



The Analysis of Per (poly) Fluorinated Compounds – Beyond UCMR3

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Perfluorinated Compounds



Perfluorinated Compounds (PFCs) are a class of compounds that have been in use since the late 1940's, early 1950's. They have been used as additives in fluoropolymer production and as surfactants for numerous consumer applications;

- Stain resistant coatings for furniture and carpeting
- Coatings for fast food wrappers and boxes
- Breathable waterproof fabrics

Perfluorinated Compounds



Perfluorinated Compounds (PFCs) were also used in Aqueous Film Forming Foams (AFFF). Developed by 3M and US Navy in the 1960's. The low surface tension and positive spreading coefficient enabled film formation on top of lighter, less dense fuels.

Perfluorinated Compounds



- Environmental release occurs through production and use in fluoropolymer production
- Leaks from storage tanks and pipelines
- Emergency activation of fire suppression systems
- Fire training exercises



Perfluorinated Compounds



Will typically see this class of compounds abbreviated in several different ways;

- PFCs - perfluorinated compounds
- PFAA – perfluorinated alkyl acids
- PFAS – polyfluorinated alkyl substances

PFAS is gaining greater recognition because not all of the chemistries are perfluorinated

Perfluorinated Compounds



There are several chemistries that are being looked at;

- perfluorinated carboxylic acids
- perfluorinated sulfonic acids/sulfonates
- perfluorinated telomer sulfonates (polyfluorinated)
- perfluorinated sulfonamides
- fluorotelomer alcohols

Perfluorinated Compounds



Perfluorobutanoic acid	Perfluorobutanesulfonate
Perfluoropentanoic acid	Perfluorohexanesulfonate
Perfluorohexanoic acid	Perfluoroheptanesulfonate
Perfluorheptanoic acid	Perfluorooctanesulfonate
Perfluorooctanoic acid	Perfluorodecanesulfonate
Perfluorononanoic acid	Perfluorooctanesulfonamide
Perfluorodecanoic acid	Methylperfluoro-1-octanesulfonamide
Perfluoroundecanoic acid	Ethylperfluoro-1-octanesulfonamide
Perfluorododecanoic acid	4:2 Fluorotelomer sulfonate
Perfluorotridecanoic acid	6:2 Fluorotelomer sulfonate
Perfluorotetradecanoic acid	8:2 Fluorotelomer sulfonate
Perfluorohexadecanoic acid	10:2 Fluorotelomer sulfonate
N-methylperfluoro-1-octanesulfonamidoacetic acid	
N-ethylperfluoro-1-octanesulfonamidoacetic acid	
2-(N-methylperfluoro-1-octanesulfamido)-ethanol	
2-(N-ethylperfluoro-1-octanesulfamido)-ethanol	

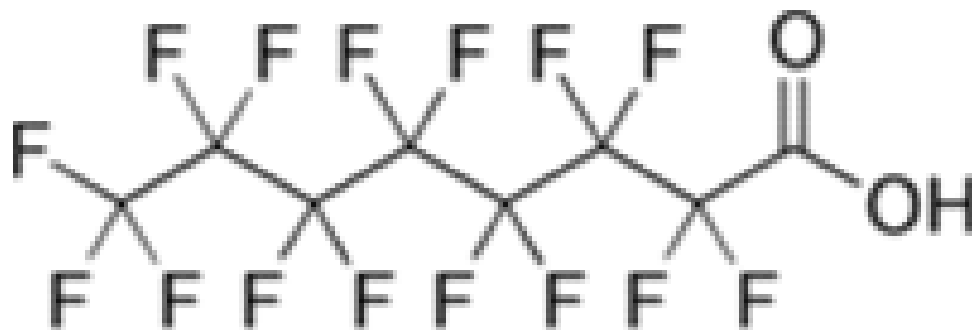
Perfluorinated Compounds



However, out of these chemistries there are two compounds that have received the most attention;

- a. PFOA - was used as a surfactant in the manufacture of fluoropolymers – DuPont
- b. PFOS - was the principle component in Scotchgard and AFFF manufactured by 3M – manufacture by 3M has been discontinued since 2002

PFCs



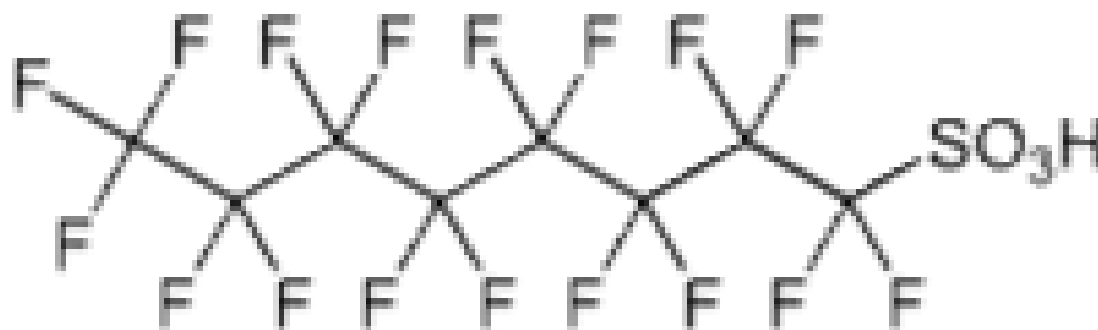
Perfluorooctanoic acid (also known as PFOA)

MW = 414 amu

BP = 189-192 °C

Density = 1.8 grams/ml

PFCs



Perfluorooctane sulfonic acid (also known as PFOS)

MW = 500 amu

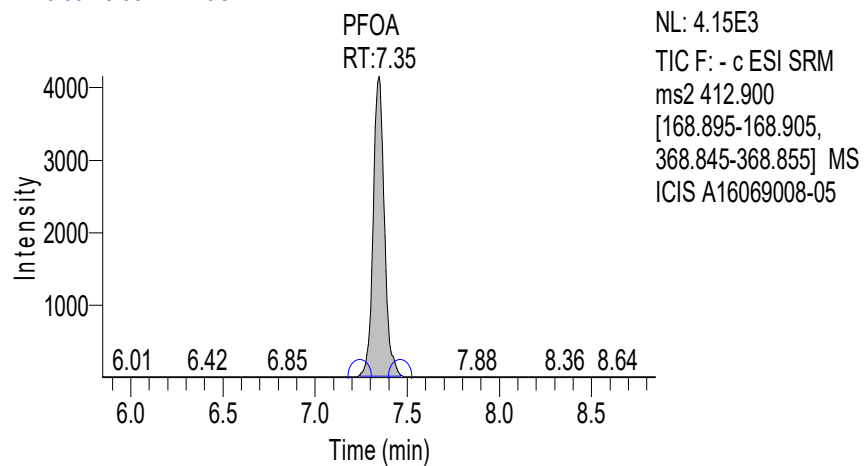
BP = 133 °C at 6 torr

Analytical Methodology

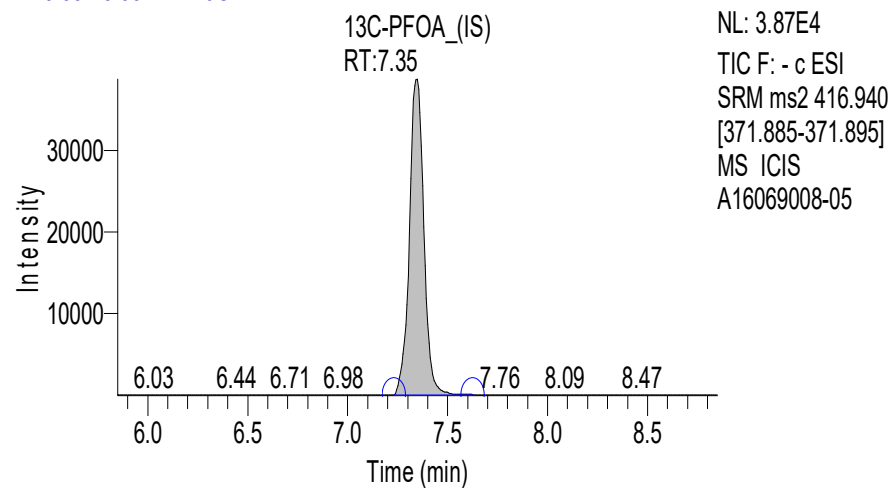


Component Name: PFOA

RT: 5.85 - 8.85 SM: 3G



RT: 5.85 - 8.85 SM: 3G



Analytical Methodology



LCMSMS ANALYSIS REPORT

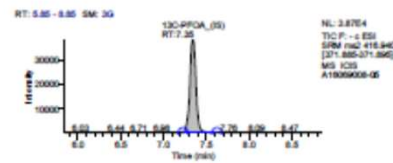
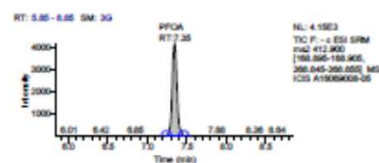
Sample Name:	CAL2	Original Data Path:	C:\XCALIBUR\PFC\2016\MCK
Sample ID:	CAL2	Instrument Method:	C:\XCalibur\PC\Acquisition
Data File:	A16069008-05	M.PFOAOS	
Acquisition Date:	03/11/16 10:23:38 AM	Dilution Factor:	1.00
Sample Type:	Std Bracket	Instrument Model:	TSQ Quantum Access
Vial:	e:4	Instrument Software Version:	2.3.0.1206 SP1
Run Time(min):	15.00	Instrument Serial Number:	TQU01408
Injection Volume(µl):	10.00	Operator:	Quantum

Quan Peak Table

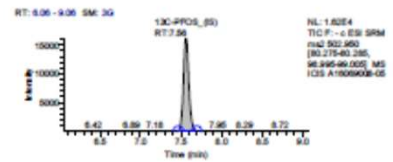
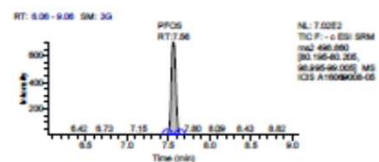
Component Name	Calculated Amount	RT	Response	ISTD Response	Response Ratio	Units
13C-PFOA_(IS)	N/A	7.35	193953.85	N/A	N/A	N/A
13C-PFOS_(IS)	N/A	7.56	75674.71	N/A	N/A	N/A
PFOA	4.787	7.35	17505.78	193953.85	0.090	ng/L
PFOS	9.023	7.56	2612.36	75674.71	0.035	ng/L

Extracted Ion Chromatogram

Component Name: PFOA



Component Name: PFOS



PFCs



- The fluorine substitution gives this class of compounds unique characteristics
- Contain a hydrophobic, fully fluorinated carbon chain
- Also contains a hydrophilic functional group
- Acids have low pKa's and therefore at environmental pHs are soluble to moderately water soluble

PFCs



- PFCs are generally chemically and biologically stable. Resist typical environmental degradation processes
- PFCs bioaccumulate and by some estimates are present in blood serum of up to 98% of wildlife
- PFOS added to Stockholm Convention list of Persistent Organic Pollutants and PFOA being considered
- Specific toxicological and eco-toxicological studies are few so exact impacts not well understood.

Advisory Limits



- EPA Office of Water established Provisional Health Advisory (PHA)*

PFOS = 0.2 ug/l PFOA = 0.4 ug/l

- Minnesota one of few states with any regulatory action limits

PFOS = 0.3 ug/l PFBS = 7 ug/l
PFOA = 0.3 ug/l PFBA = 7 ug/l

- New Jersey preliminary health based guidance

PFOA = 0.04 ug/l PFNA = 0.01 ug/l
PFOS = 0.2 ug/l

- EPA Region 4 levels in soils

PFOS = 6 mg/kg PFOA = 16 mg/kg

Advisory Limits - Update



- * The U.S. Environmental Protection Agency (EPA) is issuing a lifetime drinking water Health Advisory (HA) for PFOA of 0.07 micrograms per liter ($\mu\text{g/L}$) based on a reference dose (RfD) derived from a developmental toxicity study in mice; the critical effects included reduced ossification in proximal phalanges and accelerated puberty in male pups following exposure during gestation and lactation.

EPA Document Number: 822-R-16-005 May 2016

The U.S. Environmental Protection Agency (EPA) is issuing a lifetime drinking water health advisory (HA) for PFOS of 0.07 micrograms per liter ($\mu\text{g/L}$) based on a reference dose (RfD) derived from a developmental toxicity study in rats; the critical effect was decreased pup body weight following exposure during gestation and lactation.

EPA Document Number: 822-R-16-004 May 2016



Perfluorinated Compounds (PFCs): EPA Method 537 included as UCMR3 List 1 Contaminants;

<u>Compound</u>	<u>MRL ug/l</u>
Perfluorooctanesulfonic acid	0.04
Perfluorooctanoic acid	0.02
Perfluorononanoic acid	0.02
Perfluorohexanesulfonic acid	0.03
Perfluoroheptanoic acid	0.01
Perfluorobutanesulfonic acid	0.09

For Comparison...



Analyte	Acronym	Water Reporting Limits LOQ (ng/L)	Soil Reporting Limits LOQ (ng/g)
Perfluorohexanoic acid	PFHxA	2	0.4
Perfluoroheptanoic acid	PFHpA	2	0.6
Perfluorooctanoic acid	PFOA	2	0.6
Perfluorononanoic acid	PFNA	2	0.4
Perfluorodecanoic acid	PFDA	2	0.4
Perfluoroundecanoic acid	PFUnDA	4	0.6
Perfluorododecanoic acid	PFDoA	4	0.8
Perfluorotridecanoic acid	PFTTrDA	4	1.2
Perfluorotetradecanoic acid	PFTeDA	4	0.8
Perfluorobutanesulfonate	PFBS	10	1.6
Perfluorohexanesulfonate	PFHxS	10	1.6
Perfluoro-octanesulfonate	PFOS	10	1.6
8:2 fluorotelomersulfonate	8:2 FtS	2	0.8

Perfluorinated Compounds



Solicitations for capabilities for analysis of PFCs often request a “UCMR3” certified lab.

“UCMR3” certified lab would have been certified for EPA Method 537, Version 1.1.

EPA Method 537, as written, has some limitations as to its application

Analytical Methodology



There is only one EPA “sanctioned” method for the analysis of perfluorinated compounds – EPA Method 537, Version 1.1

- Drinking water method – prescriptive list of compounds
- Uses LC/MS/MS which is the analytical technique of choice
- Has some limitations in the range of compounds that can be accommodated
- Many labs reference a 537 Modified

Analytical Methodology



- ISO Method 25101: 2009 often referenced, more amenable to surface water and wastewater
- ASTM Methods D7979-15 and D7968-14 address water, sludges and soils but have not been subject to an EPA validation
- No established method for soils, so often certify to lab SOP

Analytical Methodology



- In general, water methods use solid phase extraction (SPE) for the removal of PFCs from aqueous matrix
- Soil methods involve extraction with solvent and/or water
- LC/MS/MS is an analytical technique that not all laboratories have mastered
- Analysis conditions important – soft ionization technique

Analytical Methodology



- Concern for potential for background contamination
- Avoid use of PTFE materials in lab and in sampling program
- Samples collected in plastic (polypropylene or polyethylene) containers
- All materials should be checked for background

Analytical Methodology



- Wastewater and groundwater may well have significant particulate matter
- Typically would centrifuge and or filter
- Is filtering appropriate?
- What about treatment of soil extracts?
- Filter? SPE?

Analytical Methodology



- Sample containers – Impact?
- Use/necessity of Trizma for waters
- Polypropylene as listed in EPA 537
- HDPE or amber glass?
- Soils and or tissues

Analytical Methodology



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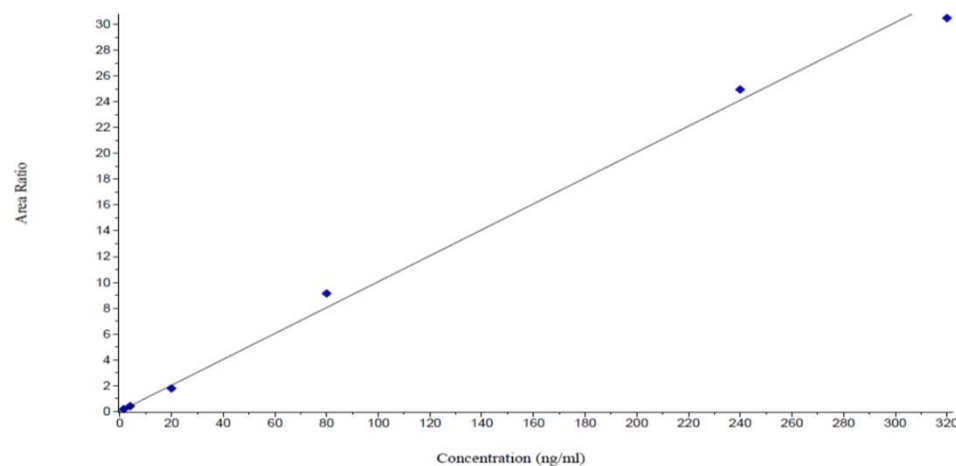
LC-MS/MS Analysis Report

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Initial Calibration
Results Table Name: 16131008.rdb

Component Name: **PFBS**

16131008.rdb (PFBS): "Linear" Regression ("1 / x" weighting):
 $y = 0.1x + 0.00694$ ($r = 0.9977$)



Standard Error Table

File Name	Sample Name	PFBS Area	13CPFHxS Area	Area Ratio	RT	Specified Amount	Calculated Amount	% Diff
A16131008\003.wiff	CAL1	32691.	190398.	0.172	8.99	1.600	1.640	2.44
A16131008\004.wiff	CAL2	79272.	197997.	0.400	9.00	4.000	3.916	-2.04
A16131008\005.wiff	CAL3	421462.	237996.	1.771	9.00	20.000	17.557	-13.90
A16131008\006.wiff	CAL4	1467808.	160655.	9.136	9.17	80.000	90.870	11.96
A16131008\007.wiff	CAL5	3167593.	126982.	24.945	9.01	240.000	248.221	3.31
A16131008\008.wiff	CAL6	3464760.	113641.	30.489	9.18	320.000	303.397	-5.47



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Analytical Methodology



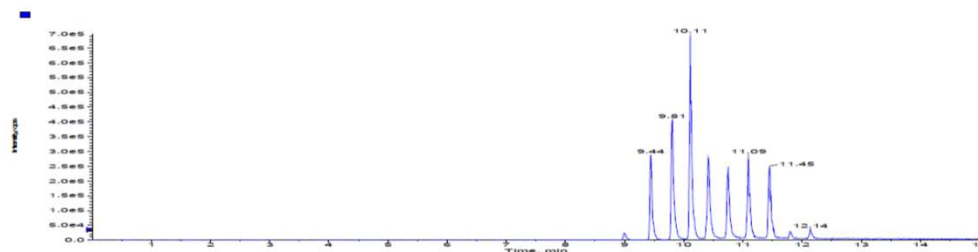
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LC-MS/MS Analysis Report

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Sample Name:	CAL2	Data File:	A16131008\004.wiff
Sample ID:	CAL2	Acquisition Date:	5/17/2016 1:47:19 AM
Sample Type:	Standard	Instrument Name:	API 4000
Sample Matrix:		Acquisition Method:	CTMale.dam
Vial:	14.	Result Table:	16131008.rdb
Dilution Factor:	1.00	Injection Vol (µl):	10.00
Batch Number:	16131001.dab	Operator:	US19_USR_INS04228

Total Ion Chromatogram



Quantitation Peak Table

Component Name	RT	Calculated Amount	Area	IS Name	ISTD Area	Area Ratio	Units
PFBS	9.00	3.916	79272.	13CPFHxS	197997.	0.400	ng/g
PFHxA	9.45	0.849	38840.	13CPFHxA	769400.	0.050	ng/g
PFHpA	9.81	0.929	52039.	13CPFHpA	913902.	0.057	ng/g
PFHxS	9.80	3.890	85616.	13CPFHxS	197997.	0.432	ng/g
PFOA	10.10	0.889	88941.	13CPFOA	1656887.	0.054	ng/g
PFNA	10.40	1.007	122504.	13CPFNA	680218.	0.180	ng/g
PFOS	10.40	3.675	39687.	13CPFOS	97694.	0.406	ng/g
PFDA	10.70	0.921	84444.	13CPFDA	678596.	0.124	ng/g
PFUnA	11.10	1.056	75519.	13CPFUnA	743309.	0.102	ng/g
PFDaA	11.40	1.642	107285.	13CPFDaA	711494.	0.151	ng/g
PFTriDA	11.80	1.742	73739.	13CPFDaA	711494.	0.104	ng/g
PFTeDA	12.10	1.676	95881.	13CPFDaA	711494.	0.135	ng/g



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Analytical Methodology

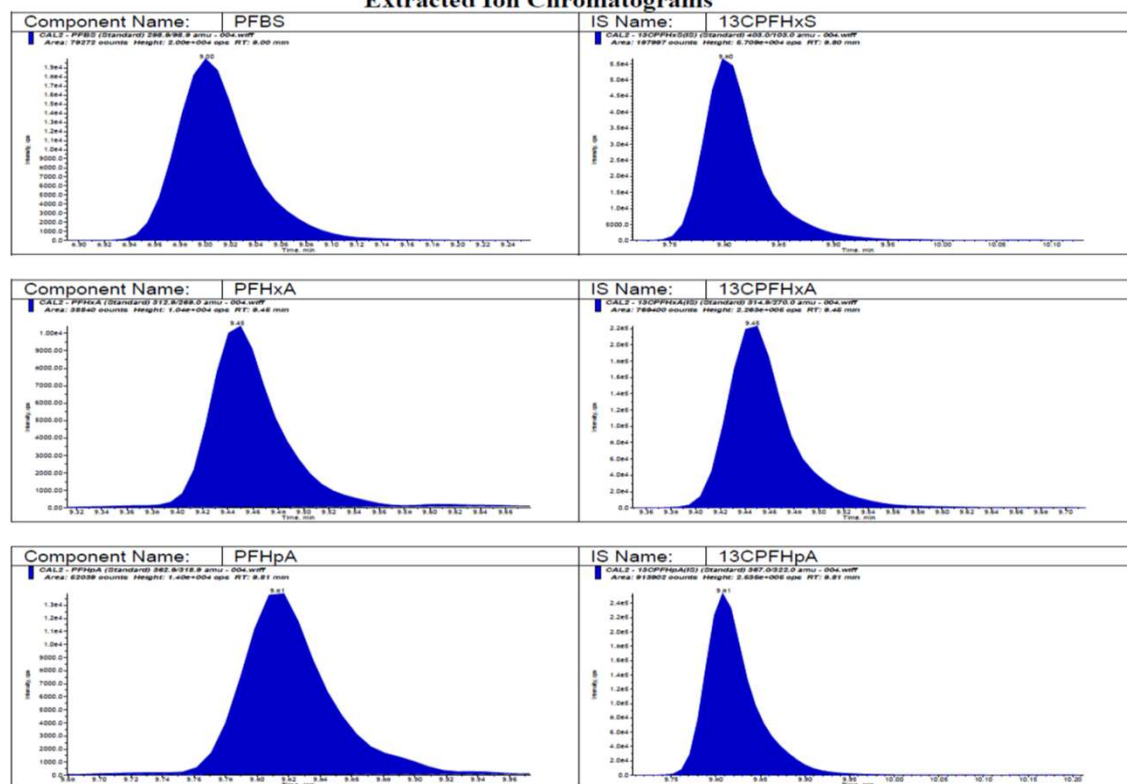


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LC-MS/MS Analysis Report

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Extracted Ion Chromatograms



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Summary



- What may have been sufficient for the UCMR3 list of 6 compounds may not be adequate for PFAS investigations going forward
- Lists of compounds of concern may be more diverse than the 3 alkyl acids and 3 alkyl sulfonates in UCMR3
- Range of matrices and diversity within matrices significantly different
- Qualification based on UCMR3 not necessarily appropriate

Questions

