

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 trifluoroacetic 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.

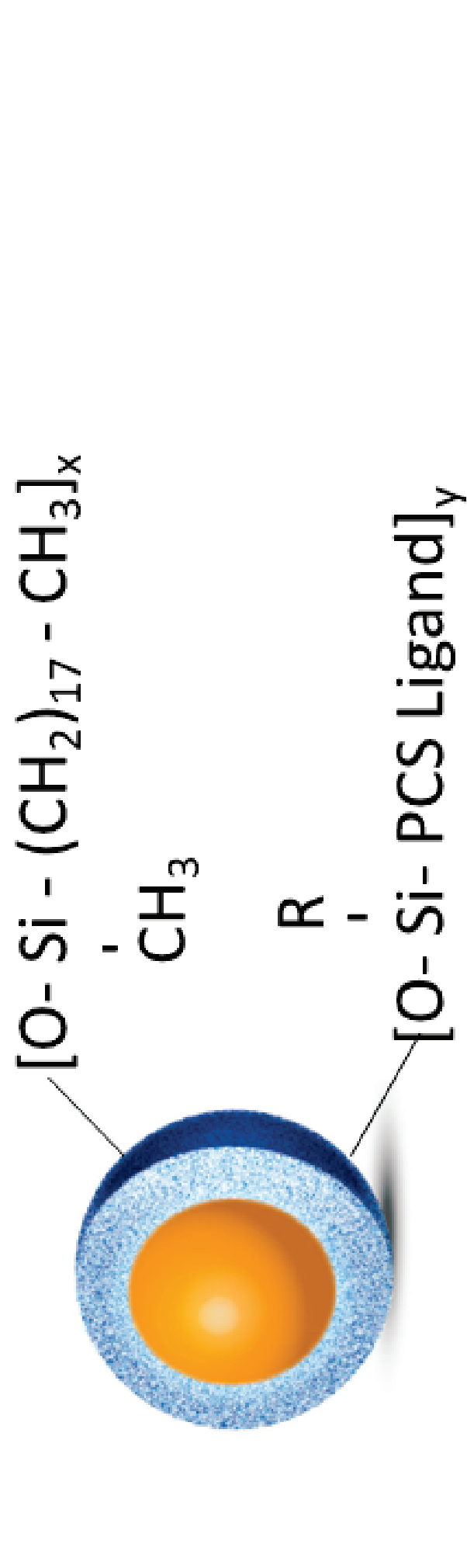


Figure 1: Common pathways for PFAS exposure released into the environment and health effects linked to PFAS

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.

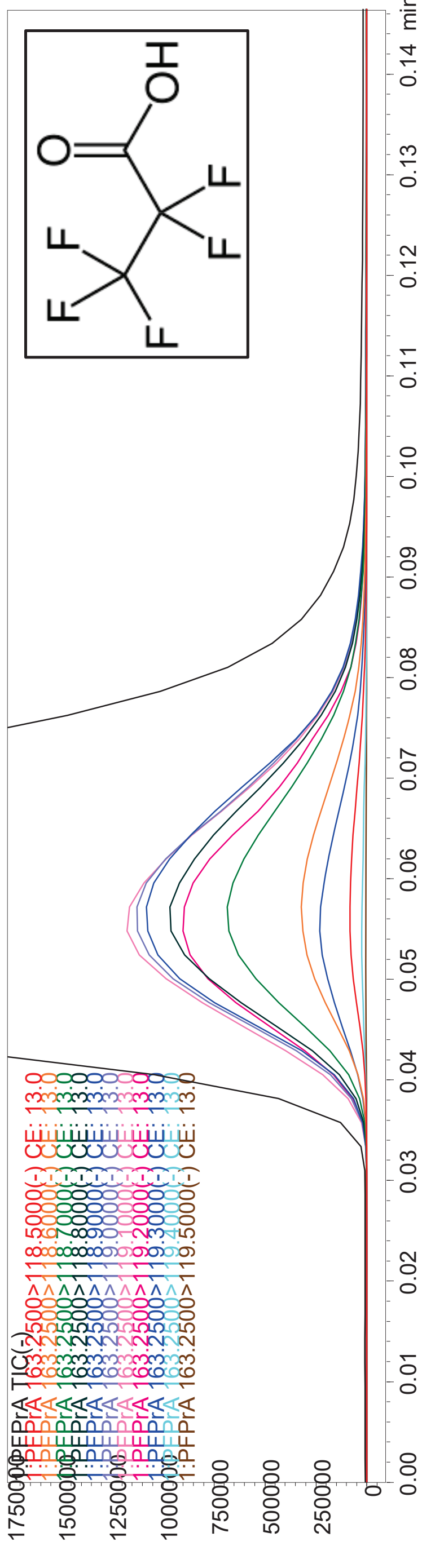
- Excellent peak shape and increased loading capacity for basic compounds
- Alternate L1 selectivity (PCS C18)
- Alternate L1.1 selectivity (PCS Phenyl-Hexyl)
- Built upon Fused-Core® technology for fast, efficient and reliable separations

HALO 90 Å, 2.7 µm PCS C18



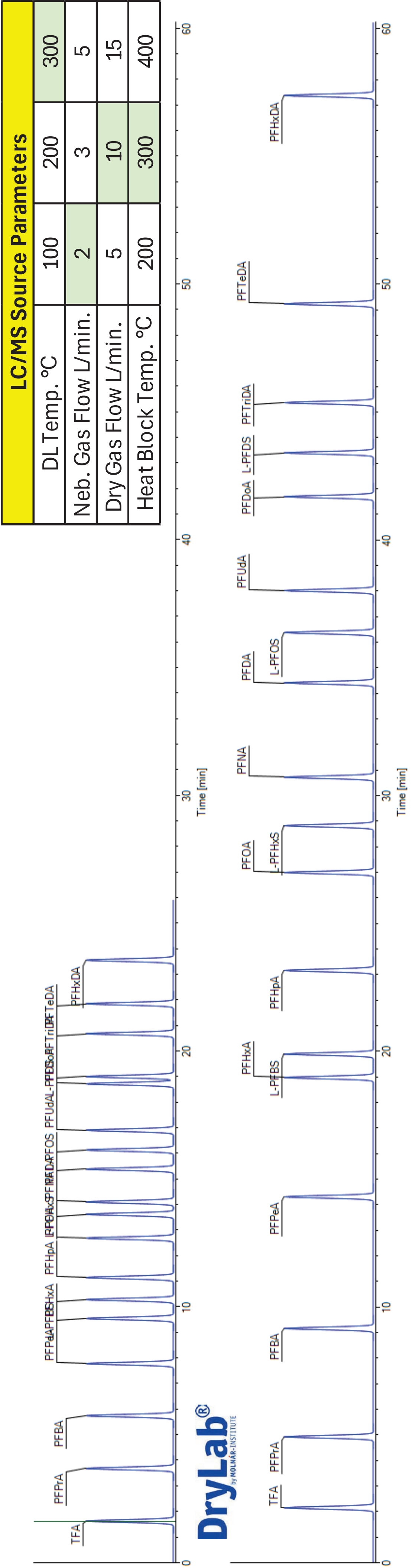
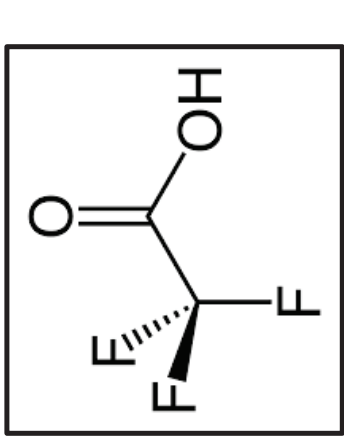
$$\begin{matrix} \text{CH}_3 & & \text{CH}_3 \\ | & & | \\ [\text{O}-\text{Si}-(\text{CH}_2)_{17}-\text{CH}_3]_x \\ | & & | \\ \text{R} & & \text{R} \\ | & & | \\ [\text{O}-\text{Si}-(\text{CH}_2)_y-\text{PCS Ligand}]_y \end{matrix}$$

LC/MS Method Optimization



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.

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

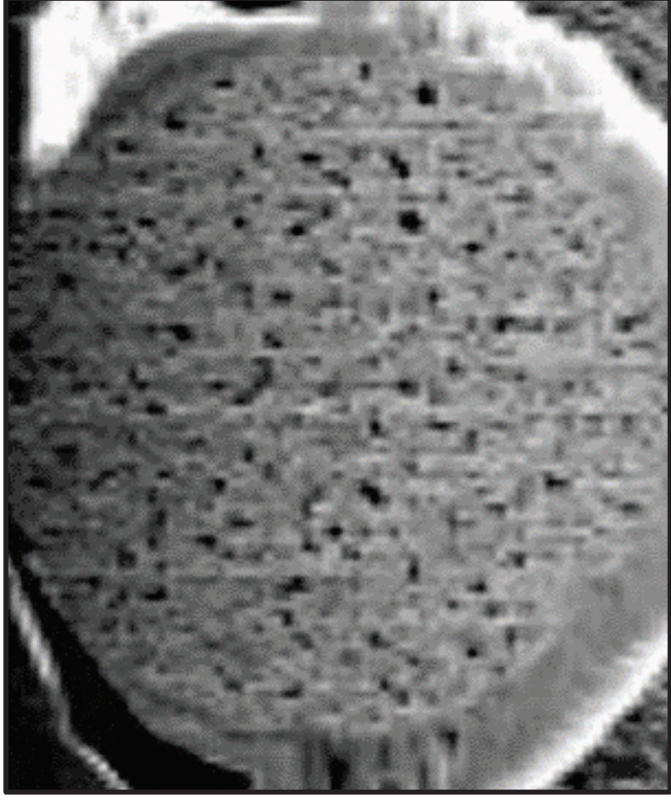
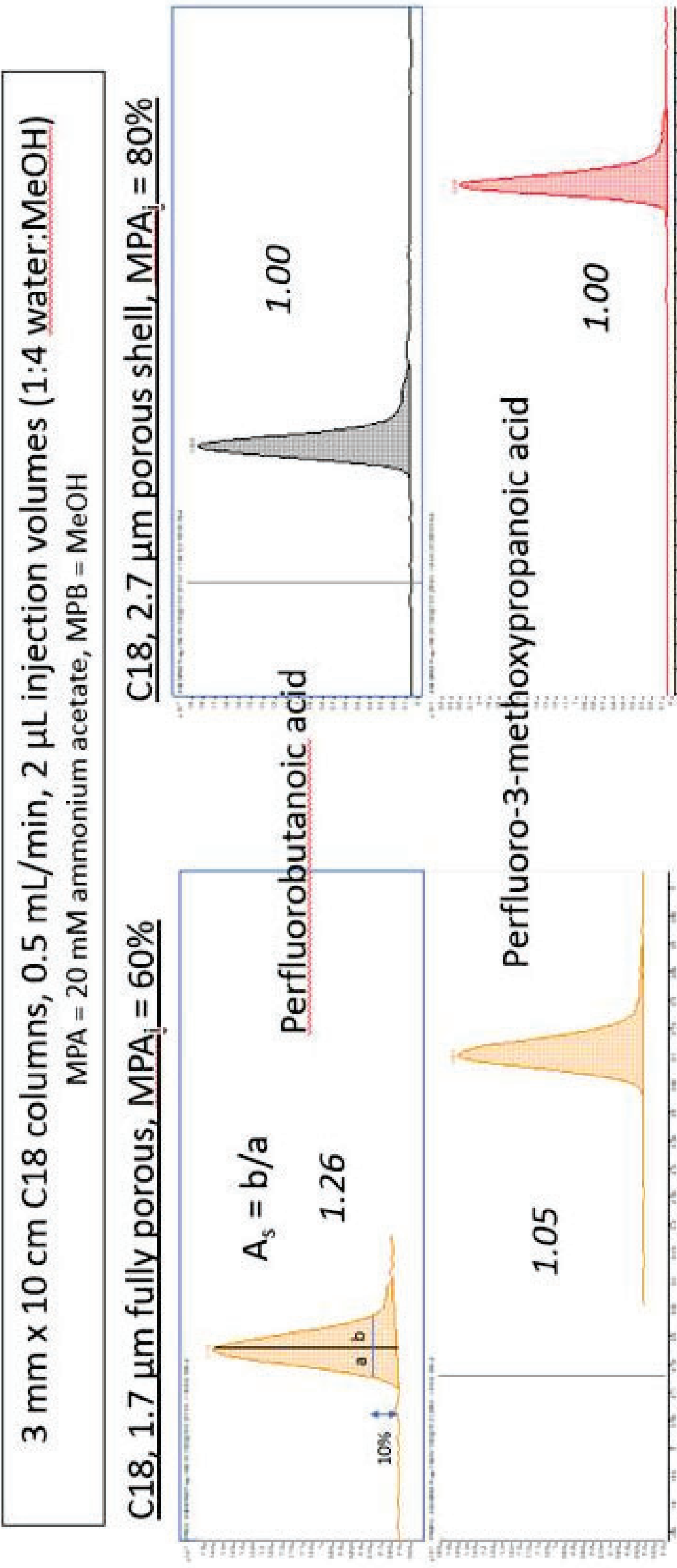


DryLab® software is utilized in order to determine adequate retention and resolution for a panel of 18 per and polyfluorinated compounds.

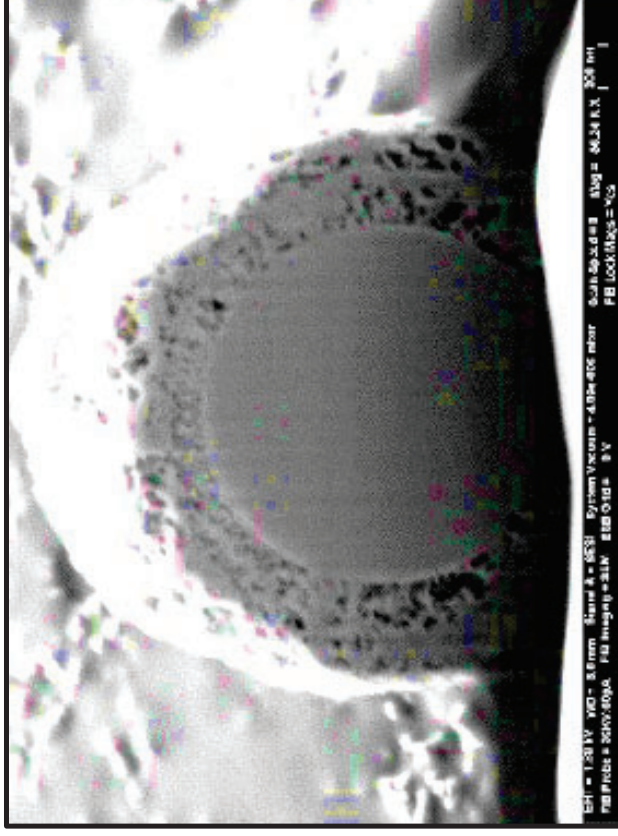
Superficially Porous (SPP) vs. Fully Porous Particles (FPP)

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.

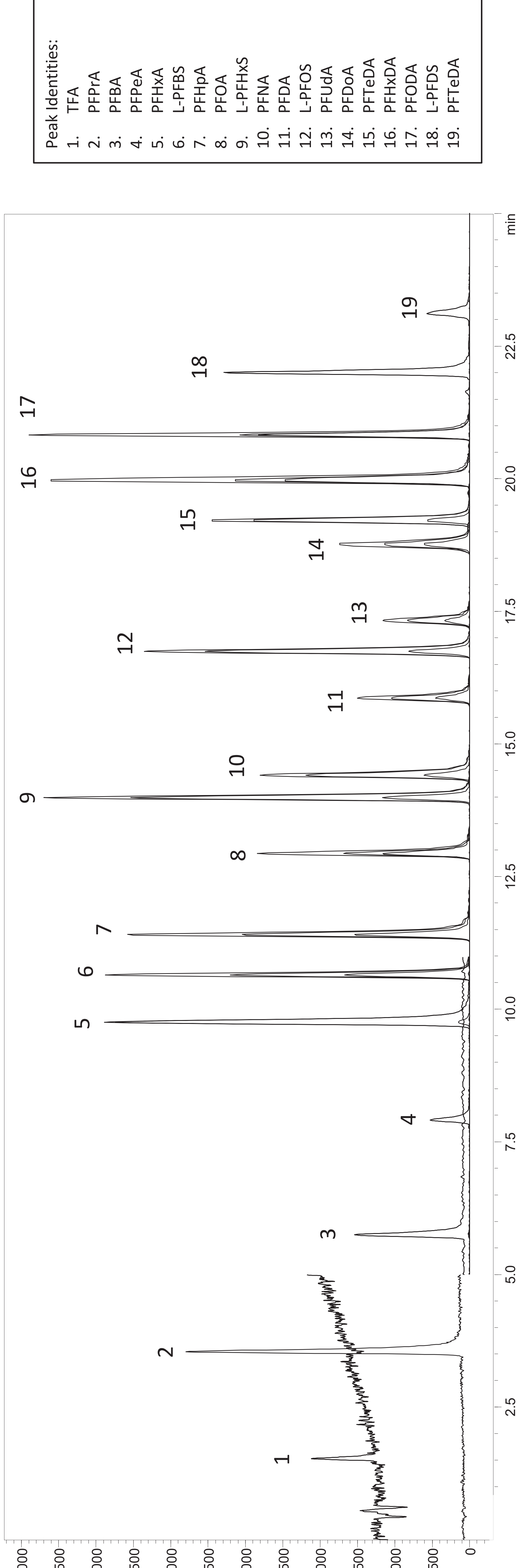


Fully Porous Particle (FPP)



Superficially Porous Particle (SPP)

Reverse Phase Positive Charge Surface: Formic Acid



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



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.