APPLICATIONS OF SEPARATION AND MASS SPECTROMETRIC TECHNIQUES FOR CHALLENGES IN THE ANALYSIS OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) IN THE ENVIRONMENT

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October 14, 2020

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Applications of Separation and Mass Spectrometric Techniques to Challenges for the Analysis of Per- and Polyfluorinated Alkyl Substances (PFAS) in the Environment

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Applications of Separation and Mass Spectrometric Techniques to Challenges for the Analysis of Per- and Polyfluorinated Alkyl Substances (PFAS) in the Environment

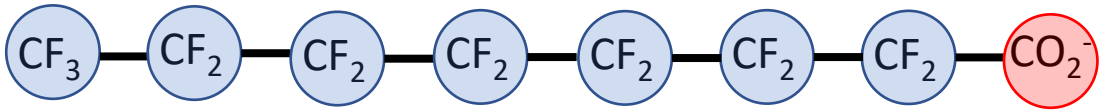
- PFAS chemistry: why is PFAS analysis so challenging?
- How have the analytical tools evolved?
- How are the challenges met in environmental analysis?
  - Sample collection
  - Sample preparation
  - Sample analysis

Caveats, Assumptions and Idiosyncrasies

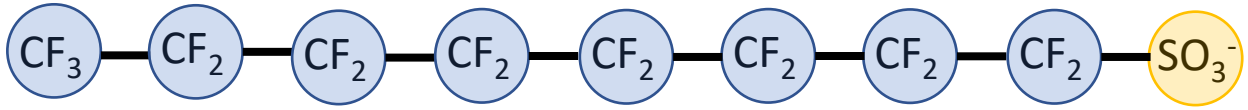
- No finger pointing, just science
- Assume good to excellent understanding of GC and LC, mixed bag on MS
- “Teflon®” and “PTFE” are not the same thing

Introduction to PFAS Chemistry

- First classes of PFAS analyzed were perfluorinated carboxylates and sulfonates



Perfluorooctanoate, perfluorooctanoic acid, PFOA, C8

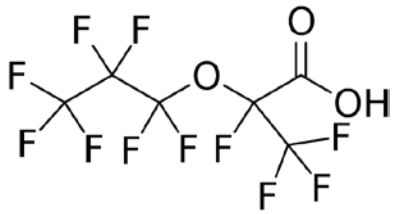


Perfluorooctane sulfonate, perfluorooctane sulfonic acid, PFOS

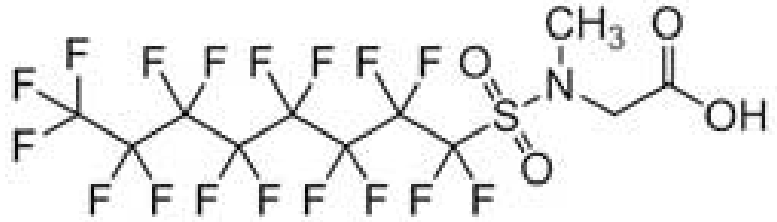
	"Short Chain" PFAS	"Long Chain" PFAS
Number of units	≤7 for Carboxylates ≤6 for Sulfonates	≥8 for Carboxylates ≥7 for Sulfonates

Introduction to PFAS Chemistry (continued)

- Many other PFAS classes were added to the discussion, including replacements and precursors



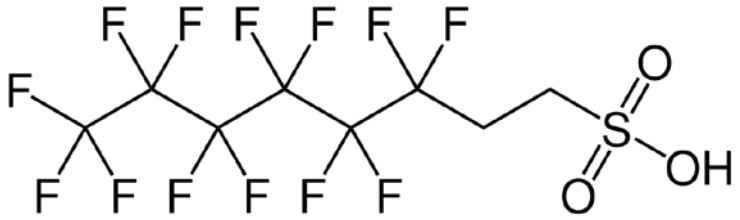
Hexafluoropropylene oxide dimer acid, HFPO-DA, GenX (PFOA replacement)



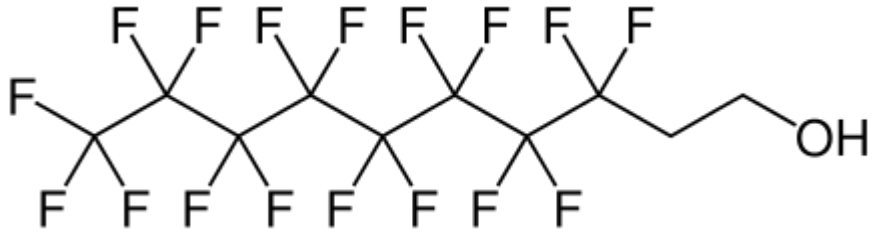
N-methyl perfluorooctanesulfonamidoacetic acid, NMeFOSAA (PFOS precursor)

Introduction to PFAS Chemistry (continued)

- Another important class of PFAS are telomers:



1H, 1H, 2H, 2H-perfluorooctane sulfonic acid, 6:2 FTS (surfactant and degradant)



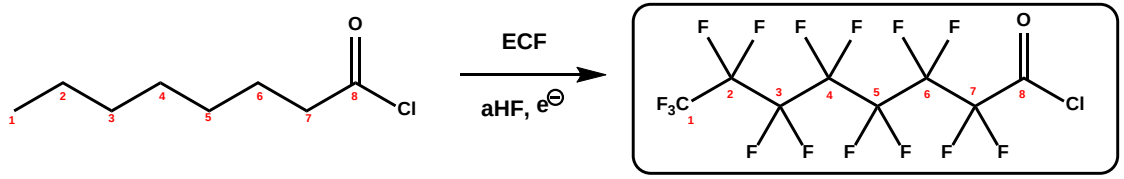
1H, 1H, 2H, 2H-perfluorooctanol, 6:2 FTOH (intermediate and degradant, *volatile*)

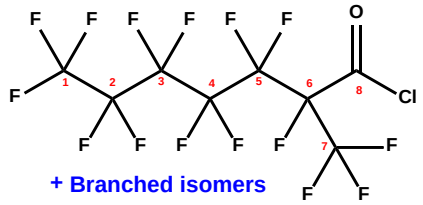
- Estimated 4000-5000 PFAS in environment now, only < 100 for which we have authentic standards

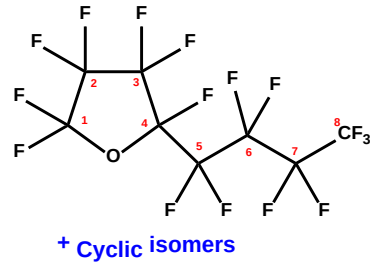
PFAS Process Chemistry

- Two major processes used to produce PFAS
  - Electrochemical fluorination (ECF)
  - Telomer

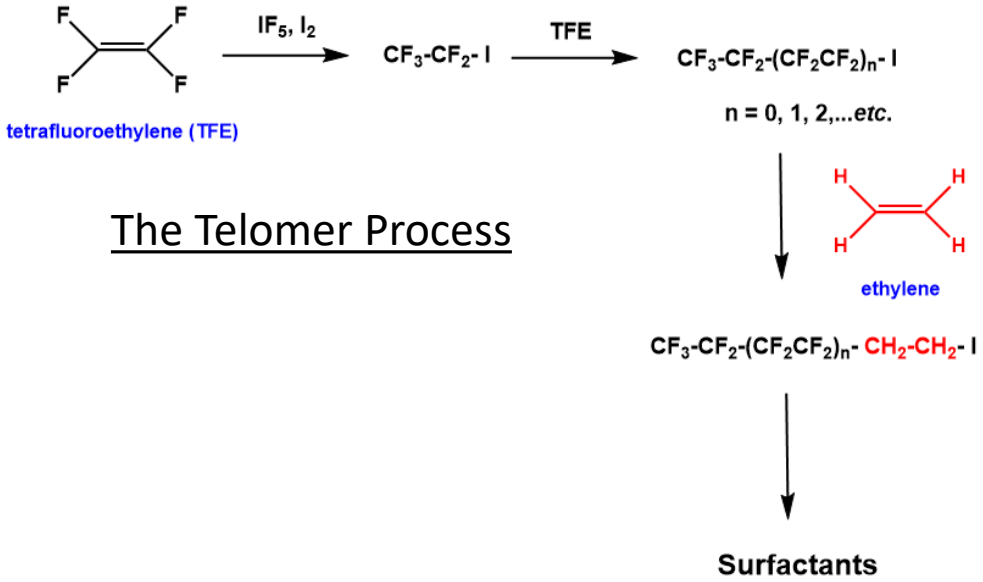
The ECF Process





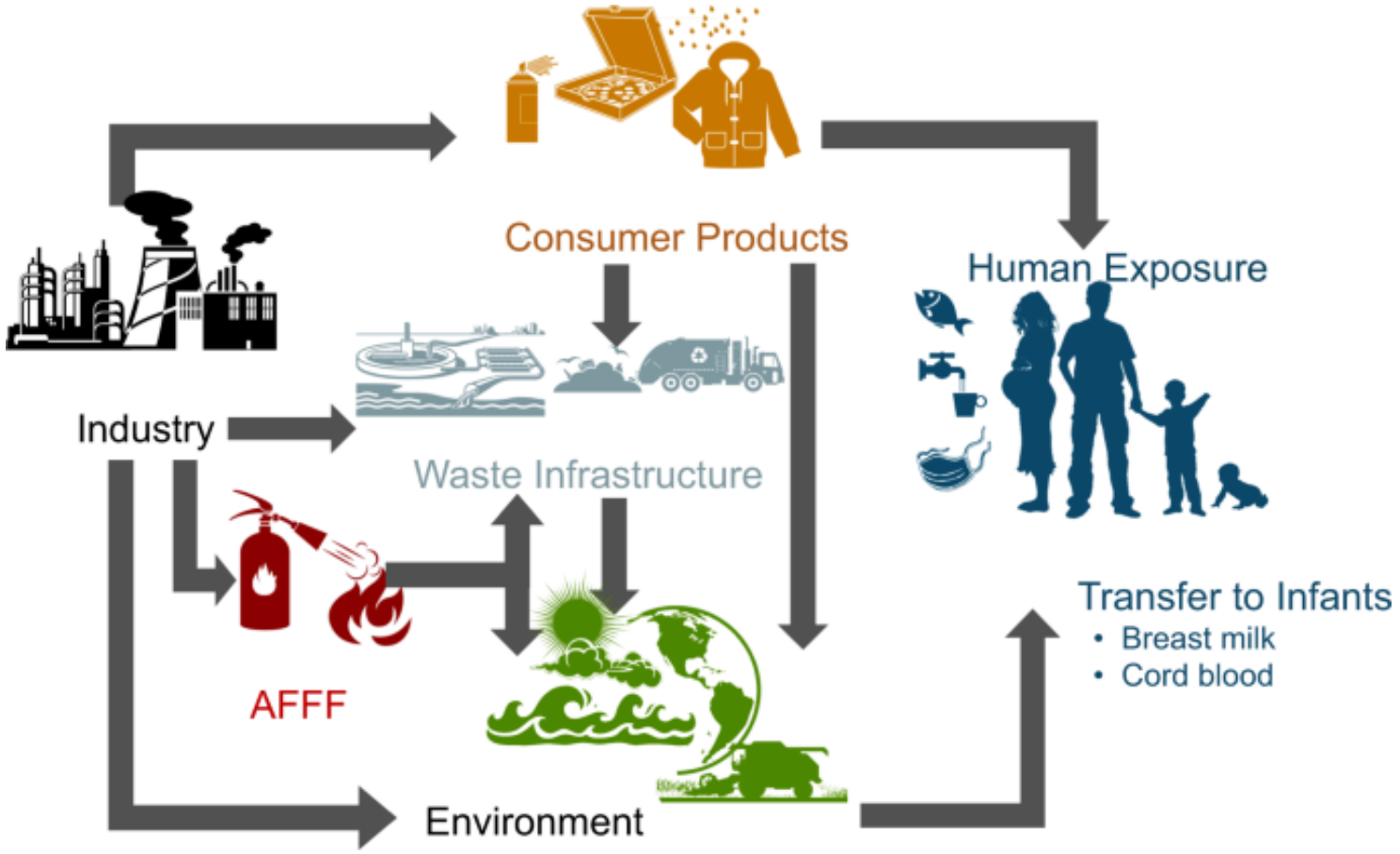


The Telomer Process



Figures courtesy of Chris Junk, CJIdeas LLC

PFAS Exposure Sources



Sunderland, E.M., Hu, X.C., Dassuncao, C. *et al. J Expo Sci Environ Epidemiol* **29,** 131–147 (2019).

Health Effects of PFAS

- Humans ingest PFAS from drinking water and foods
  - Major source is thought to be drinking water
  - Foods contain PFAS as well
    - Wrapping papers
    - Application of WWTP biosolids to farms (affects mostly meat and dairy)
    - PFAS biomagnify up the food chain
- Known health effects (epidemiological studies)
  - Low infant birth weights
  - Immune system suppression
  - Cancer, especially prostate (PFOA)
  - Thyroid hormone disruption (PFOS)
  - Increased cholesterol levels

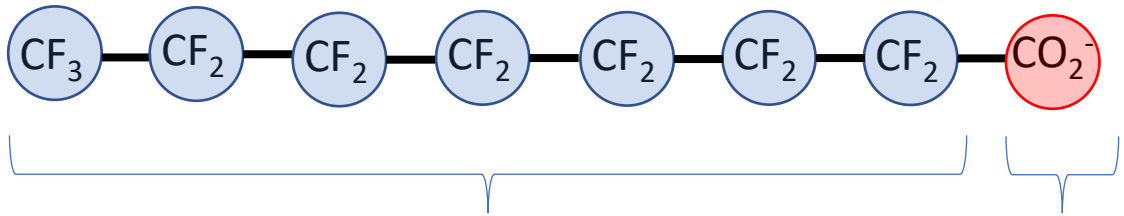
Why is PFAS Analysis so Challenging?

- PFAS need to be determined in drinking water samples at part-per-trillion (ppt or 1 ng/L) levels.
  - 1 ppt corresponds to ~3 sec in 100,000 years!
  - They also need to be determined in other environmental samples and human blood serum at ppb levels. 1 ppb corresponds to 1 bumblebee in a football stadium
- Sample and laboratory contamination is very common due to the ubiquitous nature of these substances
  - PFTE components
  - Sample containers
  - Contact with carpeting or upholstery
  - Non-stick foils and papers
  - Clothing (Gore-Tex®, Tyvek®)
  - Cosmetics, moisturizers, hand cream
  - Food wrappers and containers

- Once the lab is contaminated, it is virtually impossible to de-contaminate!

Why is PFAS Analysis so Challenging? (cont'd)

- The troublesome properties of PFAS:
  - PFAS compounds are surfactants:
    - Very difficult to clean up – prefer interfaces



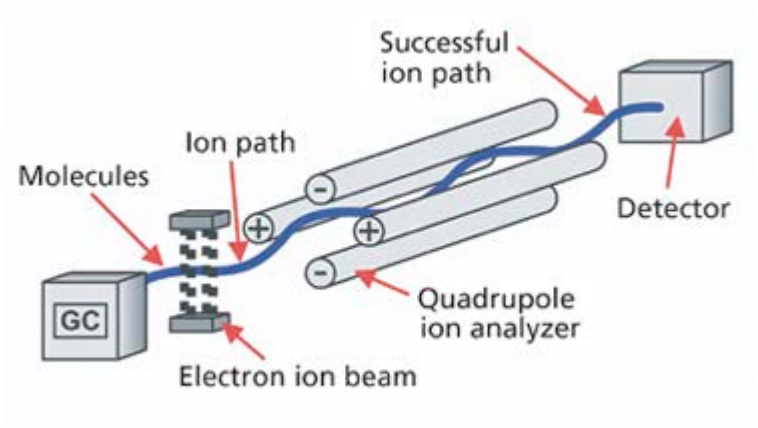
- Hydrophobic tail made of carbon and fluorine
- Prefers soils, fats
- Hydrophilic head made of carbon and oxygen
- Prefers water

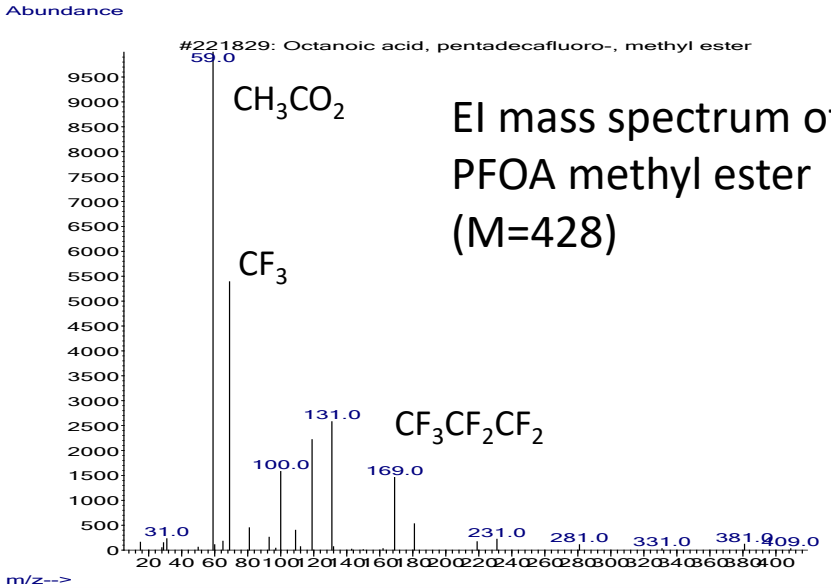
  - PFAS compounds are perfluorinated
    - Does not stick to cleaning agents like soaps
  - C-F and C-C bonds are the strongest chemical bonds known
    - Cannot destroy them with bleach, etc.

The Evolution of PFAS Analysis

Pre-2000

- Environmental analysis – early focus on water and blood serum
  - Best choice for PFOA and related carboxylates was gas chromatography (GC)
    - Detection usually by EI-quadrupole mass spectrometry
    - Poor electron capture response
  - PFAS are not volatile enough for GC but carboxylates (not sulfonates) could be chemically derivatized.



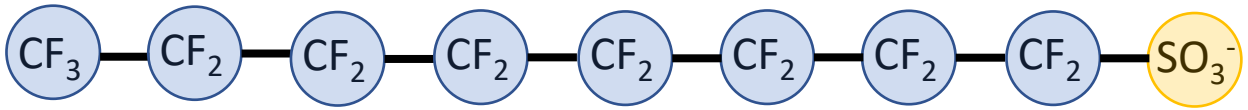


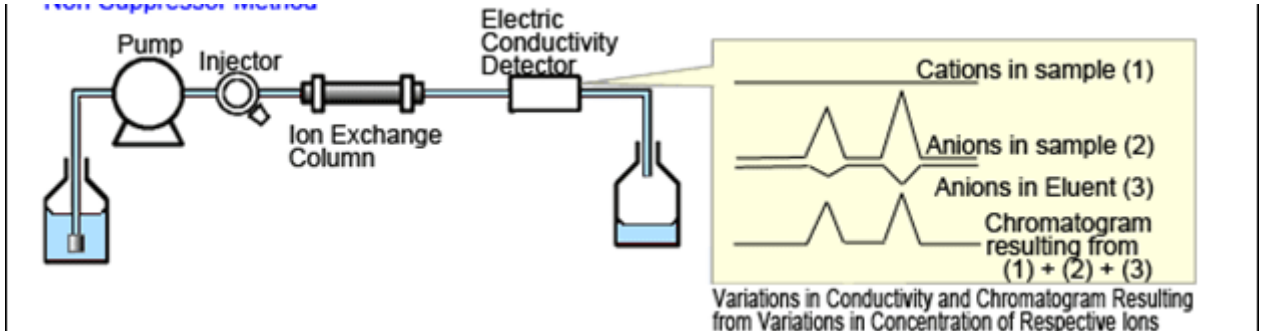
EI mass spectrum of PFOA methyl ester (M=428)

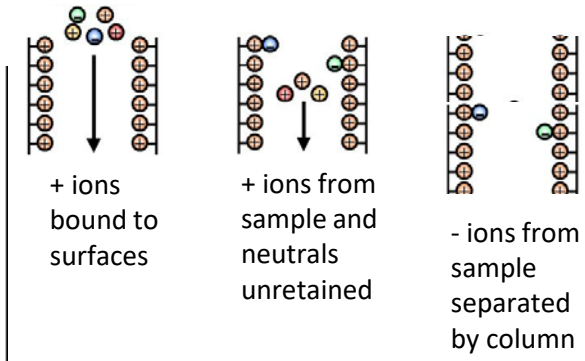
The Evolution of PFAS Analysis

Pre-2000 (cont'd)

- Environmental analysis – focus on water (continued)
  - Best choice for PFOS and related sulfonates was ion chromatography (IC)
    - Detection usually by conductivity



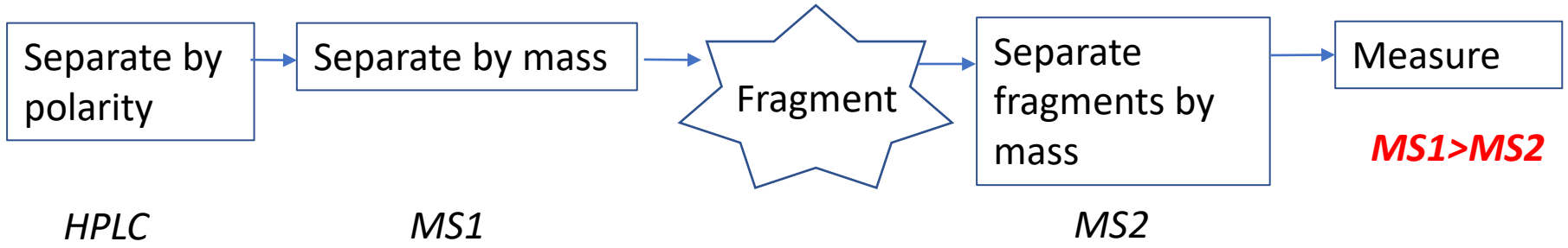




The Evolution of PFAS Analysis

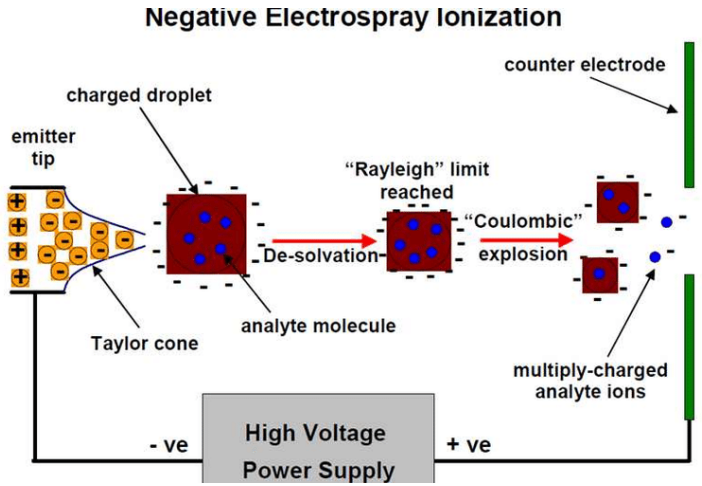
Post-2000

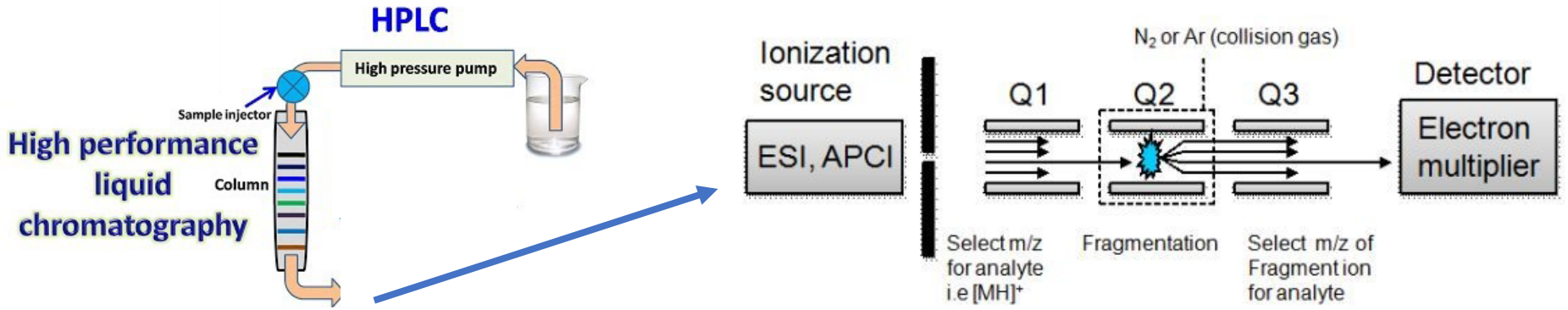
- The electrospray interface for coupling liquid chromatography to mass spectrometry (LC-MS) was commercialized ca. 1998
  - Game changer – before this LCMS was not particularly quantitative or sensitive
  - High performance LC coupled to a tandem mass spectrometer (LC-MS/MS) quickly became the analytical tool of choice for determining low levels of PFAS in environmental and biological (human blood serum) samples.



HPLC-MS/MS

- The PFAS determined in environmental and biological samples exist as anions (sulfonates and carboxylates)
- The major ionization process used is therefore negative ion electrospray.
- The analyte gas phase ions are then selected by the first quadrupole, fragmented and the characteristic fragments are selected by the second quadrupole.
- ***The precursor to fragment selection plus LC retention time is extremely selective for PFAS analytes. Excellent rejection of interferents and chemical noise.***

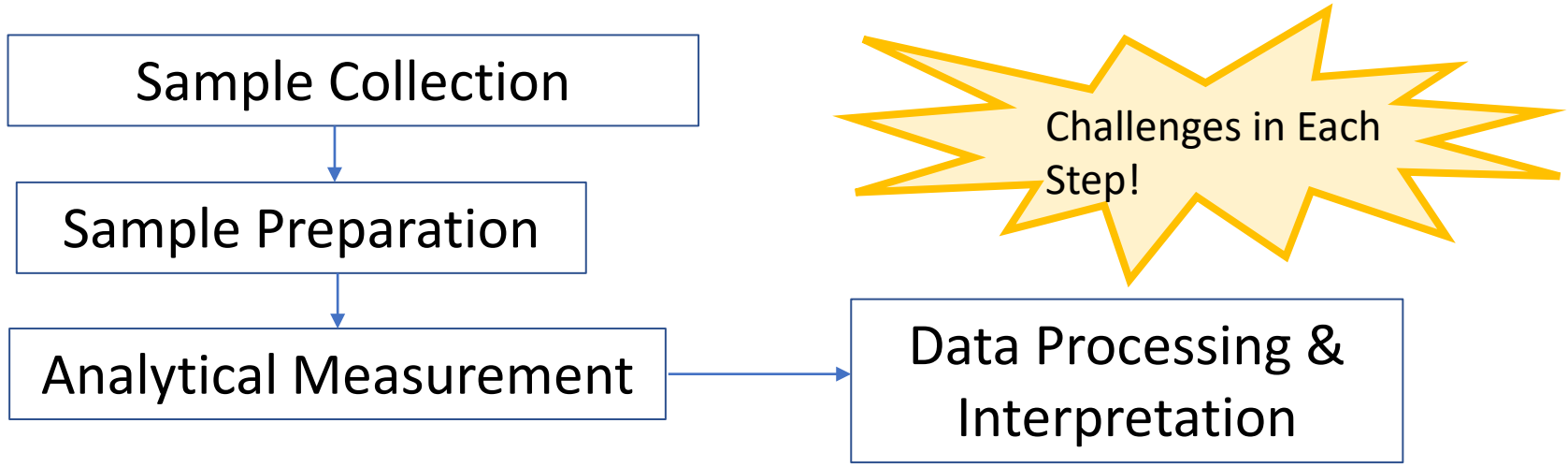




PFAS Determination in Drinking Water

- Most likely, the leading analysis in the environmental PFAS field is determination in drinking water-related samples.
  - Most water companies require reporting limits around 1-2 ng/L (parts per trillion) in finished water.
- The type of analysis done is called a targeted analysis:
  - Know what analytes you are looking for
  - Have authentic analytical standards of each (for both verification and quantification)
  - Narrow subset of PFAS

Flow diagram of a trace-level PFAS water method:



Selection of an Analytical Method

- Methods for drinking water should be standard across multiple laboratories and recognized by regulatory agencies.
- Currently only two such methods for drinking water:
  - USEPA Method 537.1 (November 2018)
  - USEPA Method 533 (November 2019)
- Non-standard methods often called “EPA 537 Modified”
  - Many versions exist
  - Different labs will often have their own unique versions
  - Often used for non-potable water samples
  - May not be recognized by relevant agencies

Which PFASs are Analyzed?

- EPA Method 537.1: emphasis on “legacy” compounds

Carboxylates	
Perfluorohexanoic acid	PFHxA *
Perfluoroheptanoic acid	PFHpA *
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTrDA
Perfluorotetradecanoic acid	PFTA
Sulfonates	
Perfluorobutanesulfonic acid	PFBS *
Perfluorohexanesulfonic acid	PFHxS *
Perfluorooctanesulfonic acid	PFOS

Replacement Chemicals	
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS (Cpd F53 Major)
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (Cpd F53 Minor)
4,8-Dioxa-3H-perfluorononanoic acid	ADONA
Hexafluoropropylene oxide dimer acid	HFPO-DA * (GenX)
PFOS Precursors	
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA

* Short chain PFAS

Which PFASs are Analyzed?

- EPA Method 533: emphasis on current compounds

Carboxylates	
Perfluorobutanoic acid	PFBA*
Perfluoropentanoic acid	PFPeA*
Perfluorohexanoic acid	PFHxA *
Perfluoroheptanoic acid	PFHpA *
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Sulfonates	
Perfluorobutanesulfonic acid	PFBS *
Perfluoropentanesulfonic acid	PFPeS*
Perfluorohexanesulfonic acid	PFHxS *
Perfluoroheptanesulfonic acid	PFHpS
Perfluorooctanesulfonic acid	PFOS

Replacement Chemicals	
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9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS
4,8-Dioxa-3H-perfluorononanoic acid	ADONA
Hexafluoropropylene oxide dimer acid	HFPO-DA *
Fluorotelomer Sulfonic Acids	
1H,1H,2H,2H-Perfluorohexane sulfonic acid	4:2 FTS*
1H,1H,2H,2H-Perfluorooctane sulfonic acid	6:2 FTS
1H,1H,2H,2H-Perfluorodecane sulfonic acid	8:2 FTS
Perfluorinated Alkyl Ether Carboxylic and Sulfonic Acids	
Perfluoro-4-methoxybutanoic acid	PFMBA*
Perfluoro-3-methoxypropanoic acid	PFMPA*
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA*
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA*

* Short chain PFAS

What Levels Are Required?

- EPA Health Advisory Level (HAL) is 70 parts per trillion (ng/L) for PFOA + PFOS in drinking water (DW)
- Recommend reporting levels of at most 2-4 ppt for current (DW) analyses
  - HAL reduction to ~10 ppt is already mandated in some states
  - HAL is the sum of multiple PFASs
- ppb (ng/g) levels appear to be sufficient for other sample types:
  - Non-potable waters
  - Soils, sludges and sediments

Potential Technical Issues

- ***CONTAMINATION***
  - PFASs from fluoropolymers and coatings are ubiquitous in common sampling and analytical equipment
  - Laboratory contamination is almost impossible to eliminate once it happens
  - Result: false positives and high reporting levels due to background
- Recovery
  - Non-standard concentration methods may not extract all PFAS components, especially short-chain
  - Long-chain compounds may stick to water sampling containers*.

	"Short Chain" PFAS	"Long Chain" PFAS
Number of units	≤7 for Carboxylates ≤6 for Sulfonates	≥8 for Carboxylates ≥7 for Sulfonates

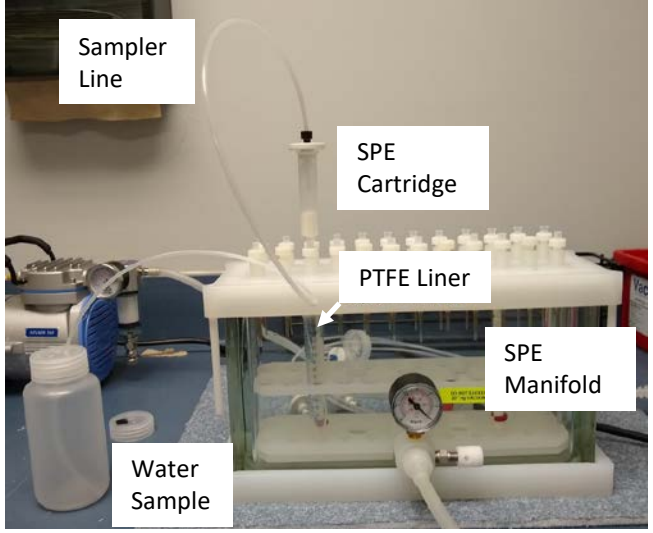
*Powley, CR et al., 2006, Organohalogen Compounds, 68, 1688

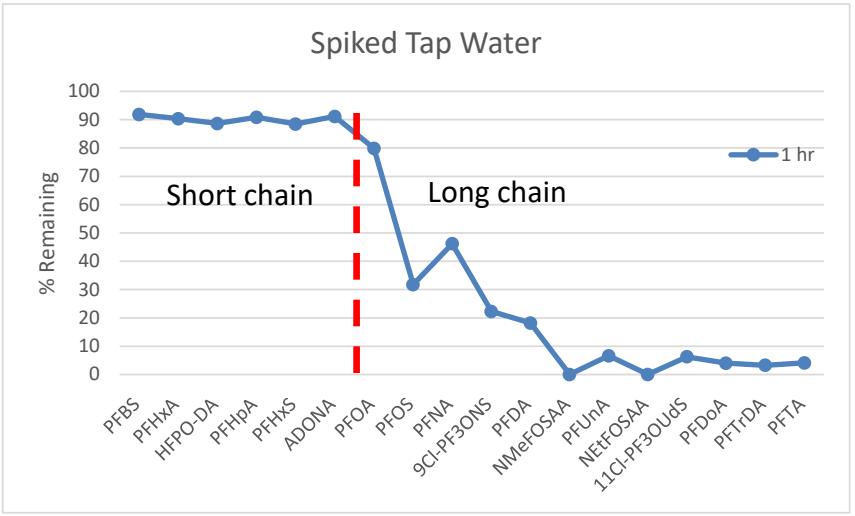
Sample Collection

- Huge potential for contamination from sampling equipment, clothing and cosmetics.
  - Remember: 1 ng/L corresponds to ~3 sec in 100,000 years!
- Blanks, blanks, blanks!
  - Use polypropylene sample collection bottles provided and tested by the laboratory
  - Lab should include 2 bottles filled with water known not to contain PFASs
    - Trip blank – water travels with empty and filled bottles
    - Field blank – water is transferred to an empty bottle at the time samples are collected.

Sample Preparation - Water

- Water samples are prepared using Solid Phase Extraction (SPE).
  - EPA 537.1 neutral polymer (SDVB) sorbent
  - EPA 533.1 weak anion exchange sorbent
- Potential for contamination from lab equipment.
  - PTFE components – replace when possible
  - Single-use PP labware including ASV's
  - Carryover from high-level samples
- More blanks!
  - Lab reagent blank: PFAS-free water carried through entire procedure and analyzed for background levels
- Incorporate solvent rinse of sample containers for long-chain compounds.





Tap water sample spiked at 300 ppt with EPA 537.1 analytes, shaken for 1 hr in PP container and direct-injected.

Sample Preparation – Soil/Sludge/Sediment

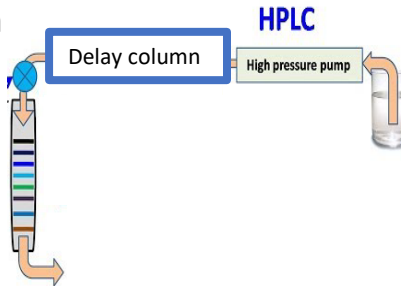
- Solid samples are extracted with a suitable organic solvent such as methanol.
  - Remove interferents using purification by Dispersive Solid Phase Extraction (DSPE) or other methods.
- Potential for contamination from lab equipment.
  - Single-use PP labware
  - Carryover from standards - isolate
- More blanks!
  - Lab reagent blank: PFAS-free solvents carried through entire procedure and analyzed for background levels.

Principle of DSPE using graphitized carbon

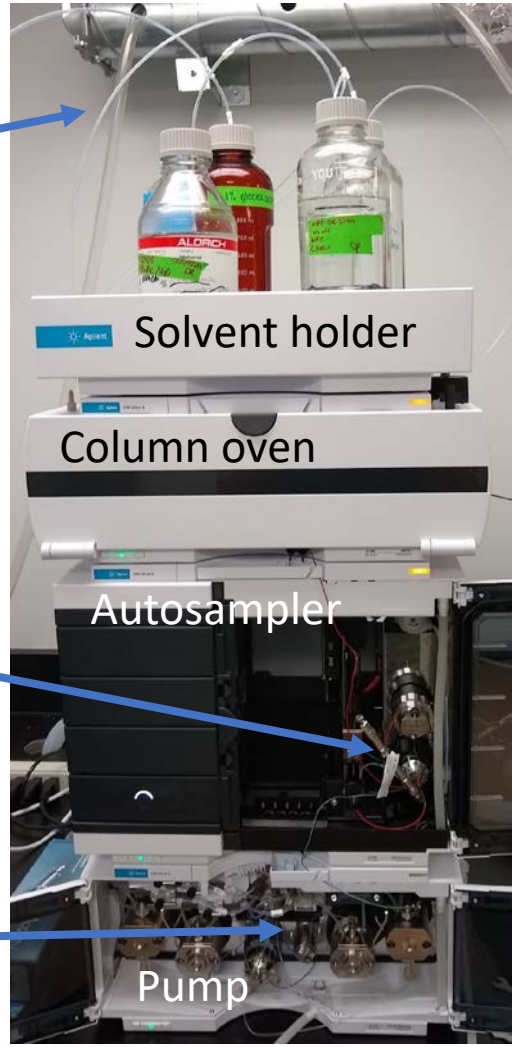
Powley CR, et al., 2005 Anal. Chem., 77, 6353

Sample Analysis by LC-MS/MS

- Sample extracts analyzed by sequential injection into an LC-MS/MS instrument.
  - Calibration standards
  - Quality control (QC) samples
    - Blanks
    - Fortifications
    - Curve check standards
- Potential for contamination from the instrument!
  - PTFE components - replace or use delay column
  - Carryover from high level standards and samples
- Even more blanks!
  - Instrument blank: Typically the dilution solvent used
    - Beginning (2-3x) and end of run
    - After series of calibration standards
    - After series of QC samples
    - After each known "high" sample



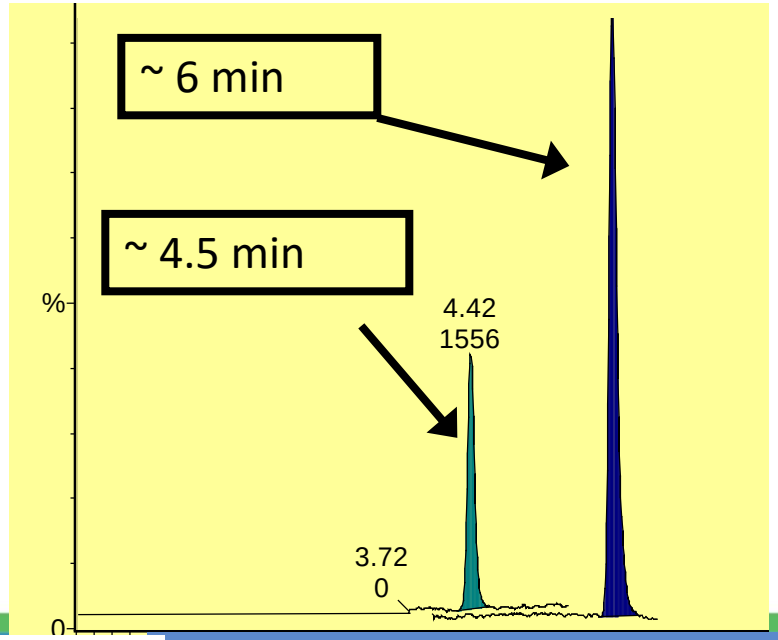
Powley CR, et al., 2005 Anal. Chem., 77, 6353

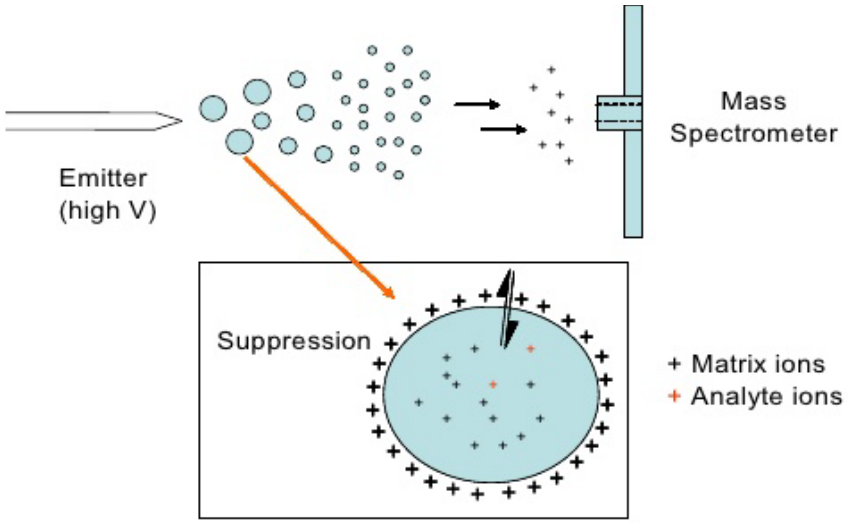


Optimizing Data Acquisition: HPLC

- Choose MPA and MPB to yield best MS sensitivity
- ACN is 20x more expensive than MeOH!
- Run time/gradient steepness
  - Typical sample load is 15 to 25 including QC's and standards.
  - Co-elution okay
  - Dirty samples can yield matrix suppression, let the column do its job!

MPA	MPB
20 mM NH_4OAc	MeOH
0.1% HOAc	ACN



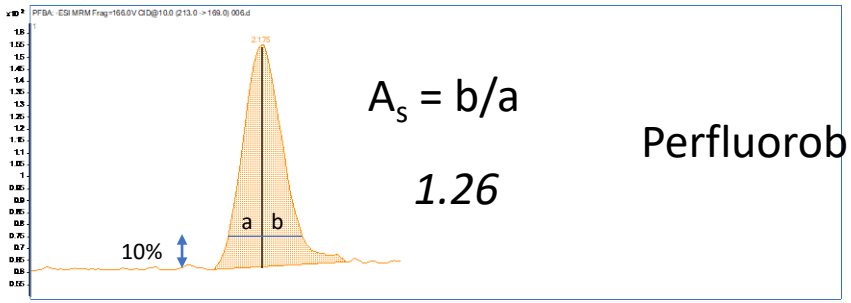


Optimizing Data Acquisition: HPLC

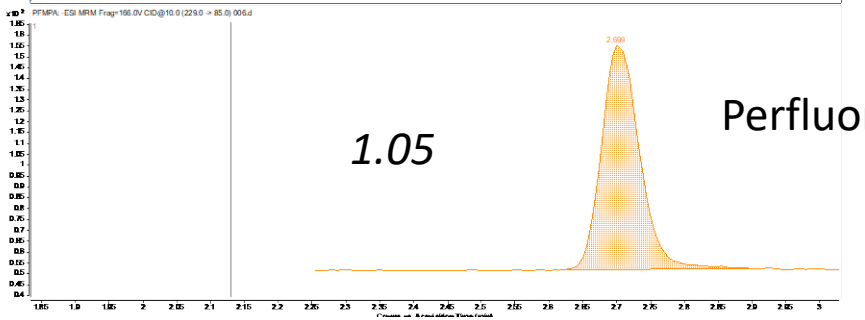
- Requirement: Peak asymmetry factor must be 0.8 – 1.5 (first two eluters)
- EPA Method 537.1 samples are in 96:4 MeOH:water
- Can be achieved with low-volume injections and lowered initial %MPA.

3 mm x 10 cm C18 columns, 0.5 mL/min, 2 µL injection volumes (1:4 water:MeOH)
MPA = 20 mM ammonium acetate, MPB = MeOH

C18, 1.7 µm fully porous, MPA_i = 40%

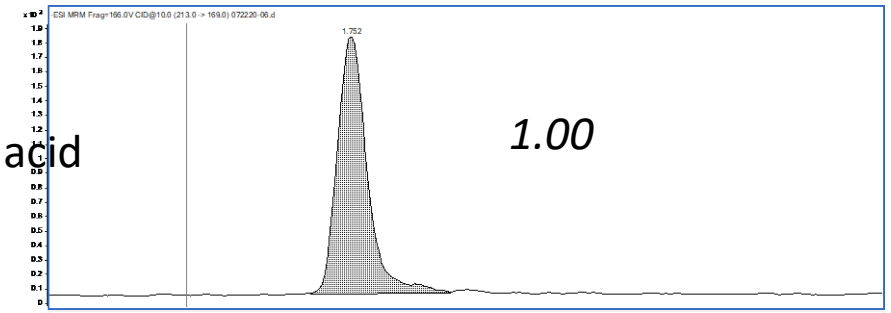


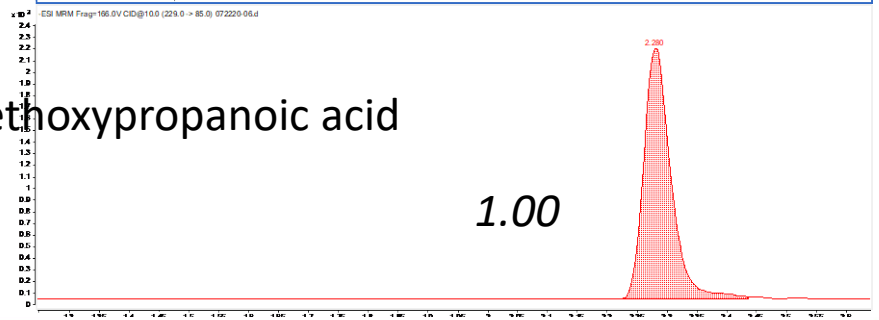
Perfluorobutanoic acid



Perfluoro-3-methoxypropanoic acid

C18, 2.7 µm porous shell, MPA_i = 20%

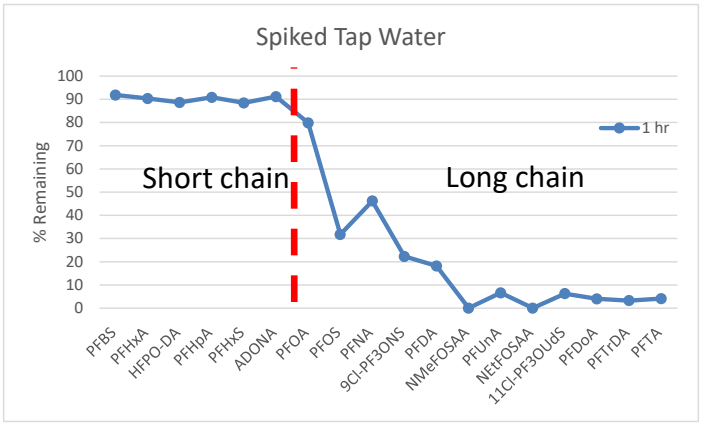


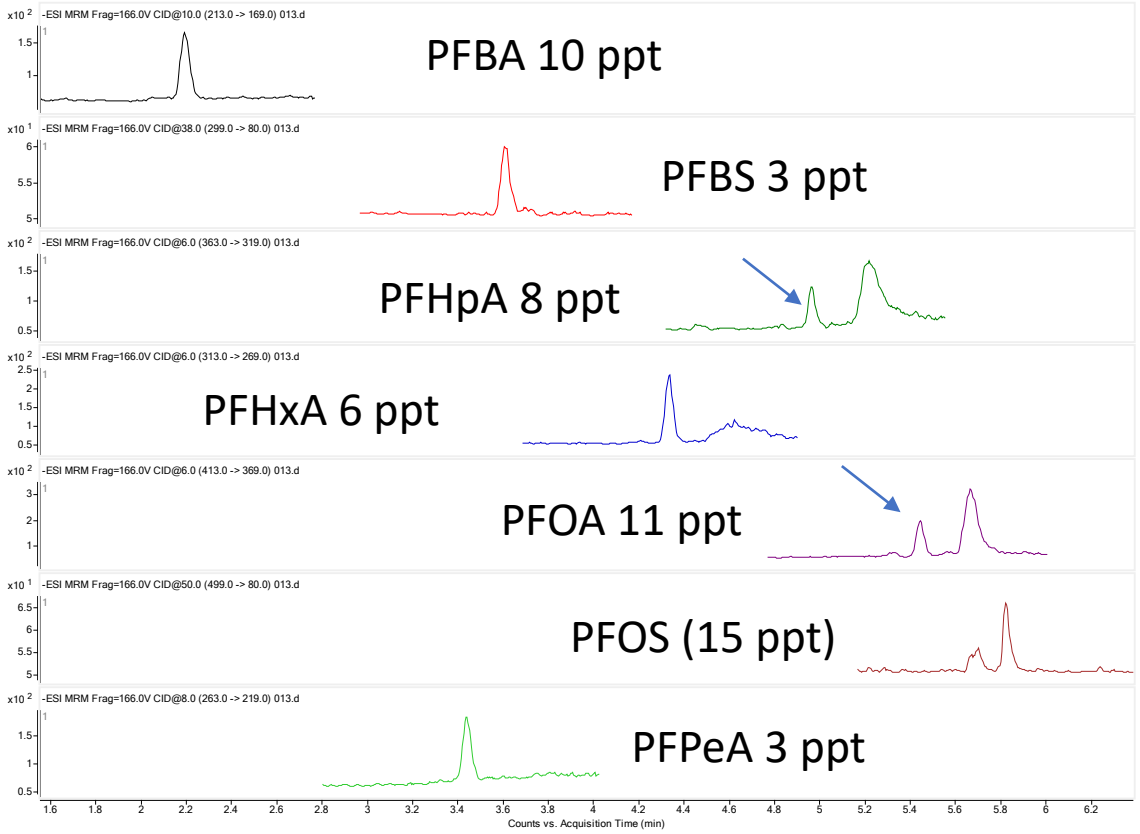


Optimizing Data Acquisition: HPLC

- Large volume injections: direct inject aliquot of 100% water samples
  - Not recommended for longer chain compounds, as losses on sample collection containers would be significant
  - PFOS and PFNA are still important analytes for DW.

20 µL injection volume (water)

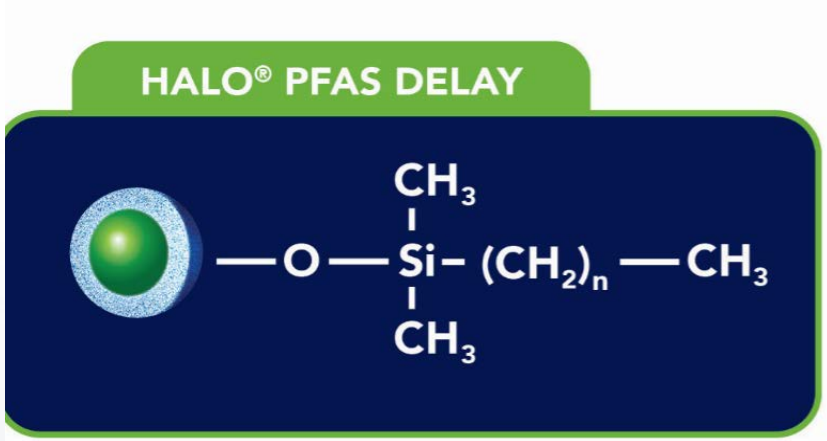


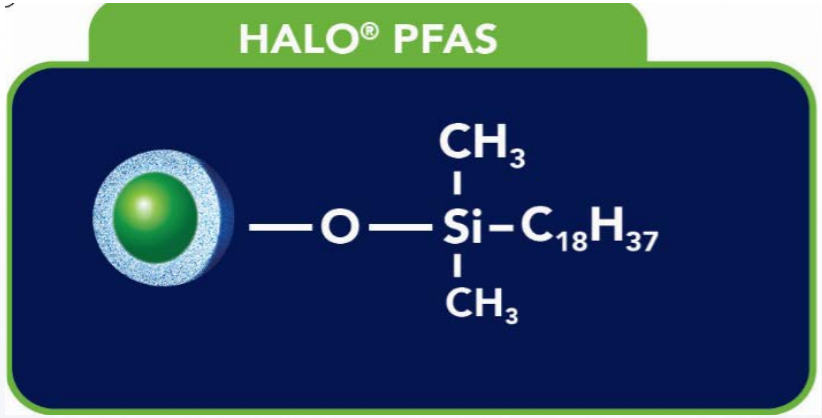


HALO® PFAS Solution

HALO®
PFAS Delay
Column

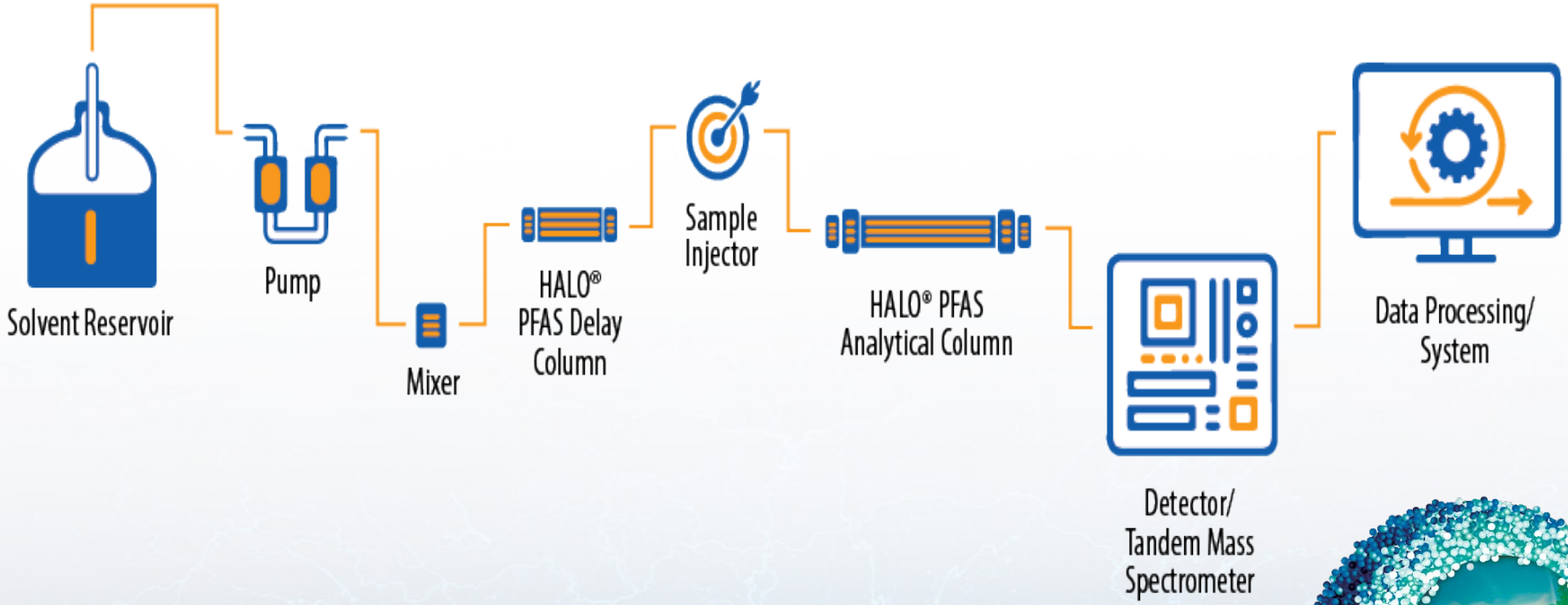
HALO® PFAS
Analytical Column



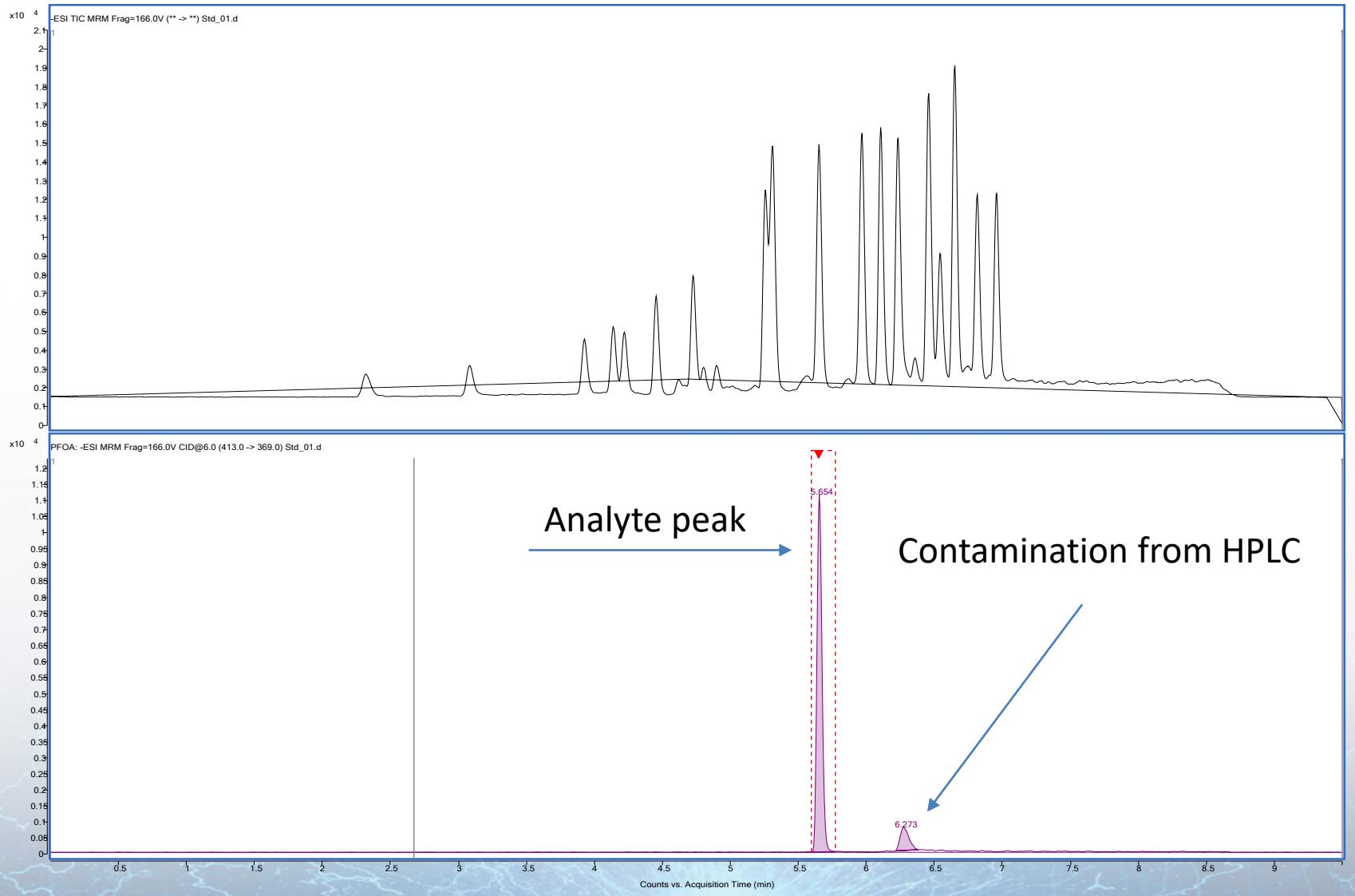


PFAS Delay Column

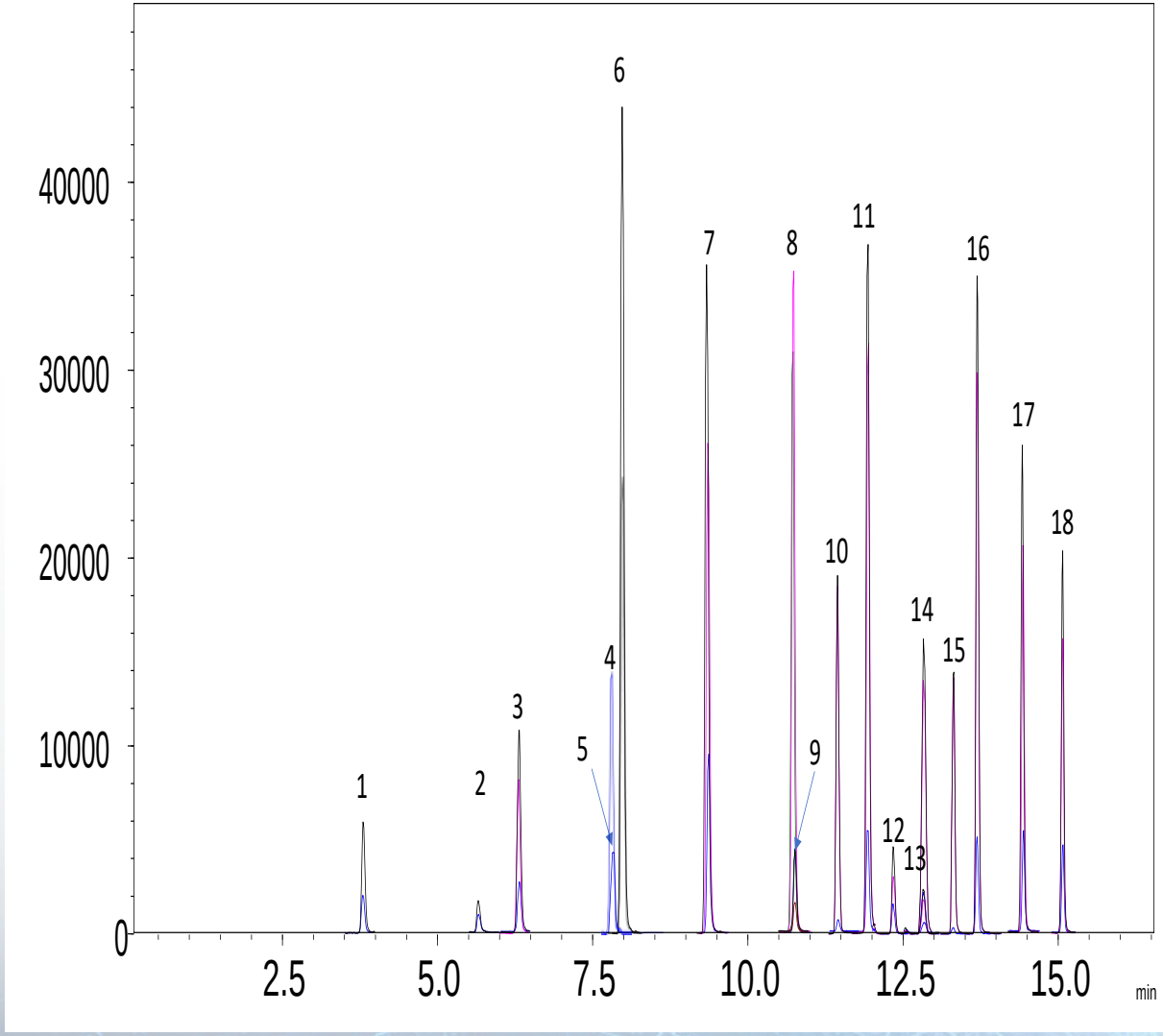
PFAS are “forever chemicals” that are almost everywhere, even in your HPLC.



Delay column effectiveness showing the delay of PFOA contamination by 0.7 minutes



EPA 537.1-Drinking Water



Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-613
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Part Number: 92113-415
Mobile Phase A: 10 mM Ammonium Acetate
Mobile Phase B: Methanol

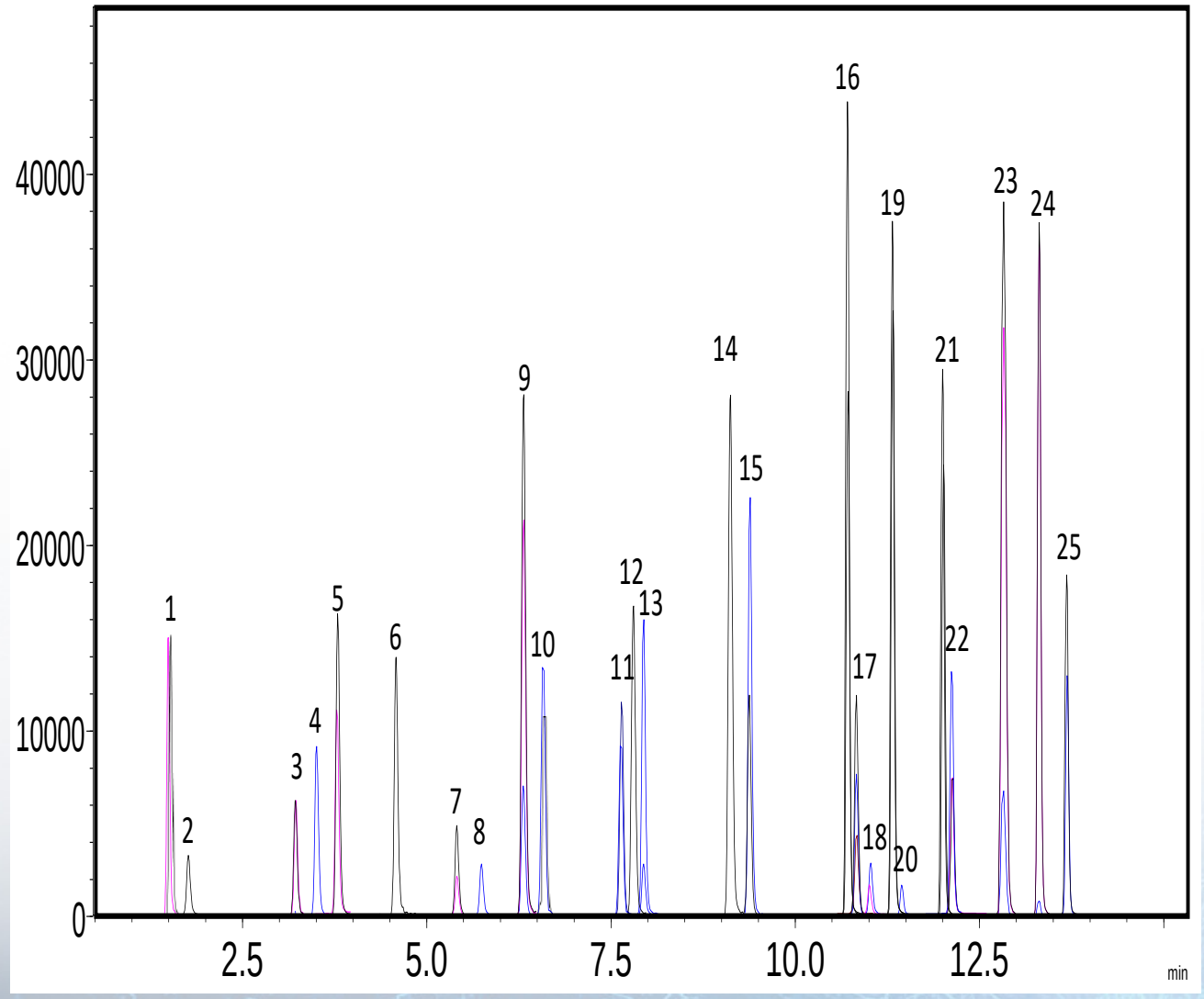
Gradient:

Time	%B
0.0	33
18.0	98
18.1	100
21.0	100
21.1	33
26.0	End

Flow Rate: 0.4 mL/min
Pressure: 485 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)

Peak Number	Compound
1	PFBS
2	PFHxA
3	HFPO-DA
4	PFHpA
5	PFHxS
6	ADONA
7	PFOA
8	PFNA
9	PFOS
10	9Cl-PF3ONS
11	PFDA
12	N-MeFOSAA
13	PFUnA
14	N-EtFOSAA
15	11Cl-PF3OUdS
16	PFDoA
17	PFTrDA
18	PFTeDA

EPA 533-Short Chain PFAS, Drinking Water



Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-613
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Part Number: 92113-415
Mobile Phase A: 10 mM Ammonium Acetate
Mobile Phase B: Methanol

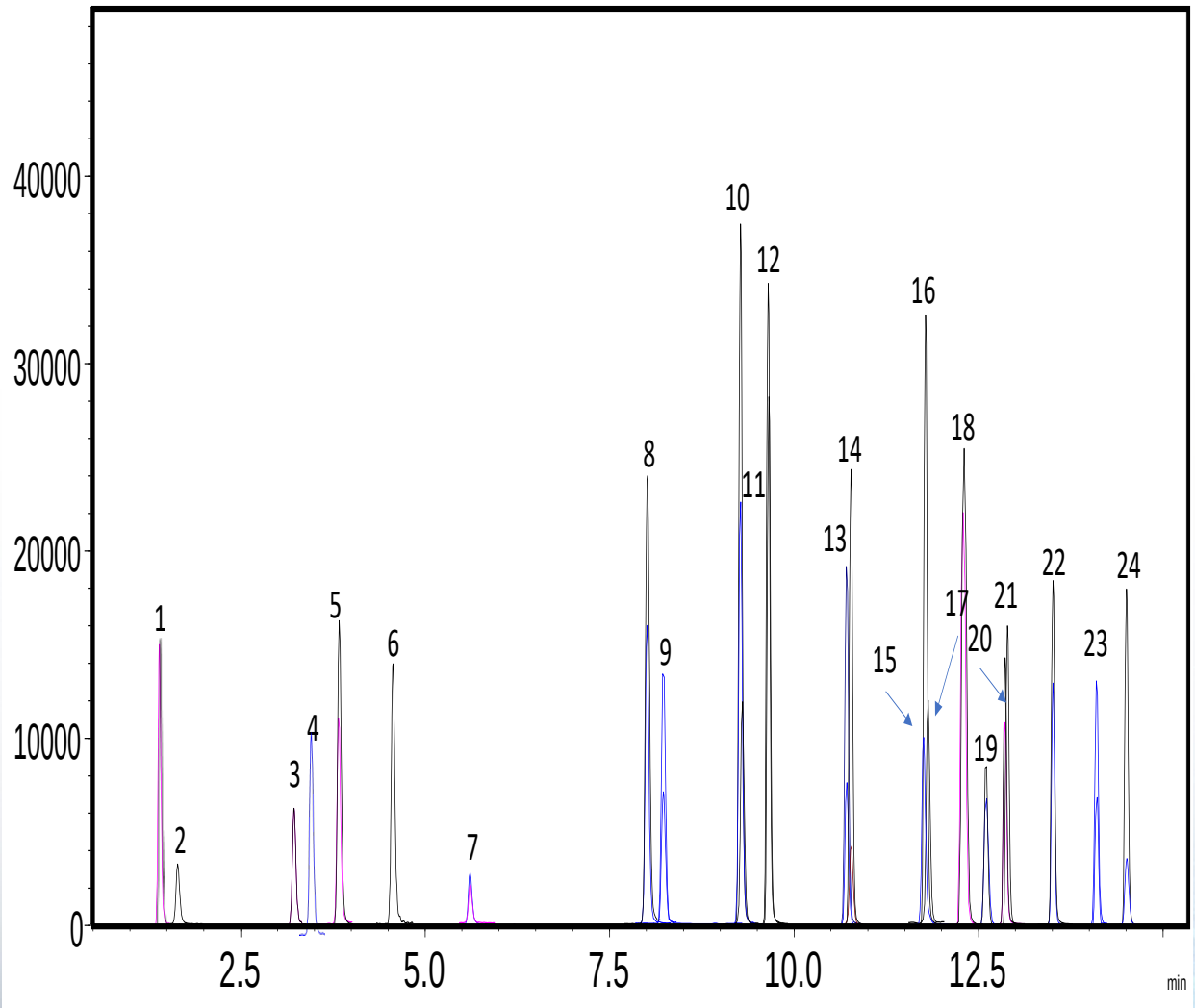
Gradient:

Time	%B
0.0	33
18.0	98
18.1	100
21.0	100
21.1	33
26.0	End

Flow Rate: 0.4 mL/min
Pressure: 485 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)

Peak number	Compound
1	PFBA
2	4:2FTS
3	PFPeA
4	PFBS
5	PFHpS
6	PFPeS
7	PFMPA
8	PFHxA
9	PFEESA
10	HFPO-DA
11	PFHpA
12	PFHxS
13	ADONA
14	PFOA
15	PFMBA
16	PFNA
17	PFOS
18	9Cl-PF3ONS
19	PFDA
20	8:2FTS
21	6:2FTS
22	NFDHA
23	PFUnA
24	11Cl-PF3OUdS
25	PFDoA

EPA 8327- Non Potable Water



Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-613
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Part Number: 92113-415
Mobile Phase A: 10 mM Ammonium Acetate
Mobile Phase B: Methanol

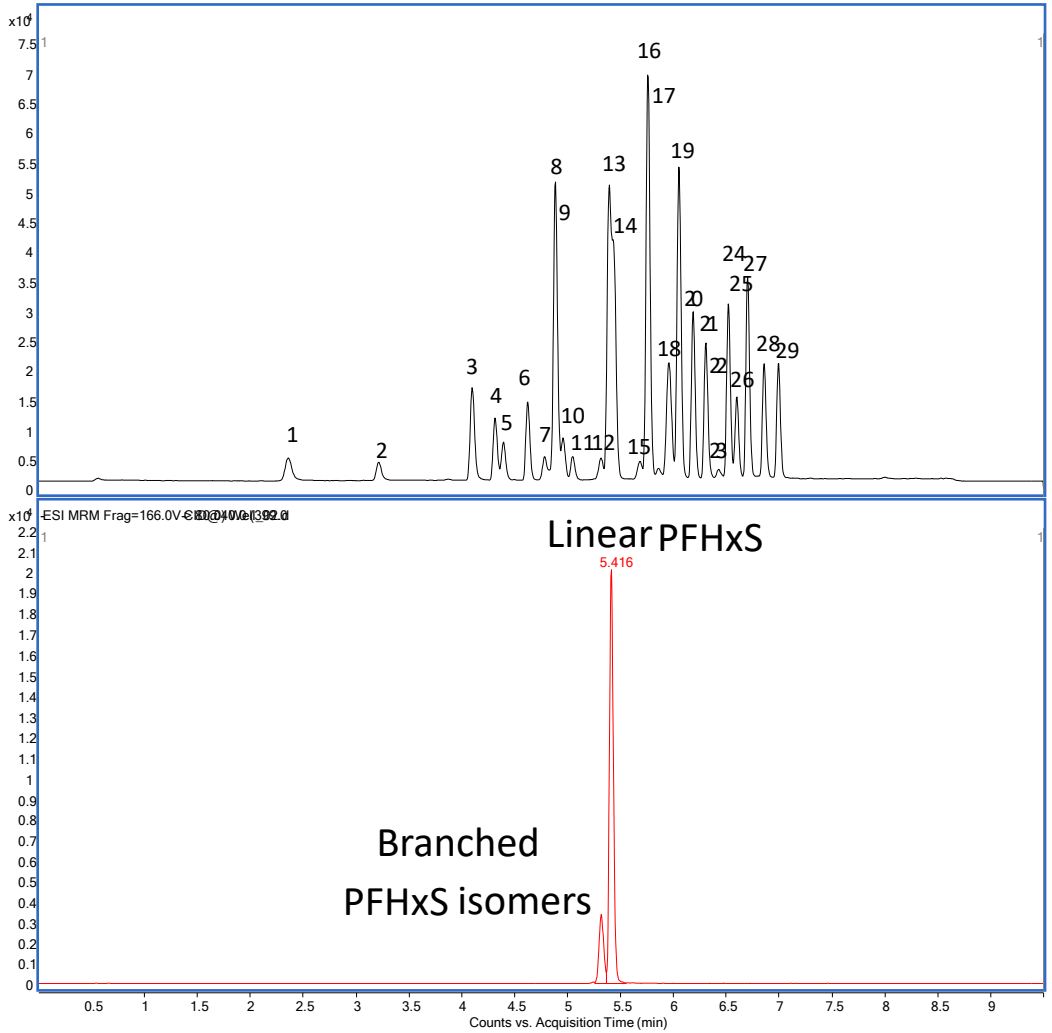
Gradient:

Time	%B
0.0	33
18.0	98
18.1	100
21.0	100
21.1	33
26.0	End

Flow Rate: 0.4 mL/min
Pressure: 485 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)

Peak number	Compound
1	PFBA
2	4:2FTS
3	PFPeA
4	PFBS
5	PFHpS
6	PFPeS
7	PFHxA
8	PFHpA
9	PFHxS
10	FOSA
11	PFOA
12	PFDS
13	PFNA
14	PFOS
15	PFNS
16	PFDA
17	8:2FTS
18	N-MeFOSAA
19	6:2FTS
20	PFUnA
21	N-EtFOSAA
22	PFDoA
23	PFTrDA
24	PFTeDA

Applications- Branched and Linear PFAS Isomers in Well Water



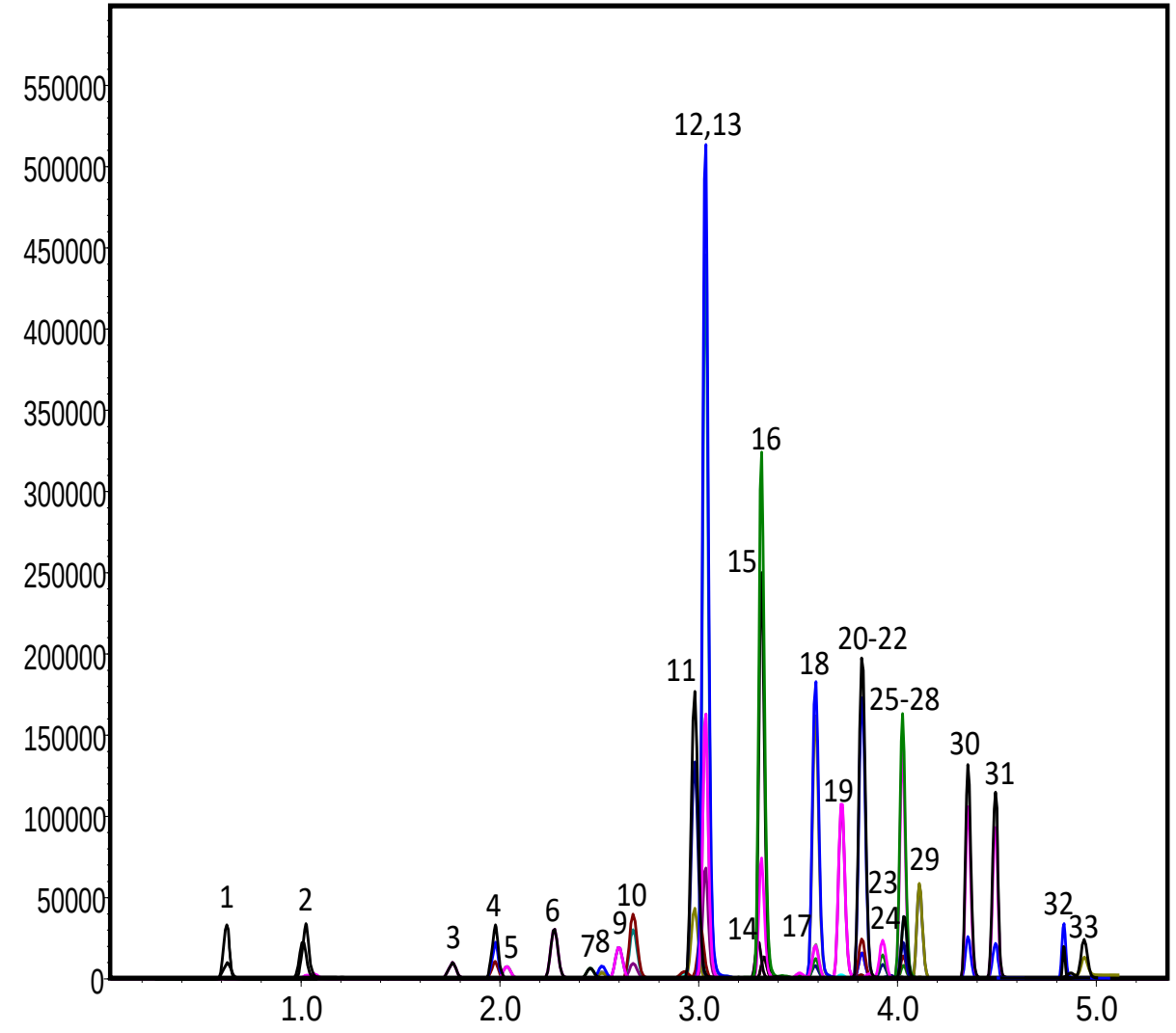
TEST CONDITIONS:
Analytical Column: HALO 90 Å PFAS, 2.7 µm 2.1 x 100 mm
Delay Column: HALO® PFAS, 3.0 x 50 mm
Part Number:
Mobile Phase A: 20 mM Ammonium Acetate
Mobile phase B: Methanol
Gradient:

Time	%B
0.0	20
5.5	90
7.5	90
8.0	20
10.5	End

Flow Rate: 0.4 mL/min
Pressure: 505 bar
Temperature: 44 °C
Detection: -ESI
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)
LC System: Agilent MS 6400

Peak number	Compound
1	PFBA
2	PFMPA
3	PFPeA
4	PFBS
5	PFMBA
6	PFEESA
7	NFDHA
8	4-2FTS
9	PFHxA
10	PFPeS
11	HFPO-DA
12	PFHpA
13	PFHxS
14	ADONA
15	6-2FTS
16	PFHpS
17	PFOA
18	PFOS
19	PFNA
20	9Cl-PF3ONS
21	PFDA
22	8-2FTS
23	NMeFOSAA
24	PFUnA
25	NEtFOSAA
26	11Cl-PF3OUdS
27	PFDoA
28	PFTrA
29	PFTA

How Can Fused-Core® Benefit PFAS Separations? = Speed



Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-613
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Part Number: 92113-415
Mobile Phase A: 10 mM Ammonium Acetate
Mobile Phase B: Methanol
Gradient:

Time	%B
0.0	33
4.0	98
4.10	100
6.00	100
6.10	33
7.50	End

Flow Rate: 0.4 mL/min
Pressure: 389 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)

Peak Number	Compound
1	PFBA
2	4:2FTS
3	PFPeA
4	PFBS
5	PFHpS
6	PFPeS
7	PFMPA
8	PFHxA
9	PFEESA
10	HFPO-DA
11	PFHxS
12	ADONA
13	NaDONA
14	FOSA
15	PFOA
16	PFMBA
17	PFHpA
18	PFOS
19	9Cl-PF3ONS
20	8:2FTS
21	PFNS
22	PFDA
23	PFNA
24	N-MeFOSAA
25	NFDHA
26	PFUnA
27	N-EtFOSAA
28	6:2FTS
29	11Cl-PF3OUdS
30	PFTrDA
31	PFDoA
32	PFTeDA
33	PFDS

The separation of 33 PFAS species found in EPA 537.1, EPA 533, and EPA 8327, completed in under 5 minutes.

Comparison: 18 min Gradient to 5 min Gradient

EPA 533

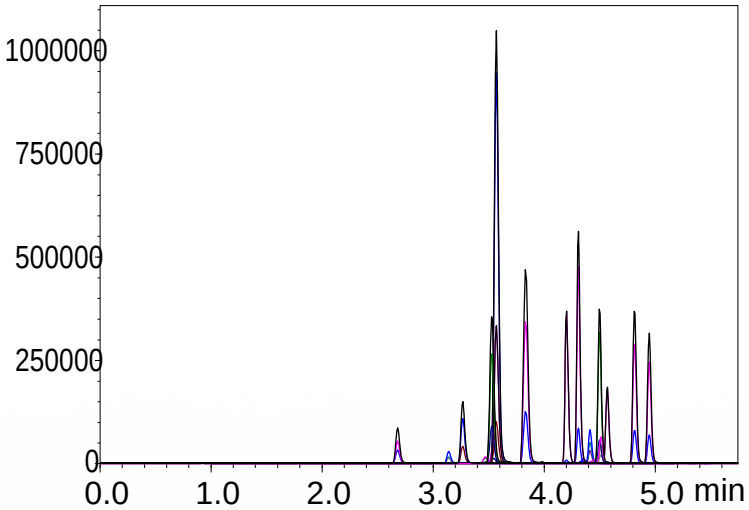
Peak #	Compound	Transition	t_R (min)
1	PFBA	213.0000>169.0000	1.358
2	4-2FTS	229.0000>85.0000	1.890
3	PFPeA	263.0000>219.0000	3.219
4	PFBS	299.0000>80.0000	3.810
5	PFHpS	279.0000>85.0000	3.967
6	PFPeS	315.0000>135.0000	4.791
7	PFmpA	327.0000>307.0000	5.431
8	PFHxA	313.0000>269.0000	5.684
9	PFEESA	349.0000>80.0000	6.099
10	HFPO-DA	285.0000>169.0000	6.335
11	PFHpA	363.0000>319.0000	7.763
12	PFHxS	399.0000>80.0000	7.985
13	ADONA	377.0000>250.9000	8.012
14	PFOA	413.0000>369.0000	9.398
15	PFmbA	449.0000>80.0000	9.512
16	PFNA	463.0000>419.0000	10.751
17	PFOS	499.0000>80.0000	10.793
18	9Cl-PF3ONS	530.9000>351.0000	11.459
19	PFDA	513.0000>469.0000	11.885
20	8-2FTS	549.0000>80.0000	11.897
21	6-2FTS	498.0000>78.0000	12.680
22	NFDHA	599.0000>80.0000	12.847
23	PFUnA	563.0000>519.0000	12.862
24	11Cl-PF3OUdS	630.7000>451.0000	13.329
25	PFDoA	613.0000>569.0000	13.708

Average: 2-3.5 times faster. No loss in sensitivity or resolution

Multi component PFAS method

Peak #	Compound	Transition	t_R (min)
1	PFBA	213.0000>169.0000	0.755
2	4:2FTS	229.0000>85.0000	1.031
3	PFPeA	263.0000>219.0000	1.762
4	PFBS	299.0000>80.0000	1.979
5	PFHpS	279.0000>85.0000	2.035
6	PFPeS	315.0000>135.0000	2.273
7	PFMPA	327.0000>307.0000	2.454
8	PFHxA	313.0000>269.0000	2.514
9	PFEESA	349.0000>80.0000	2.599
10	HFPO-DA	285.0000>169.0000	2.670
11	PFHxS	399.0000>80.0000	3.013
12	NaDonna	377.0000>251.0000	3.033
13	ADONA	377.0000>250.9000	3.034
14	FOSA	427.0000>407.0000	3.299
15	PFOA	413.0000>369.0000	3.316
16	PFMBA	449.0000>80.0000	3.328
17	PFHpA	363.0000>319.0000	3.388
18	PFOS	499.0000>80.0000	3.588
19	9Cl-PF3ONS	530.9000>351.0000	3.719
20	8:2FTS	549.0000>80.0000	3.816
21	PFNS	527.0000>507.0000	3.820
22	PFDA	513.0000>469.0000	3.822
23	N-MeFOSAA	570.0000>419.0000	3.925
24	PFNA	463.0000>419.0000	3.942
25	NFDHA	599.0000>80.0000	4.015
26	PFUnA	563.0000>519.0000	4.025
27	N-EtFOSAA	584.0000>419.0000	4.029
28	6:2FTS	498.0000>78.0000	4.033
29	11Cl-PF3OUdS	630.7000>451.0000	4.110
30	PFTrDA	663.0000>619.0000	4.355
31	PFDoA	613.0000>569.0000	4.496
32	PFTeDA	713.0000>669.0000	4.745
33	PFDS	295.0000>201.0000	4.921

EPA-537.1 Reproducibility



Injection 1

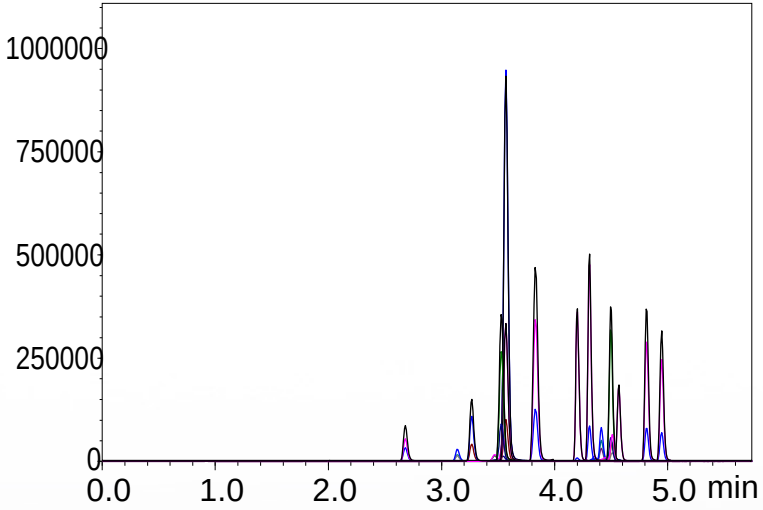
Peak Number	Compound	Retention Time (min)
1	PFBS	2.682
2	PFHxA	3.141
3	HFPO-DA	3.269
4	PFHpA	3.472
5	PFHxS	3.531
6	ADONA	3.569
7	PFOA	3.57
8	PFNA	3.834
9	PFOS	3.911
10	9Cl-PF3ONS	4.201
11	PFDA	4.309
12	N-MeFOSAA	4.355
13	PFUnA	4.451
14	N-EtFOSAA	4.499
15	11Cl-PF3OUdS	4.57
16	PFDoA	4.814
17	PFTrDA	4.948
18	PFTeDA	4.978

Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-613
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Part Number: 92113-415
Mobile Phase A: 10 mM Ammonium Acetate
Mobile Phase B: Methanol

Gradient:

Time	%B
0.0	33
4.0	98
4.10	100
6.00	100
6.10	33
7.50	End

Flow Rate: 0.4 mL/min
Pressure: 389 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)



Injection 300

Peak Number	Compound	Retention Time (min)
1	PFBS	2.702
2	PFHxA	3.212
3	HFPO-DA	3.254
4	PFHpA	3.488
5	PFHxS	3.583
6	ADONA	3.590
7	PFOA	3.591
8	PFNA	3.801
9	PFOS	3.899
10	9Cl-PF3ONS	4.195
11	PFDA	4.319
12	N-MeFOSAA	4.401
13	PFUnA	4.461
14	N-EtFOSAA	4.510
15	11Cl-PF3OUdS	4.569
16	PFDoA	4.822
17	PFTrDA	4.910
18	PFTeDA	4.931

Acknowledgements

- Charles Powley – STRIDE Center for PFAS Solutions

Q&A with the Presenters