Improving Short Chain PFAS Analysis using Reversed Phase Conditions

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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 amongst other government agencies.

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.

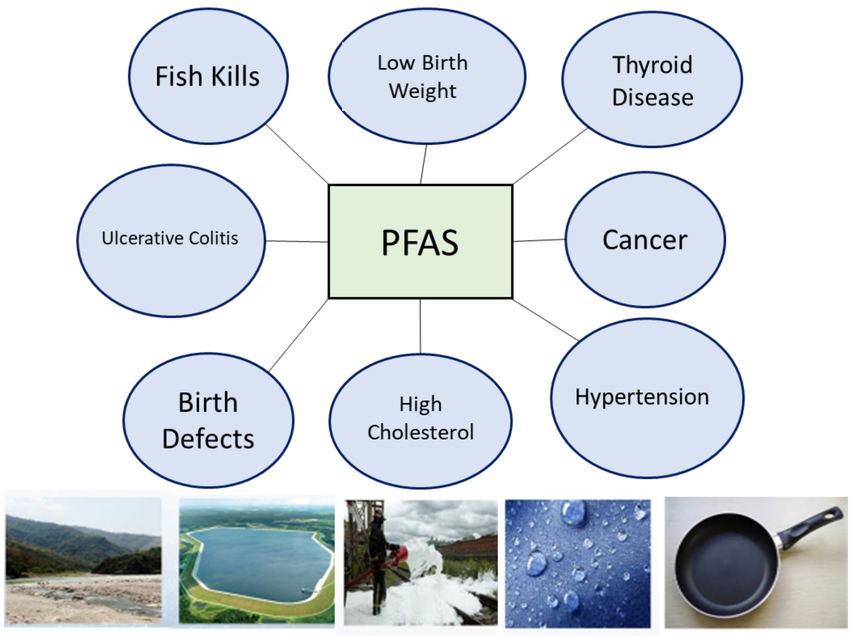
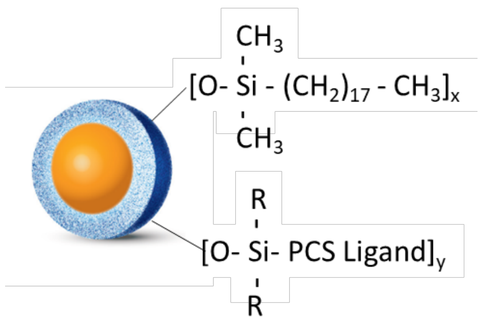


Figure 1: Common pathways for PFAS exposure released into the environment and health effects linked to PFAS

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.

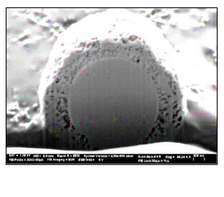
HALO 90 Å PCS C18

- 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

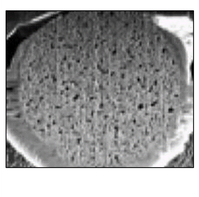


SUPERFICIALLY POROUS VS. FULLY POROUS PARTICLES

Superficially Porous Particle (SPP)



Fully Porous Particle (FPP)



The design of the HALO® SPP with a solid core surrounded by a bonded phase shell provides higher efficiencies with less back pressure compared to FPP columns. These design advantages aid in meeting chromatographic requirements for PFAS methods.

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

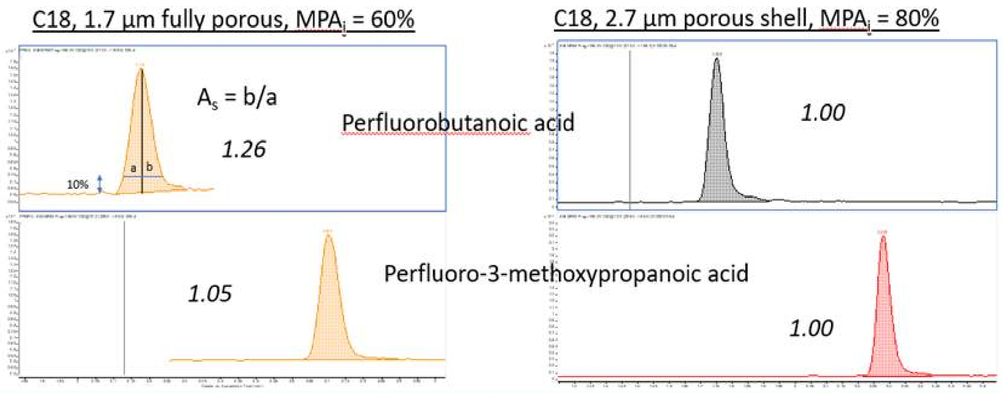
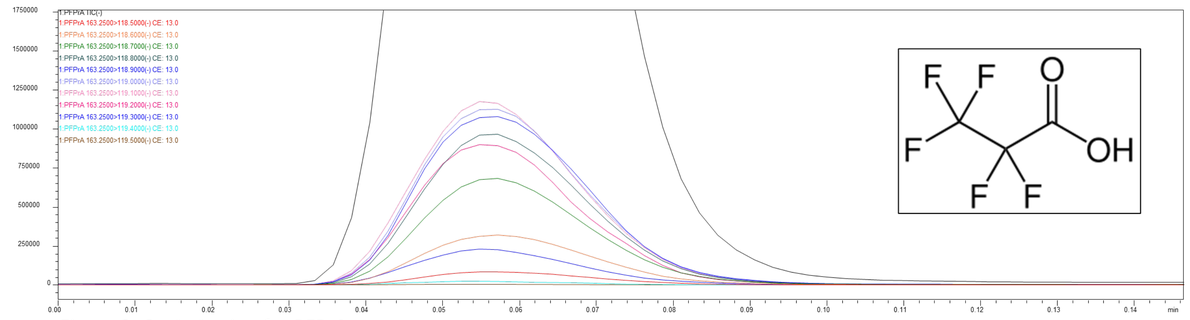


Figure 1: Comparison of peak asymmetry for PFBA and PFMA using FPP vs. SPP columns

Requirement: Peak Asymmetry factor must be 0.8-1.5 (first two eluting compounds)

LC/MS METHOD OPTIMIZATION

DryLab® software was utilized for method optimization to determine adequate retention and resolution for a panel of 18 per and polyfluorinated compounds which included "ultra-short" chain compounds.



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

Trifluoroacetic acid (TFA) is an organofluorine compound and considered an ultra-short chain perfluorocarboxylic acid (PFCA). One challenge analyzing TFA is achieving retention on column.

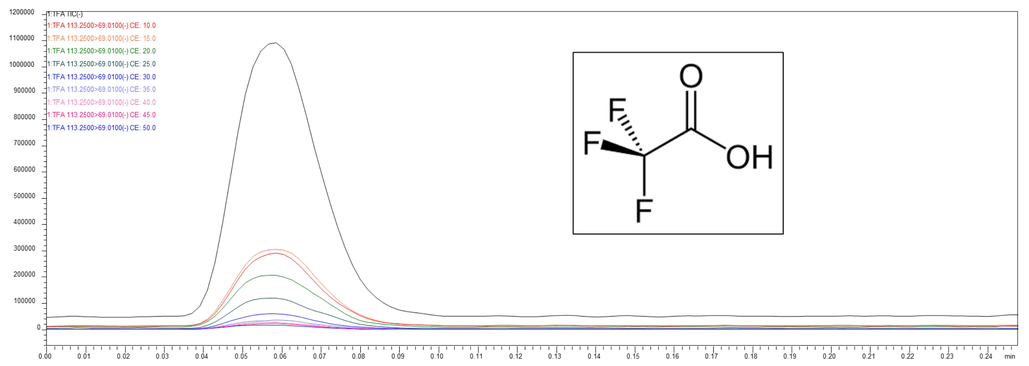
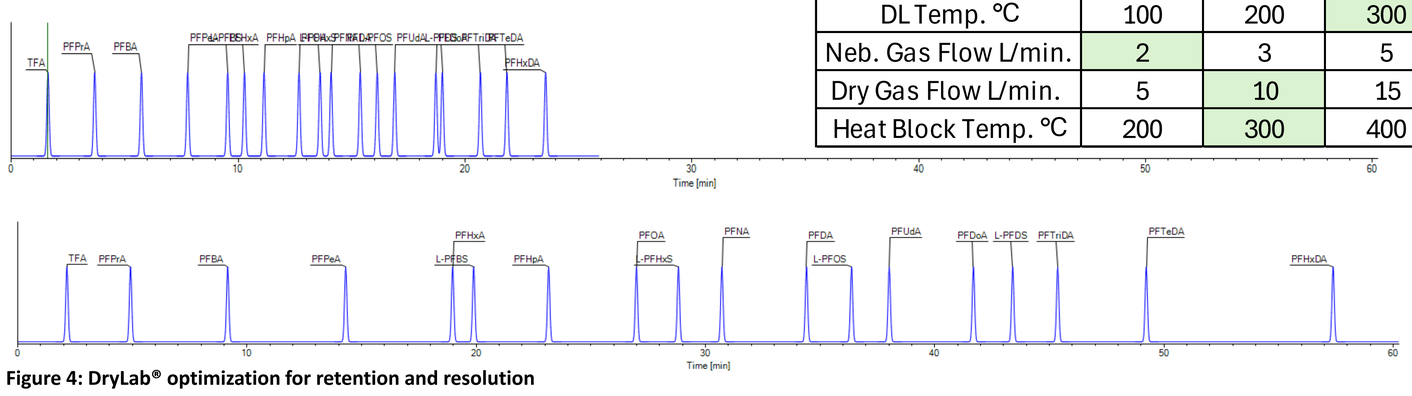


Figure 3: Optimization for TFA

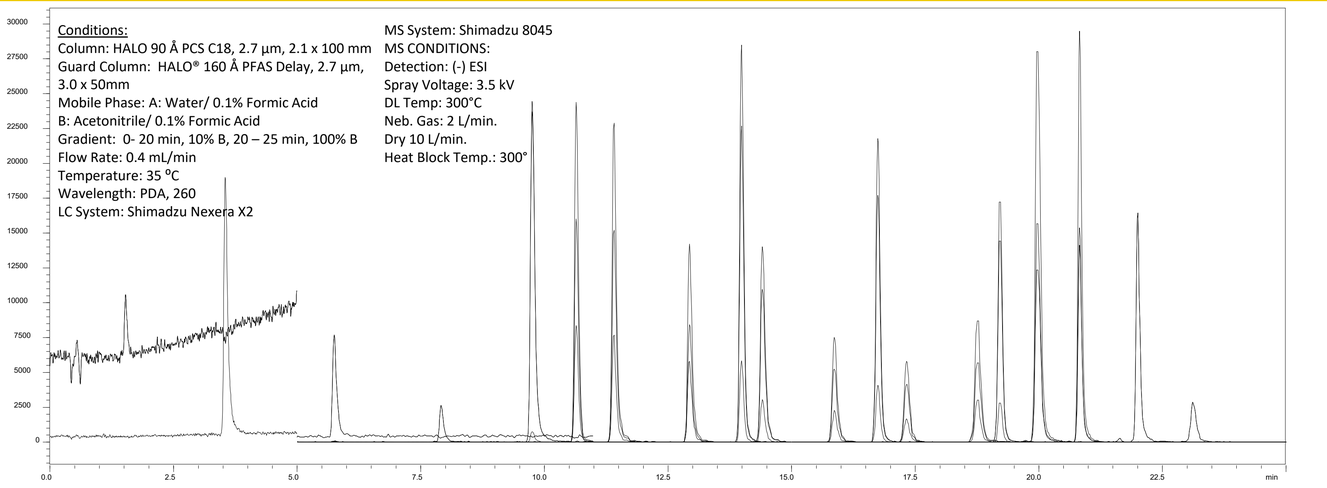
DryLab® by MOLNÁR-INSTITUTE



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

Figure 4: DryLab® optimization for retention and resolution

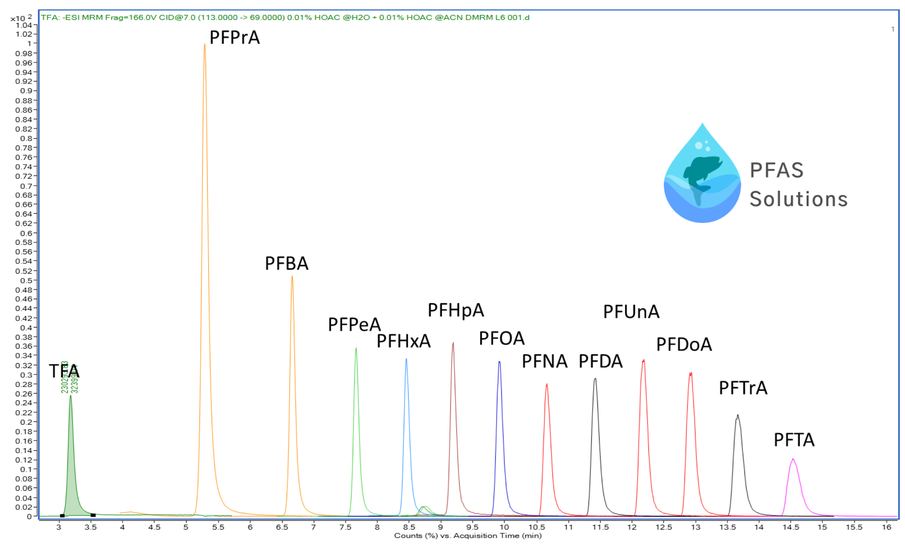
REVERSE PHASE POSITIVE CHARGE SURFACE: FORMIC ACID



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

Figure 5: A separation of 19 per and polyfluorinated compounds including TFA and PFPrA is performed on a HALO® PCS C18 column under formic acid conditions.

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

Figure 6: 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 shape 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 increase signal intensity while reducing solvent consumption.