

The Telomerization and ECF Processes

Although perfluorinated products were historically produced using electrochemical fluorination, today the majority of industrially manufactured perfluorinated compounds are obtained through the telomerization process. This process generates a perfluoroalkyl iodide intermediate which can be utilized to produce a variety of fully and partially fluorinated compounds. The flow-chart below illustrates the synthesis of common perfluorinated products from a perfluoroalkyl iodide (*Integr Environ Assess Manag*, **2011**, 7, 513-541).



Perfluoroalkanesulfonates (PFAS) and perfluoroalkanesulfonyl fluorides are still being produced using electrochemical fluorination (ECF). This method commonly results in a mixture of linear and branched perfluorinated isomers and homologues.



Summary of LC/MS/MS Tune Parameters and Transitions

Perfluoroalkylcarboxylic Acids						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
PFBA	C ₄ HF ₇ O ₂	214.0396	10	8	213	169
PFBA [M+4]	¹³ C ₄ HF ₇ O ₂	218.0090	10	8	217	172
PFPeA	C ₅ HF ₉ O ₂	264.0474	10	9	263	219
PFPeA [M+3]	¹³ C ₃ ¹² C ₂ HF ₉ O ₂	267.0244	10	9	266	222
PFPeA [M+5]	¹³ C ₅ HF ₉ O ₂	269.0091	10	9	268	223
PFHxA	C ₆ HF ₁₁ O ₂	314.0552	10	9	313	269
PFHxA [M+2]	¹³ C ₂ ¹² C ₄ HF ₁₁ O ₂	316.0399	10	9	315	270
PFHxA [M+5]	¹³ C ₅ ¹² C ₁ HF ₁₁ O ₂	319.0169	10	9	318	273
PFHpA	C ₇ HF ₁₃ O ₂	364.0630	15	11	363	319
PFHpA [M+4]	¹³ C ₄ ¹² C ₃ HF ₁₃ O ₂	368.0324	15	11	367	322
PFOA	C ₈ HF ₁₅ O ₂	414.0708	15	11	413	369
PFOA [M+2]	¹³ C ₂ ¹² C ₆ HF ₁₅ O ₂	416.0555	15	11	415	370
PFOA [M+4]	¹³ C ₄ ¹² C ₄ HF ₁₅ O ₂	418.0402	15	11	417	372
PFOA [M+8]	¹³ C ₈ HF ₁₅ O ₂	422.0096	15	11	421	376
PFNA	C ₉ HF ₁₇ O ₂	464.0786	15	11	463	419
PFNA [M+5]	¹³ C ₅ ¹² C ₄ HF ₁₇ O ₂	469.0404	15	11	468	423
PFNA [M+9]	¹³ C ₉ HF ₁₇ O ₂	473.0098	15	11	472	427
PFDA	C ₁₀ HF ₁₉ O ₂	514.0864	15	13	513	469
PFDA [M+2]	¹³ C ₂ ¹² C ₈ HF ₁₉ O ₂	516.0711	15	13	515	470
PFDA [M+6]	¹³ C ₆ ¹² C ₄ HF ₁₉ O ₂	520.0405	15	13	519	474
PFuDA	C ₁₁ HF ₂₁ O ₂	564.0942	15	13	563	519
PFuDA [M+2]	¹³ C ₂ ¹² C ₉ HF ₂₁ O ₂	566.0789	15	13	565	520
PFuDA [M+7]	¹³ C ₇ ¹² C ₄ HF ₂₁ O ₂	571.0407	15	13	570	525
PFDoA	C ₁₂ HF ₂₃ O ₂	614.1020	20	13	613	569
PFDoA [M+2]	¹³ C ₂ ¹² C ₁₀ HF ₂₃ O ₂	616.0867	20	13	615	570
PFTrDA	C ₁₃ HF ₂₅ O ₂	664.1098	22	15	663	619
PFTeDA	C ₁₄ HF ₂₇ O ₂	714.1176	15	14	713	669
PFHxDA	C ₁₆ HF ₃₁ O ₂	814.1332	25	15	813	769
PFODA	C ₁₈ HF ₃₅ O ₂	914.1488	25	15	913	869

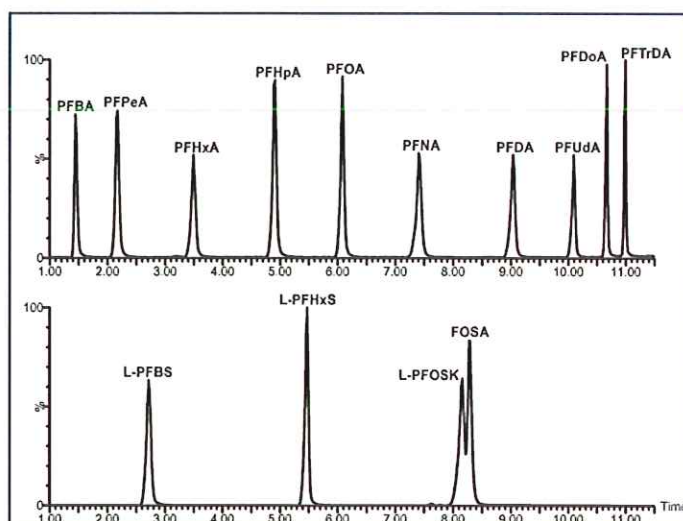
Perfluoroalkylsulfonates						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
KPFBS	C ₄ F ₉ SO ₃ K	338.1901	40	25	299	99
NaPFHxS	C ₆ F ₁₃ SO ₃ Na	422.0972	50	30	399	99
NaPFHxS [M+3]	¹³ C ₃ ¹² C ₃ F ₁₃ SO ₃ Na	425.0743	50	30	402	99
NaPFHxS [M+4]	C ₆ F ₁₃ ¹⁸ O ₂ ¹⁶ ONa	426.0968	50	30	403	103
NaPFHpS	C ₇ F ₁₅ SO ₃ Na	472.1050	60	35	449	99
KPFOS	C ₈ F ₁₇ SO ₃ K	538.2214	60	40	499	99
NaPFOS	C ₈ F ₁₇ SO ₃ Na	522.1129	62	40	499	99
NaPFOS [M+4]	¹³ C ₄ ¹² C ₄ F ₁₇ SO ₃ Na	526.0823	62	40	503	99
NaPFOS [M+8]	¹³ C ₈ F ₁₇ SO ₃ Na	530.0517	62	40	507	99
NaPFDS	C ₁₀ F ₂₁ SO ₃ Na	622.1285	70	50	599	99
NaPFDoS	C ₁₂ F ₂₅ SO ₃ Na	722.1441	80	50	699	99

Summary of LC/MS/MS Tune Parameters and Transitions

Perfluorooctanesulfonamides						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
FOSA	C ₈ H ₂ F ₁₇ NO ₂ S	499.1462	40	30	498	78
FOSA [M+8]	¹³ C ₈ H ₂ F ₁₇ NO ₂ S	507.0851	40	30	506	78
N-MeFOSA	C ₉ H ₄ F ₁₇ NO ₂ S	513.1731	45	25	512	169
N-MeFOSA [M+3]	C ₉ ² H ₃ HF ₁₇ NO ₂ S	516.1913	45	25	515	169
N-EtFOSA	C ₁₀ H ₆ F ₁₇ NO ₂ S	527.2000	40	25	526	169
N-EtFOSA [M+5]	C ₁₀ ² H ₅ HF ₁₇ NO ₂ S	532.2303	40	25	531	169

Perfluorooctanesulfonamidoethanols						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
N-MeFOSE	C ₁₁ H ₈ F ₁₇ NO ₃ S	557.2263	40	35	556	122
N-MeFOSE [M+7]	C ₁₁ ² H ₇ HF ₁₇ NO ₃ S	564.2694	40	35	563	126
N-EtFOSE	C ₁₂ H ₁₀ F ₁₇ NO ₃ S	571.2532	40	33	570	136
N-EtFOSE [M+9]	C ₁₂ ² H ₉ HF ₁₇ NO ₃ S	580.3086	40	33	579	142

Perfluorooctanesulfonamidoacetic acids						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
FOSAA	C ₁₀ H ₄ F ₁₇ NO ₄ S	557.1829	35	25	556	498
N-MeFOSAA	C ₁₁ H ₆ F ₁₇ NO ₄ S	571.2098	35	20	570	419
N-MeFOSAA [M+3]	C ₁₁ ² H ₅ H ₃ F ₁₇ NO ₄ S	574.2280	32	20	573	419
N-EtFOSAA	C ₁₂ H ₈ F ₁₇ NO ₄ S	585.2367	35	20	584	419
N-EtFOSAA [M+5]	C ₁₂ ² H ₇ H ₃ F ₁₇ NO ₄ S	590.2670	32	20	589	419



The LC/MS/MS parameters presented were determined using a Micromass Quattro micro API MS and are meant as starting points only. Further optimization is recommended.

Summary of LC/MS/MS Tune Parameters and Transitions

Fluorinated Telomer Alcohols						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
4:2 FTOH	C ₆ H ₅ F ₉ O	264.0907	15	12	263	203
4:2 FTOH [M+4]	C ₆ ² H ₄ HF ₉ O	268.1150	15	12	266	204
6:2 FTOH	C ₈ H ₅ F ₁₃ O	364.1063	13	9	363	303
6:2 FTOH [M+4]	¹³ C ₂ ¹² C ₆ ² H ₂ H ₃ F ₁₃ O	368.1032	13	9	367	306
7:2 sFTOH	C ₉ H ₅ F ₁₅ O	414.1141	20	14	393	219
8:2 FTOH	C ₁₀ H ₅ F ₁₇ O	464.1220	14	12	463	403
8:2 FTOH [M+4]	¹³ C ₂ ¹² C ₈ ² H ₂ H ₃ F ₁₇ O	468.1188	14	12	467	406
10:2 FTOH	C ₁₂ H ₅ F ₂₁ O	564.1376	13	11	563	503
10:2 FTOH [M+4]	¹³ C ₂ ¹² C ₁₀ ² H ₂ H ₃ F ₂₁ O	568.1344	13	11	567	506

Fluorinated Telomer Acids						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
6:2 FTA	C ₈ H ₃ F ₁₃ O ₂	378.0899	15	15	377	293
6:2 FTA [M+2]	¹³ C ₂ ¹² C ₆ H ₃ F ₁₃ O ₂	380.0746	15	15	379	294
8:2 FTA	C ₁₀ H ₃ F ₁₇ O ₂	478.1055	14	15	477	393
8:2 FTA [M+2]	¹³ C ₂ ¹² C ₈ H ₃ F ₁₇ O ₂	480.0902	14	15	479	394
10:2 FTA	C ₁₂ H ₃ F ₂₁ O ₂	578.1211	15	15	577	493
10:2 FTA [M+2]	¹³ C ₂ ¹² C ₁₀ H ₃ F ₂₁ O ₂	580.1058	15	15	579	494
3:3 FTA	C ₆ H ₅ F ₇ O ₂	242.0933	15	8	241	177
5:3 FTA	C ₈ H ₅ F ₁₁ O ₂	342.1089	15	10	341	237
7:3 FTA	C ₁₀ H ₅ F ₁₅ O ₂	442.1245	15	10	441	337

Fluorinated Telomer Unsaturated Acids						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
6:2 FTUA	C ₈ H ₂ F ₁₂ O ₂	358.0835	14	21	357	293
6:2 FTUA [M+2]	¹³ C ₂ ¹² C ₆ H ₂ F ₁₂ O ₂	360.0682	14	21	359	294
8:2 FTUA	C ₁₀ H ₂ F ₁₆ O ₂	458.0991	14	21	457	393
8:2 FTUA [M+2]	¹³ C ₂ ¹² C ₈ H ₂ F ₁₆ O ₂	460.0838	14	21	459	394
10:2 FTUA	C ₁₂ H ₂ F ₂₀ O ₂	558.1147	14	21	557	493
10:2 FTUA [M+2]	¹³ C ₂ ¹² C ₁₀ H ₂ F ₂₀ O ₂	560.0995	14	21	559	494

Fluorinated Telomer Sulfonates						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
4:2 FTS	C ₆ H ₄ F ₉ SO ₃ Na	350.1354	25	20	327	307
6:2 FTS	C ₈ H ₄ F ₁₃ SO ₃ Na	450.1510	25	20	427	407
8:2 FTS	C ₁₀ H ₄ F ₁₇ SO ₃ Na	550.1666	25	25	527	507

Summary of LC/MS/MS Tune Parameters and Transitions

Perfluoroalkylphosphonic acids						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
PFHxPA	C ₆ H ₂ F ₁₃ PO ₃	400.0331	40	35	399	79
PFOPA	C ₈ H ₂ F ₁₇ PO ₃	500.0487	40	35	499	79
PFDDPA	C ₁₀ H ₂ F ₂₁ PO ₃	600.0643	45	35	599	79
Cl-PFHxPA	C ₆ H ₂ ClF ₁₂ PO ₃	416.4877	40	35	415	79

Sodium Perfluoroalkyl Phosphinates						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
6:6PFPI	C ₁₂ F ₂₆ PO ₂ Na	724.0528	80	45	701	401
6:8PFPI	C ₁₄ F ₃₀ PO ₂ Na	824.0685	80	45	801	501
8:8PFPI	C ₁₆ F ₃₄ PO ₂ Na	924.0841	80	45	901	501

Mono-Substituted Polyfluorinated Phosphate Esters						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
6:2PAP	C ₈ H ₄ F ₁₃ PO ₄ Na ₂	488.0500	25	20	443	97
6:2PAP [M+2]	¹³ C ₂ ¹² C ₆ H ₄ F ₁₃ PO ₄ Na ₂	490.0347	25	20	445	97
8:2PAP	C ₁₀ H ₄ F ₁₇ PO ₄ Na ₂	588.0656	25	20	543	97
8:2PAP [M+2]	¹³ C ₂ ¹² C ₈ H ₄ F ₁₇ PO ₄ Na ₂	590.0503	25	20	545	97

Di-Substituted Polyfluorinated Phosphate Esters						
Compound	Molecular Formula	Molecular Weight	Cone (V)	Collision (eV)	Precursor Ion (m/z)	Product Ion (m/z)
6:2diPAP	C ₁₆ H ₈ F ₂₆ PO ₄ Na	812.1592	30	20	789	443
6:2diPAP [M+4]	¹³ C ₄ ¹² C ₁₂ H ₈ F ₂₆ PO ₄ Na	816.1286	30	20	793	445
8:2diPAP	C ₂₀ H ₈ F ₃₄ PO ₄ Na	1012.1904	35	25	989	543
8:2diPAP [M+4]	¹³ C ₄ ¹² C ₁₆ H ₈ F ₃₄ PO ₄ Na	1016.1598	35	25	993	545

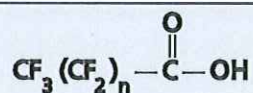
The masses utilized to calculate the molecular weights stated in this reference guide are as follows:

¹² C = 12.011	N = 14.0067	P = 30.97376
¹³ C = 13.003355	O = 15.9994	Na = 22.9898
H = 1.00794	F = 18.998403	K = 39.0983
² H = 2.014	S = 32.064	

Reference = <http://web/utk.edu/~bartmess/massabun.txt>

The LC/MS/MS parameters presented were determined using a Micromass Quattro micro API MS and are meant as starting points only. Further optimization is recommended.

Perfluoroalkylcarboxylic Acids (PFCAs)



Acronyms

n=2	PFBA	n=7	PFNA	n=12	PFTeDA
n=3	PFPeA	n=8	PFDA	n=13	PFPeDA
n=4	PFHxA	n=9	PFUdA	n=14	PFHxDA
n=5	PFHpA	n=10	PFDoA	n=15	PFHpDA
n=6	PFOA	n=11	PFTTrDA	n=16	PFODA

Stability

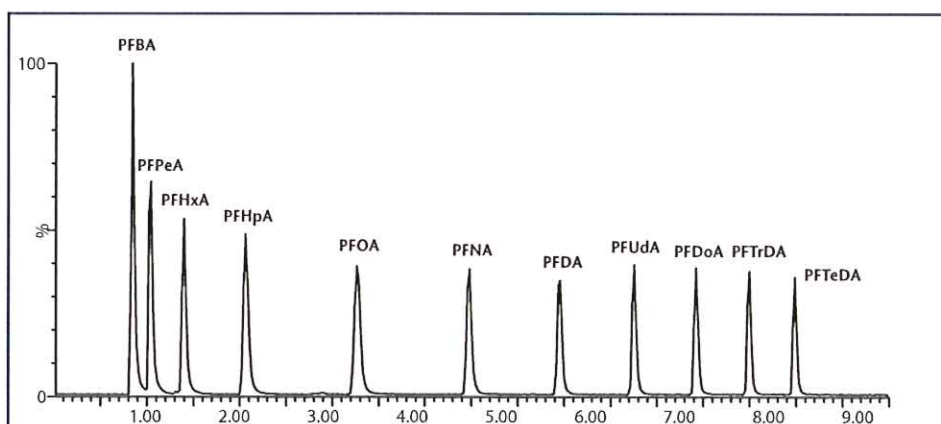
- Methanolic solutions of PFCAs will lead to the formation of methyl esters unless at least 1 molar equivalent of base is present in solution to prevent this reaction.

Analytical Challenges

- The limited solubility of the higher molecular weight PFCAs could affect the chromatography of these compounds if a high water gradient is used.
- PFC contamination may arise from Teflon lines, caps, solvents and other sources.

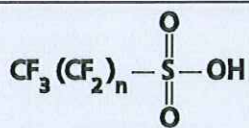
Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.
- Standard solutions should be stored at refrigerator temperatures to further decrease the likelihood of esterification and also minimize the evaporation of methanol.



LC Elution Profile for the C4 to C14 PFCAs.

Please contact us if additional information is desired.



Perfluoroalkylsulfonates (PFASs)

Acronyms

n=3	PFBS	n=8	PFNS
n=4	PFPeS	n=9	PFDS
n=5	PFHxS	n=10	PFUdS
n=6	PFHpS	n=11	PFDoS
n=7	PFOS		

Stability

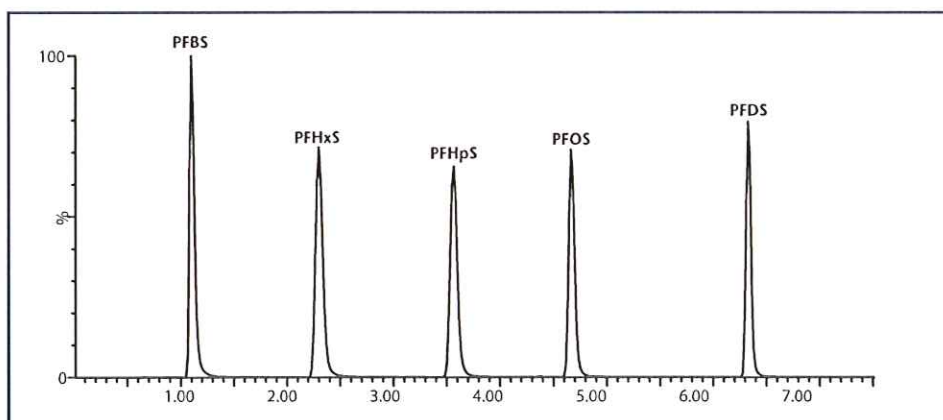
- PFASs should have unlimited stability in methanol.

Analytical Challenges

- Commercially available technical PFOS samples differ in purity and therefore should not be used as quantitative standards without accounting for purity and counter-ion.
- It has been reported that ^{18}O -mass labelled perfluoroalkylsulfonates can undergo isotopic exchange with water under certain conditions thus lowering the isotopic purity of the standards over time.

Recommended Storage

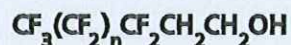
- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.
- Please be aware that solid salts of these compounds tend to absorb water from the atmosphere to form hydrates.



LC Elution Profile for the C4, C6, C7, C8 and C10 PFASs.

Please contact us if additional information is desired.

Telomer Alcohols (FTOHs)



Acronyms

n=2	4:2 FTOH (FBET)
n=4	6:2 FTOH (FHET)
n=6	8:2 FTOH (FOET)
n=8	10:2 FTOH (FDET)

Stability

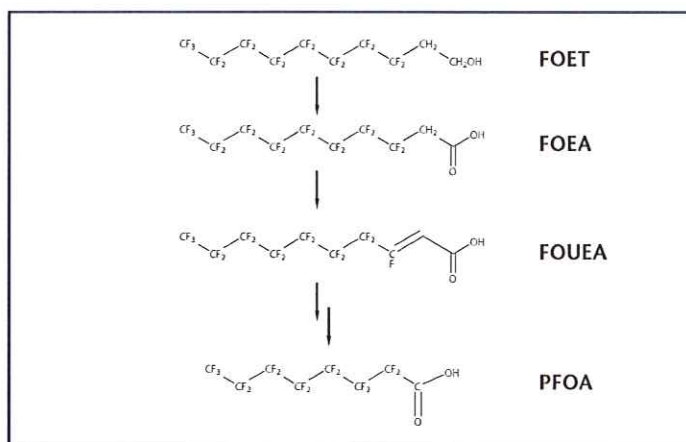
- It is possible to form the unsaturated alcohol through loss of HF.
- Oxidation of these compounds to form the corresponding saturated and unsaturated telomer acids is also possible.

Analytical Challenges

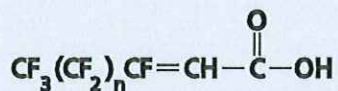
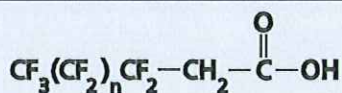
- Telomer alcohols are much more difficult to ionize than the PFCAs or PFASs.
- The hydroxyl group proton is not removed during electrospray ionization. Deprotonation of the second carbon gives rise to the charged species.
- These compounds form adducts readily. Therefore in order to detect the $[\text{M}-\text{H}]^-$ ion in negative electrospray ionization, it is necessary to remove all buffer from the LC system.
- The LC/MS system can be purged of the acetate buffer through extensive flushing. Formate adducts arising from the methanol can be reduced by sonicating the mobile phase and then flushing the system.
- It may be possible to modify MS parameters to decluster adducts in the source.
- The response for the alcohols can be lower relative to that obtained for some of the acetate adducts.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.
- Storage of these solutions at refrigerator temperatures will slow degradation.



Possible Degradation Products of the 8:2 Telomer Alcohol



X:2 Saturated and Unsaturated Telomer Acids (X:2 FTAs and X:2 FTUAs)

Acronyms

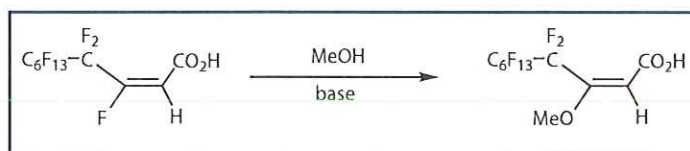
	<u>Saturated</u>	<u>Unsaturated</u>
n=4	6:2 FTA (FHEA)	6:2 FTUA (FHUEA)
n=6	8:2 FTA (FOEA)	8:2 FTUA (FOUEA)
n=8	10:2 FTA (FDEA)	10:2 FTUA (FDUEA)

Stability of Saturated Acids

- Conversion of the saturated telomer acid to its unsaturated form is easily achieved in the presence of base.
- Storage of these compounds at 4°C in isopropanol (IPA) with a small amount of HCl significantly extends their shelf-life.
- The basicity of the glass that these compounds are stored in also has an impact on their dehydrofluorination rates with more basic glassware leading to increased formation of the unsaturated species.

Stability of Unsaturated Acids

- It is known that unsaturated telomer acids can react with methanol in the presence of base to form methoxy-substituted unsaturated telomer acids at a rate of approximately 1% per year at ambient temperature.
- Storage of these compounds at 4°C reduces the rate of the methoxy formation.



Conversion of FOUEA to MeO-FOUEA.

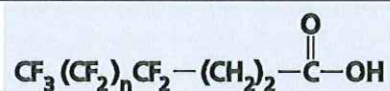
Analytical Challenges

- The saturated telomer acids and their unsaturated counterparts are difficult to separate using conventional C18 columns. Utilization of a UPLC, or columns with embedded polar groups or a perfluorinated stationary phase, improves separation.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.
- Avoid contact with base and store saturated standards in IPA in the presence of HCl.

X:3 Saturated Telomer Acids (X:3 FTAs)



Acronyms

n=1	3:3 FTA (FPrPA)
n=3	5:3 FTA (FPePA)
n=5	7:3 FTA (FHpPA)

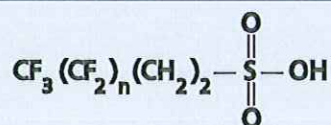
Stability

- It is possible to form the unsaturated X:3 FTA through loss of HF, however the probability of this process occurring is significantly lower than in the X:2 FTAs since an additional carbon is insulating the perfluoroalkyl chain from the carboxylic functional group.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.

X:2 Telomer Sulfonates (X:2 FTSs)



Acronyms

n=3	4:2FTS
n=5	6:2FTS
n=7	8:2FTS

Stability

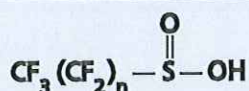
- It is possible to form the unsaturated X:2 telomer sulfonates in the presence of strong acid or base.

Analytical Challenges

- Matrix effects can have a large impact on the ionization of these compounds. For this reason, mass-labelled perfluoroalkylsulfonates do not make ideal surrogates.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.



Perfluoroalkylsulfonates (PFASis)

Acronyms

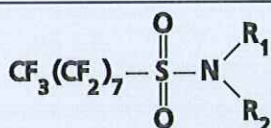
n=3	PFBSi	n=7	PFOSi
n=5	PFHxSi	n=9	PFDSi

Stability

- Sulfonates will easily oxidize to sulfonates in the presence of oxygen.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.
- It is difficult to avoid some oxidation of the sulfonates to their corresponding sulfonates. Storage of the standard solutions at refrigerator temperatures will slow this conversion.



Perfluorooctanesulfonamides (FOSAs)

Acronyms

R ₁ =R ₂ =H	FOSA
R ₁ =H, R ₂ =CH ₃	N-MeFOSA
R ₁ =R ₂ =CH ₃	N,N-Me ₂ FOSA
R ₁ =H, R ₂ =CH ₂ CH ₃	N-EtFOSA

Stability

- Oxidation of perfluorooctanesulfonamides can result in the formation of PFOS and PFOA.

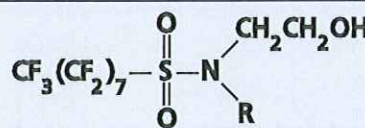
Analytical Challenges

- The N,N-Me₂FOSA is not detectable using negative electrospray ionization.
- The secondary amides have proven to be of limited utility as surrogates for the primary amide.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.

Perfluorooctanesulfonamidoethanols (FOSEs)



Acronyms

R=CH ₃	N-MeFOSE
R=CH ₂ CH ₃	N-EtFOSE

Stability

- Oxidation of perfluorooctanesulfonamidoethanols may result in the formation of PFOS and PFOA.

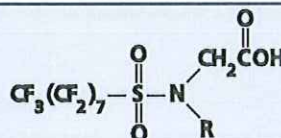
Analytical Challenges

- These compounds form adducts readily. Therefore in order to detect the [M-H]⁻ ion in negative electrospray, it is necessary to remove all buffer from the LC system.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.

Perfluorooctanesulfonamidoacetic acids (FOSAAs)



Acronyms

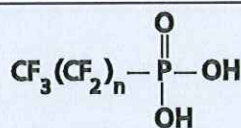
R=H	FOSAA
R=CH ₃	N-MeFOSAA
R=CH ₂ CH ₃	N-EtFOSAA

Stability

- Oxidation of perfluorooctanesulfonamidoacetic acids may result in the formation of PFOS and PFOA.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.



Perfluoroalkylphosphonic acids (PFAPAs)

Acronyms

n=5	PFHxPA
n=7	PFOPA
n=9	PFDPA

Stability

- It is possible for phosphonic anhydrides to form when heating these compounds under vacuum.
- These compounds also tend to form hydrates.

Analytical Challenges

- HPLC mobile phases may have to be adjusted to achieve adequate chromatography. We recommend using an aqueous mobile phase adjusted to pH 9 with ammonium hydroxide and diluting the PFAPA solution with 75:25 MeOH:aqueous ammonia (pH 9).
- All PFAPAs were detected as the phosphonate monoanion using our LC/ESI-MS conditions.
- These compounds tend to strongly adhere to some surfaces such as metals.

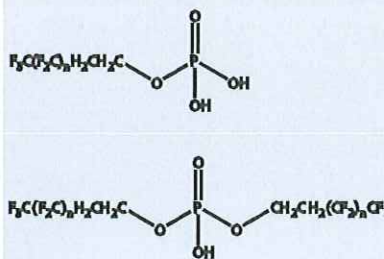
Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.

Approximate pKa Values

Compound	pK ₁	pK ₂
PFHxPA	2.1	4.4
PFOPA	2.4	4.5
PFDPA	3.4	5.6
Cl-PFHxPA	2.1	4.5

Polyfluorinated Phosphate Esters (PAPs & diPAPs)



Acronyms

	<u>PAPs</u>	<u>diPAPs</u>
n=5	6:2PAP	6:2diPAP
n=7	8:2PAP	8:2diPAP

Stability

- The phosphate ester linkages for both mono- and di-PAPs have been shown to be stable to abiotic hydrolysis.

Analytical Challenges

- The affinity of these compounds to metal surfaces can result in peak tailing during HPLC analysis.
- The response of the monoPAPs can be optimized, and peak tailing minimized, by utilizing a methanol:water gradient where the pH of the water has been adjusted to 11 with ammonium hydroxide.
- Increasing the pH of the mobile phase to 11 may suppress the formation of aggregates thus improving chromatography and signal response.
- Laboratory contamination of native PAPs and diPAPs may be an issue since these compounds are commonly used to treat paper products.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.

Approximate pKa Values

Compound	pK ₁	pK ₂
6:2PAP	3.0	7.0
8:2PAP	3.2	6.3



Acronyms

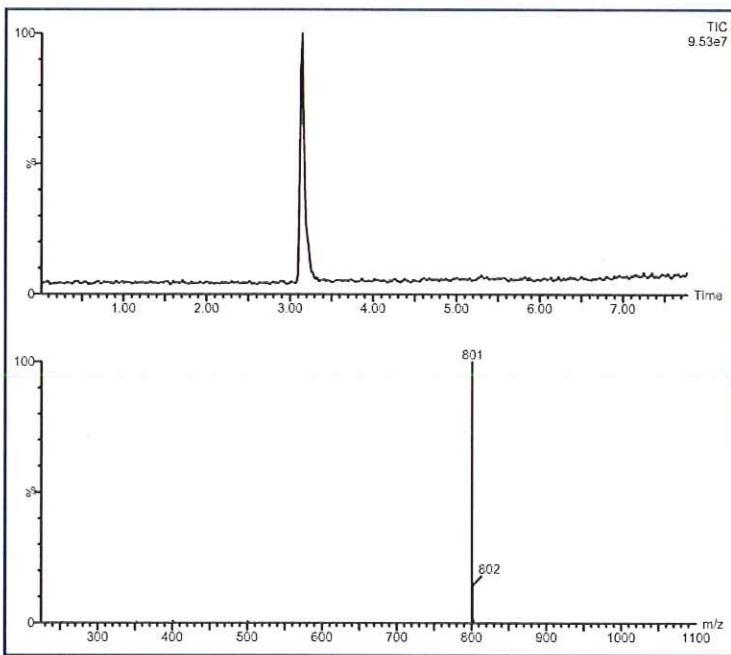
n=m=4	6:6PFPi
n=4, m=6	6:8PFPi
n=m=6	8:8PFPi

Stability

- No issues regarding the stability of perfluoroalkylphosphinates in methanol have been identified.

Recommended Storage

- All diluted solutions should be stored in glassware that has been thoroughly rinsed with methanol.
- Teflon lined caps should not be used in order to avoid contamination with small amounts of residual perfluorinated compounds.



UPLC full scan chromatogram and mass spectrum of 6:8PFPi.
Please contact us if additional information is desired.

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