HPLC Separation Improvements for Short Chain PFAS

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of chemicals used to make fluoropolymer coatings and products that resist heat, oil, stains, grease, and water. These toxic "forever chemicals" are a concern to our health and environment and are now being regulated by the Environmental Protection Agency.

Short chain PFAS such as trifluoracetic acid (TFA) are challenging to separate due to low retention and poor peak shape. Some techniques such as mixed mode hydrophilic interaction liquid chromatography (HILIC) have been demonstrated to show improved retention, however, these techniques have their limitations.

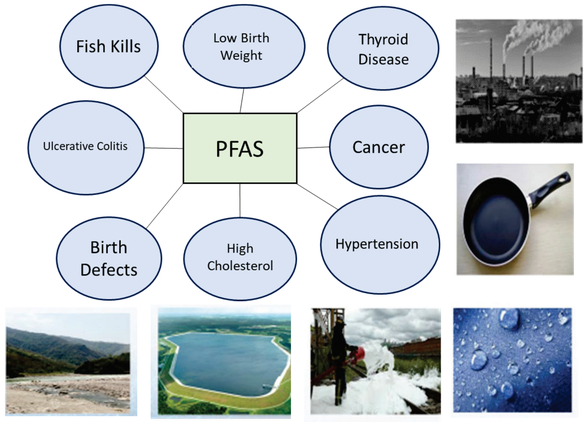
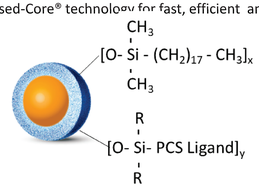


Figure 1: Common pathways for PFAS exposure released into the environment and health effects linked to PFAS

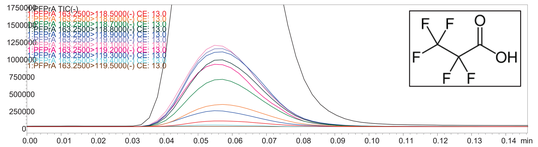
A new reverse phase, superficially porous particle (SPP) with a positive charge surface chemistry incorporated has shown separation advantages for short chain PFAS while using low ionic strength mobile phases such as formic/acetic acid.

HALO 90 Å, 2.7 µm PCS C18

- Excellent peak shape and increased loading capacity for basic compounds
- Alternate L1 selectivity (PCS C18)
- Alternate L11 selectivity (PCS Phenyl-Hexyl)
- Built upon Fused-Core® technology for fast, efficient and reliable separations

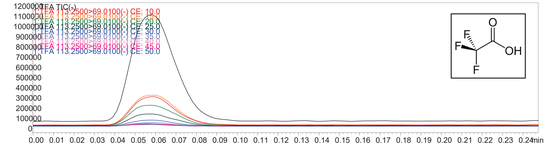


LC/MS Method Optimization

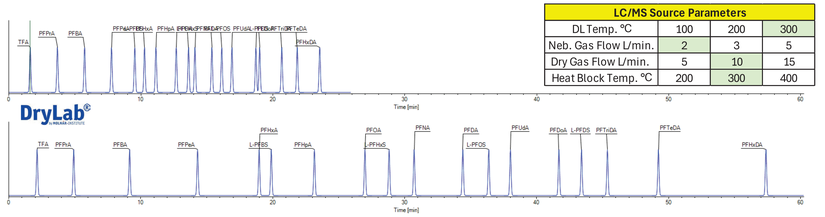


Perfluoropropionic acid (PFPrA) is an ultra-short chain perfluoroalkyl carboxylic acid. PFPrA is optimized on a Shimadzu 8045 LC/MS.

Trifluoroacetic acid (TFA) is an organofluorine compound and considered an ultra-short chain perfluoroalkyl carboxylic acid. One challenge analyzing TFA is having enough retention on column.



LC/MS Source Parameters			
DL Temp. °C	100	200	300
Neb. Gas Flow L/min.	2	3	5
Dry Gas Flow L/min.	5	10	15
Heat Block Temp. °C	200	300	400



DryLab® software is utilized in order to determine adequate retention and resolution for a panel of 18 per and polyfluorinated compounds.

Superficially Porous (SPP) vs. Fully Porous Particles (FPP)

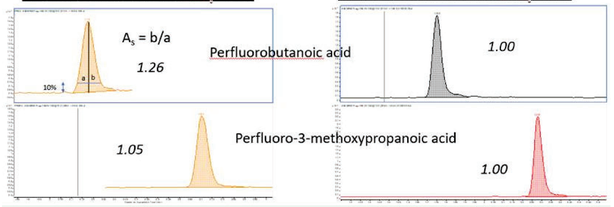
Optimizing Data Acquisition: HPLC

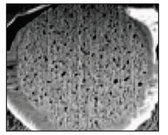
- Requirement: Peak asymmetry factor must be 0.8 – 1.5 (first two eluters)
- EPA Method 537.1 samples are in 96:4 MeOH:water
- Can be achieved with low-volume injections and lowered initial %MPA.

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

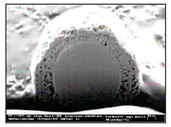
C18, 1.7 µm fully porous, MPA_c = 60%

C18, 2.7 µm porous shell, MPA_c = 80%



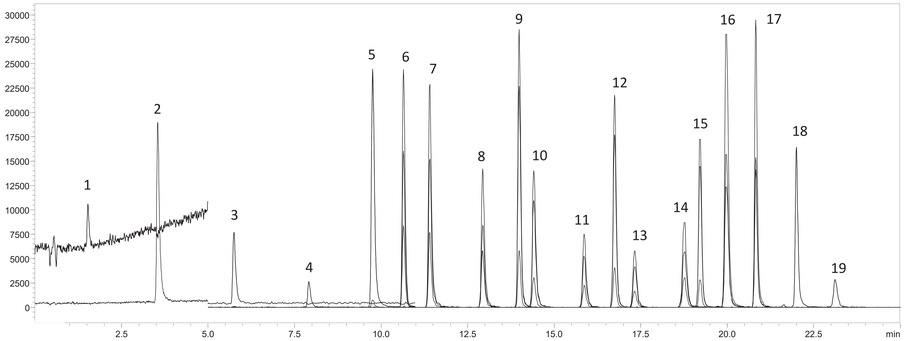


Fully Porous Particle (FPP)



Superficially Porous Particle (SPP)

Reverse Phase Positive Charge Surface: Formic Acid



Peak Identities:
1. TFA
2. PFPrA
3. PFBA
4. PFPeA
5. PFHxA
6. L-PFBS
7. PFHpA
8. PFOA
9. L-PFHxS
10. PFNA
11. PFDA
12. L-PFOS
13. PFUdA
14. PFDoA
15. PFTeDA
16. PFHxDA
17. PFODA
18. L-PFDS
19. PFTeDA

A separation of 19 per and polyfluorinated compounds including TFA and PFPrA is performed on a HALO® PCS C18 column under formic acid conditions.

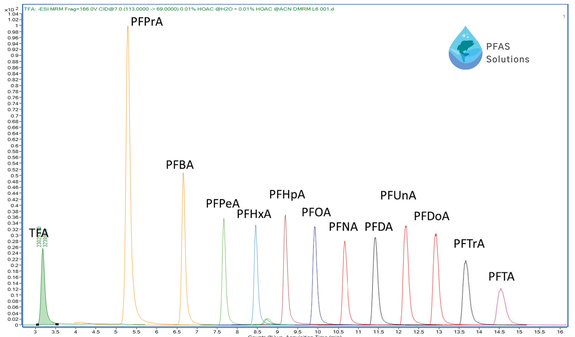
Testing Conditions:
Column: HALO 90 Å PCS C18, 2.7 µm, 2.1 x 100 mm
Part Number: 92812-617
Guard Column: HALO® 160 Å PFAS Delay, 2.7 µm, 3.0 x 50mm
Part Number: 92113-415
Mobile Phase: A: Water/ 0.1% Formic Acid
B: Acetonitrile/ 0.1% Formic Acid
Gradient:

Time	%B
0.0	10
20.0	100
25.0	100

Flow Rate: 0.4 mL/min
Temperature: 35 °C
Wavelength: PDA, 260
LC System: Shimadzu Nexera X2
MS System: Shimadzu 8045

MS CONDITIONS:
Detection: (-) ESI
Spray Voltage: 3.5 kV
DL Temp: 300°C
Neb. Gas: 2 L/min.
Dry 10 L/min.
Heat Block Temp.: 300°C

Reverse Phase Positive Charge Surface: Acetic Acid



Parameter	Value
Flow Rate	0.5 mL/min
Oven Temperature	40°C
Injection volume	2 µL
MPA	0.01% HOAc in water
MPB	0.01% HOAc in ACN

Time (min)	% MPA	% MPB
0	80	20
5	20	80
12	10	90
18	10	90
18.1	80	20

A separation of short chain PFAS is performed using acetic acid as an acidic modifier. Adequate retention and peak shape is observed while maintaining resolution for other long chain PFAS compounds.

Conclusions

A new positive charge surface (PCS) stationary phase from Advanced Materials Technology shows adequate retention and peak shape for short chain PFAS analytes such as TFA and PFPrA in combination with a HALO PFAS Delay column.

The superficially porous particle technology shows an advantage in peak widths due to the solid silica core when compared to fully porous particle material.

Future work will include LOD experiments along with temperature comparisons in order to speed up the analysis time. Moving the column dimension down to a 1.5mm ID will also be explored in order to boost sensitivity while reducing solvent consumption.