Simultaneous Quantitation of Ultrashort-, Short- and Long-chain PFAS in Different Water Matrices

Presented by: Kendra J. Adams, PhD

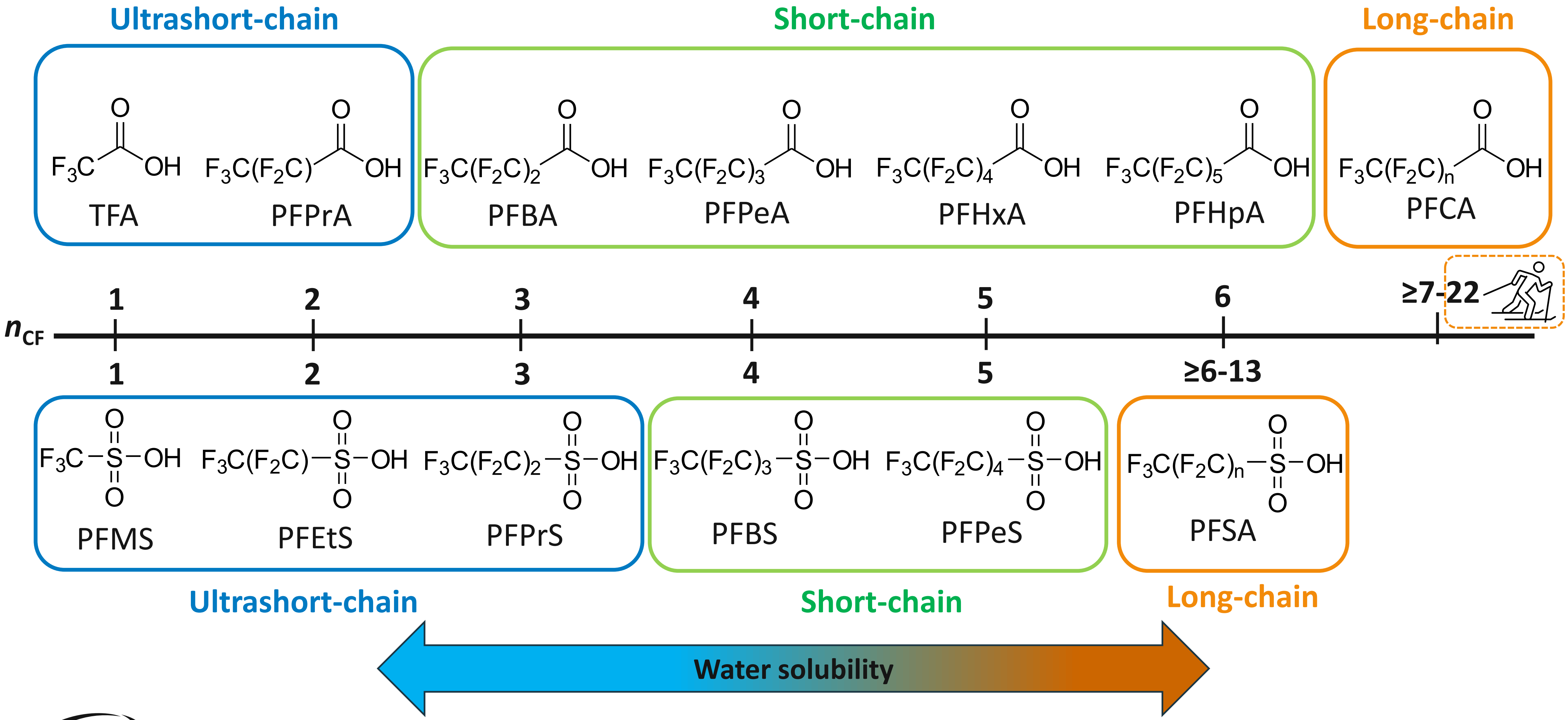
Holly Lee[1], Simon Roberts[2], Craig M. Butt[2], Sam Lodge[3], RenXi Ye[4], Cora Young[4] and Trevor VandenBoer[4]

SCIEX, Canada[1]; Sciex, USA[2], Phenomenex, USA[3]; York University, Canada[4]

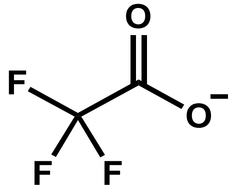
The power of precision

MKT-34340-A

Relevant perfluorocarboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) in water



Why are these ultrashort-chain PFAS so hard to analyze?

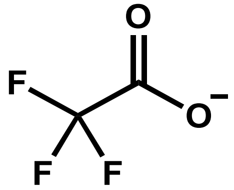


Matrix effects

- Susceptible to matrix effects from early eluting co-extractables like organic anions

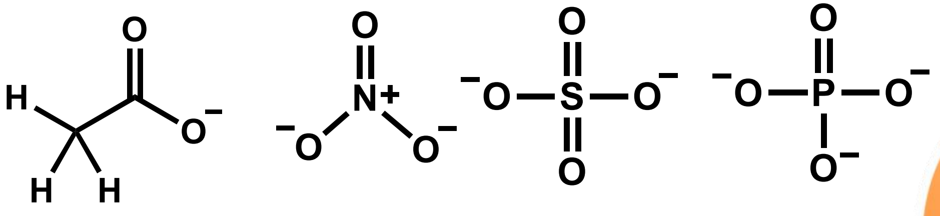
d

Why are these ultrashort-chain PFAS so hard to analyze?



Matrix effects

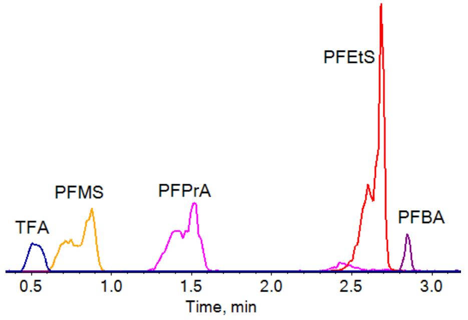
- Susceptible to matrix effects from early eluting co-extractables like organic anions

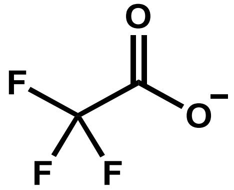


Very small Q1 and Q3 masses

- Higher instrumental baselines may impact LOQs
- Limited fragmentation for second transition

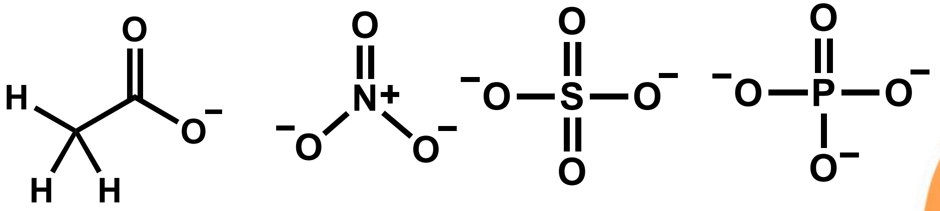
Why are these ultrashort-chain PFAS so hard to analyze?





Matrix effects

- Susceptible to matrix effects from early eluting co-extractables like organic anions



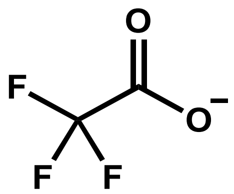
Very small Q1 and Q3 masses

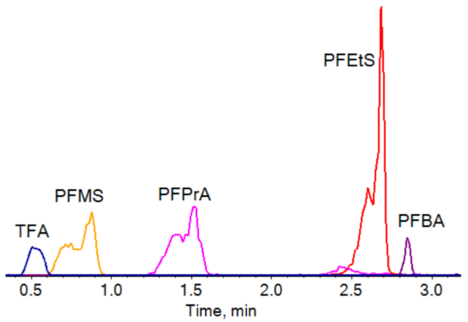
- Higher instrumental baselines may impact LOQs
- Limited fragmentation for second transition

Polar and low hydrophobicity

- Poor retention on reverse phase LC

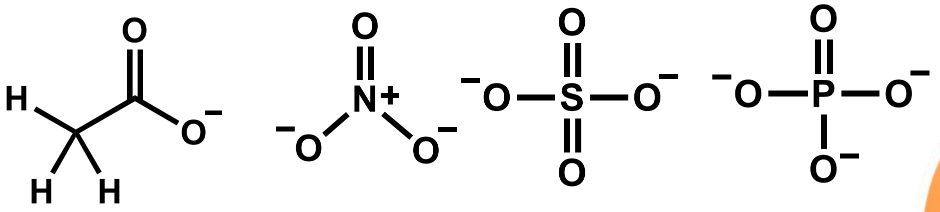
Why are these ultrashort-chain PFAS so hard to analyze?





Matrix effects

- Susceptible to matrix effects from early eluting co-extractables like organic anions



Polar and low hydrophobicity

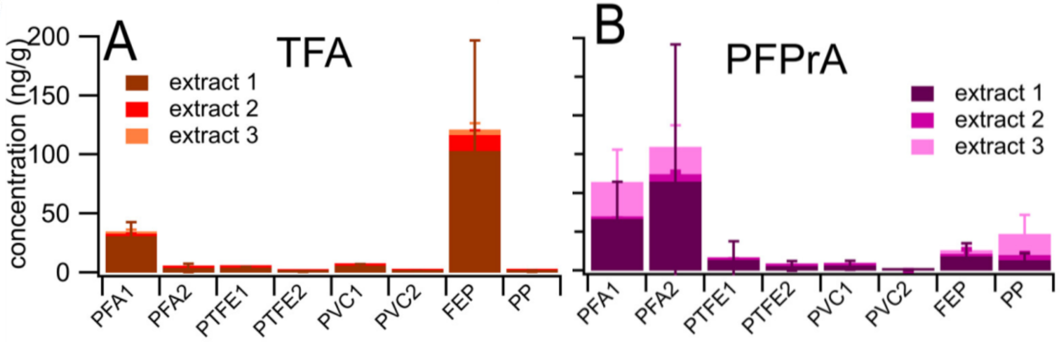
- Poor retention on reverse phase LC

Contamination

- TFA commonly used in reagents, lab consumables and solvent modifiers

Very small Q1 and Q3 masses

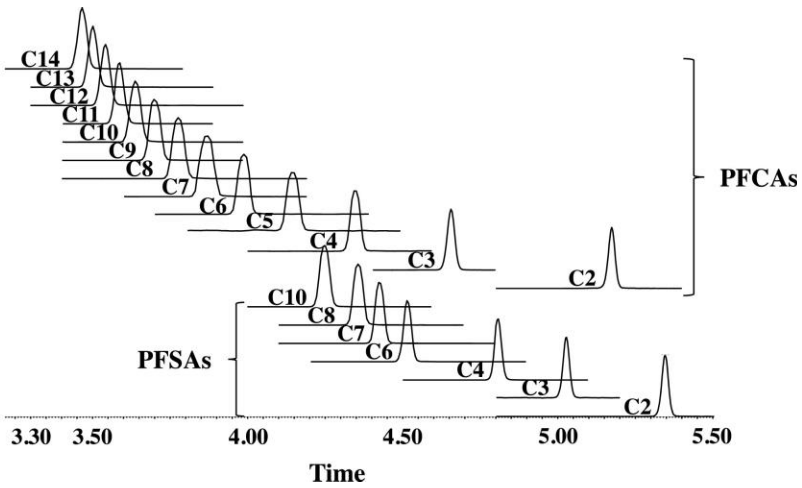
- Higher instrumental baselines may impact LOQs
- Limited fragmentation for second transition



Joudan *et al. Environ. Sci. Technol. Lett.* **2024.**

SCIEX

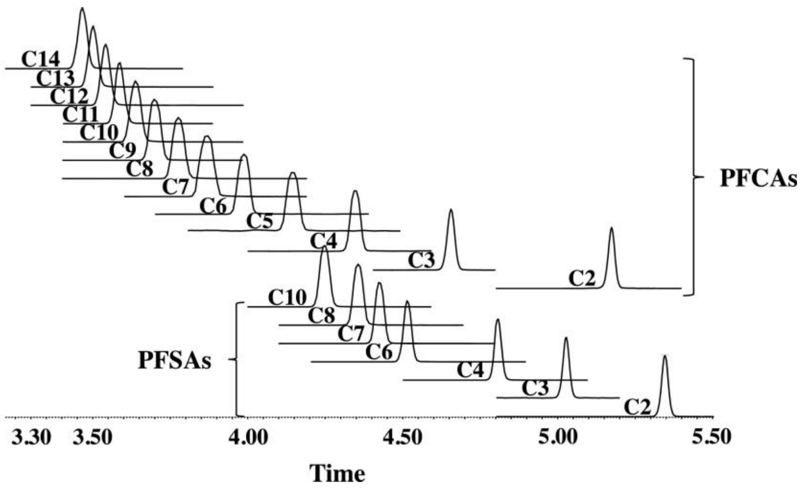
Chromatographic techniques for ultrashort-chain PFAS in the literature



Supercritical fluid chromatography

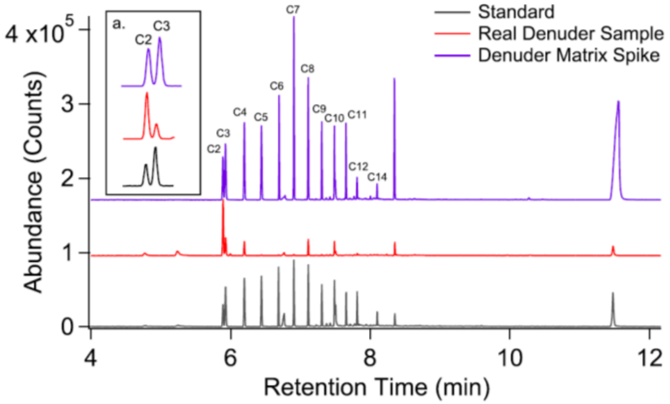
Yeung *et al. J. Chrom. A.* **2017**.

Chromatographic techniques for ultrashort-chain PFAS in the literature



Supercritical fluid chromatography

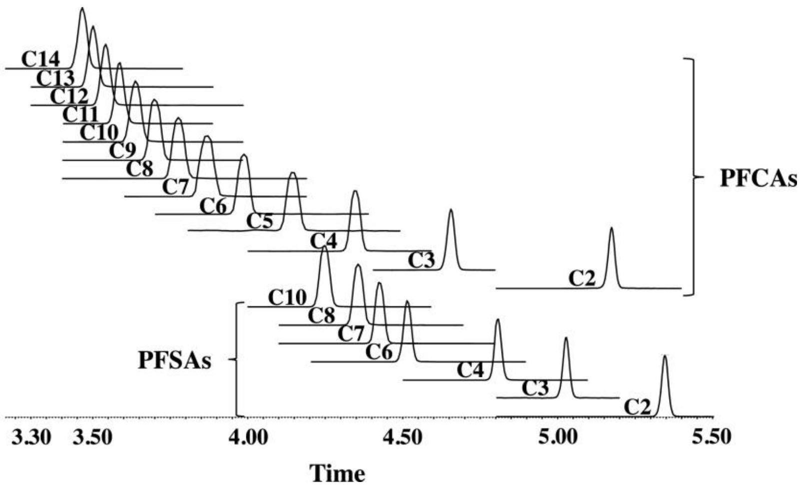
Yeung *et al. J. Chrom. A.* **2017**.



Derivatization for GC-MS

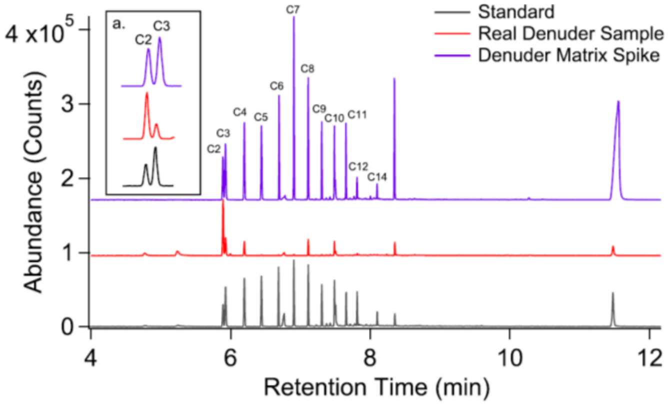
Ye *et al. Anal. Chem.* **2023**.

Chromatographic techniques for ultrashort-chain PFAS in the literature



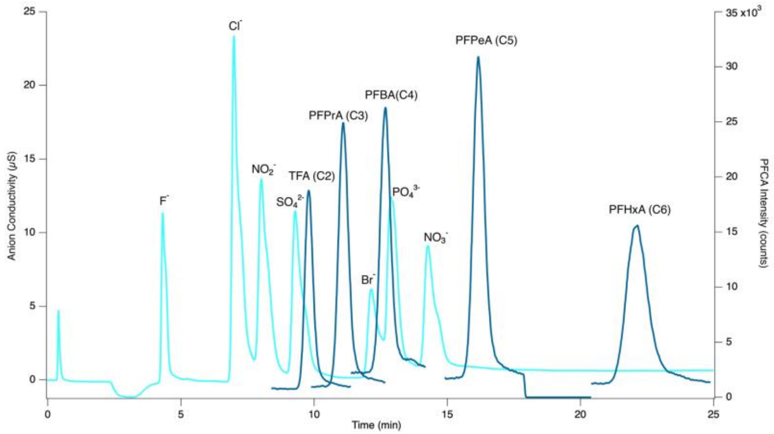
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



Derivatization for GC-MS

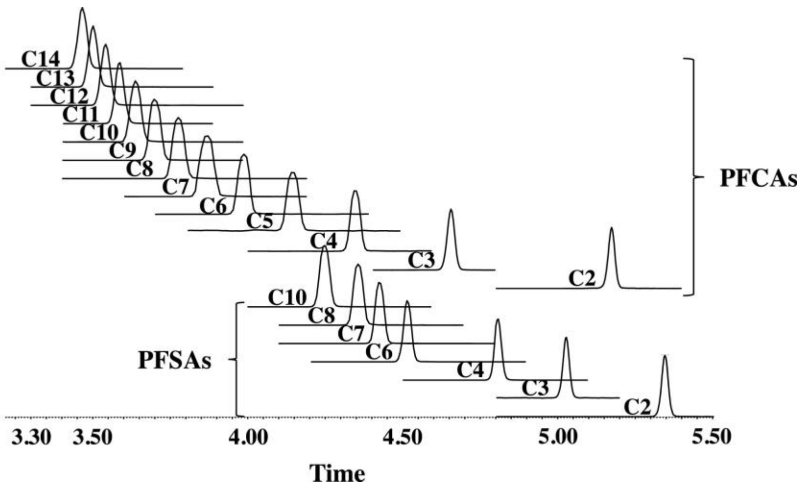
Ye *et al. Anal. Chem.* **2023**.



IC-MS

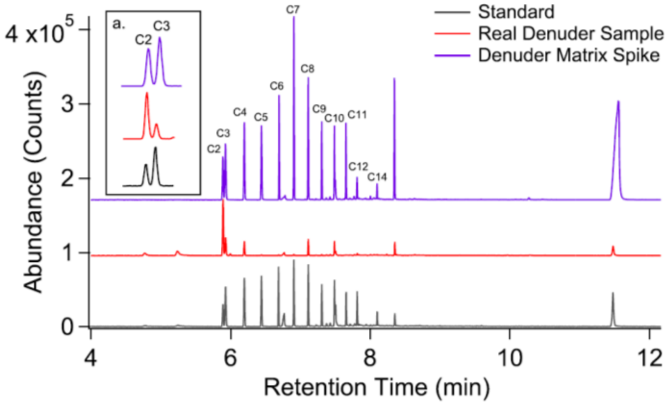
Cloutier *et al.* in prep.

Chromatographic techniques for ultrashort-chain PFAS in the literature



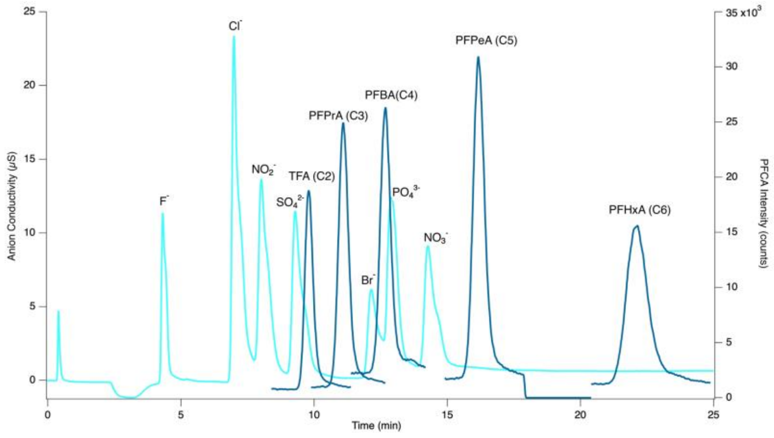
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



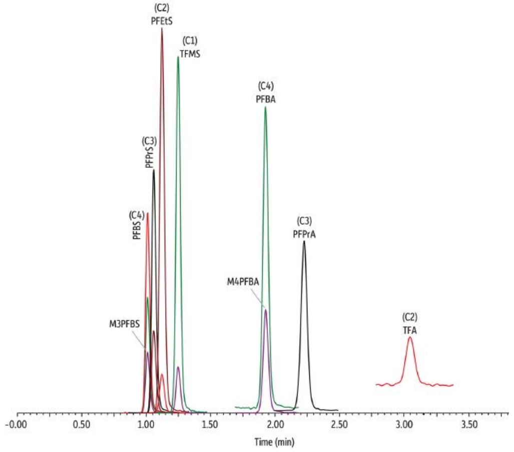
Derivatization for GC-MS

Ye *et al. Anal. Chem.* **2023**.



IC-MS

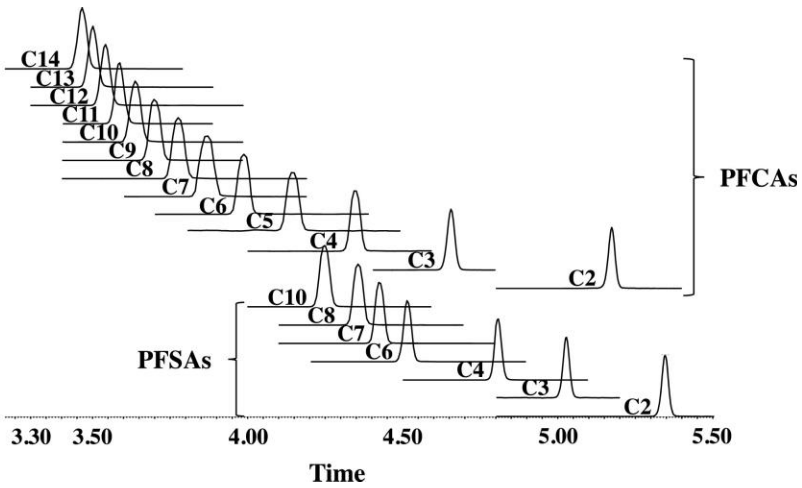
Cloutier *et al.* in prep.



Hybrid HILIC/ion exchange

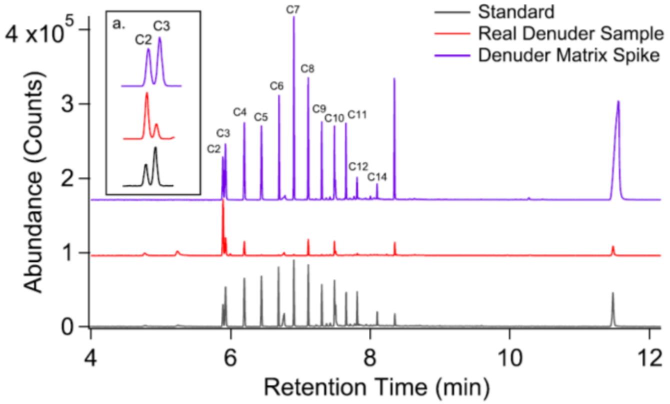
Liang *et al. J. Chrom. Open.* **2023**.

Chromatographic techniques for ultrashort-chain PFAS in the literature



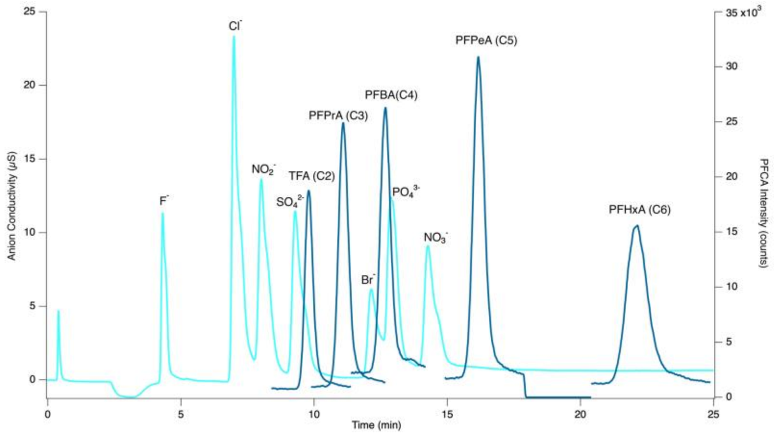
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



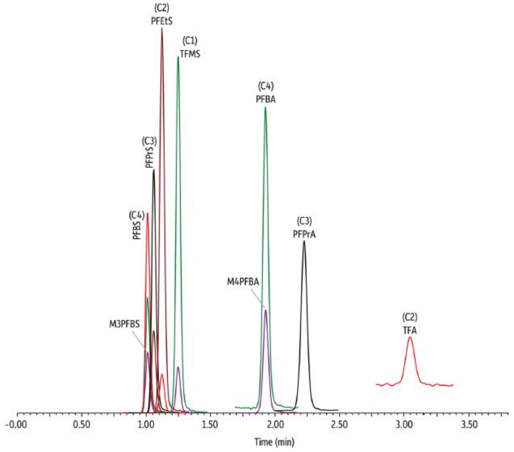
Derivatization for GC-MS

Ye *et al. Anal. Chem.* **2023**.



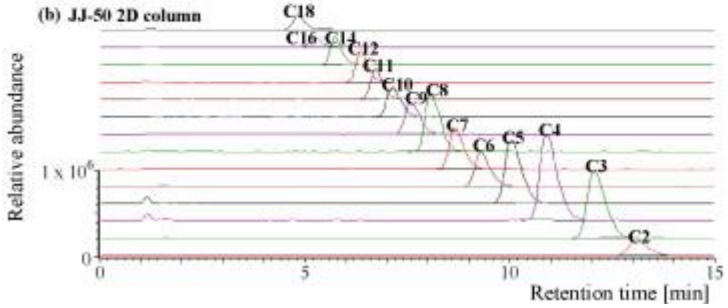
IC-MS

Cloutier *et al.* in prep.



Hybrid HILIC/ion exchange

Liang *et al. J. Chrom. Open.* **2023**.

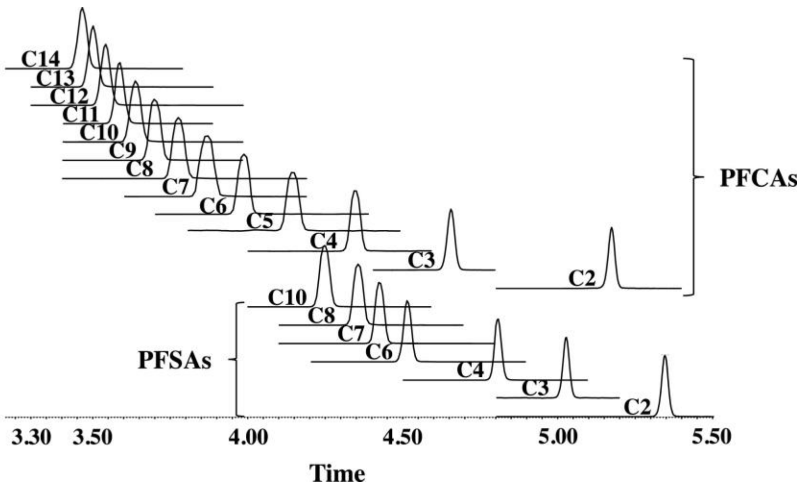


Mixed mode ion-exchange/C18 LC

Taniyasu *et al. Anal. Chim. Acta.* **2008**.

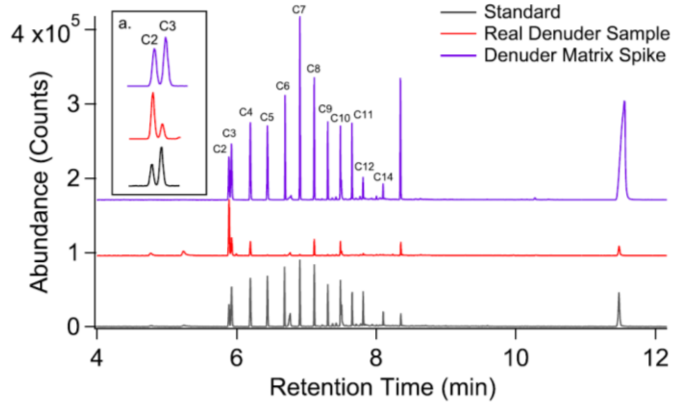
SCIEX

Chromatographic techniques for ultrashort-chain PFAS in the literature



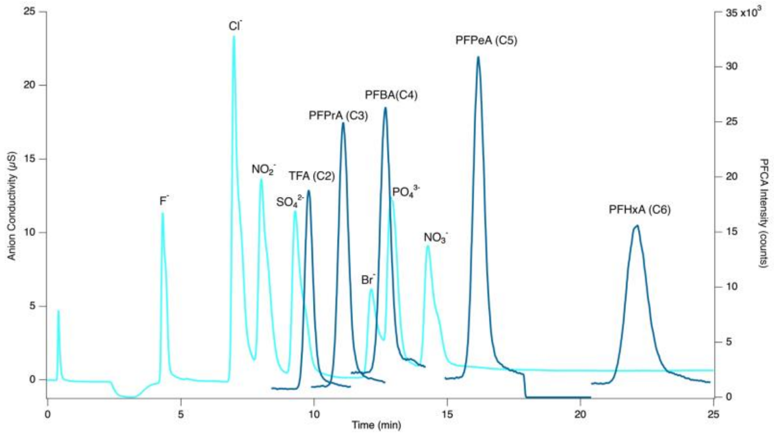
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



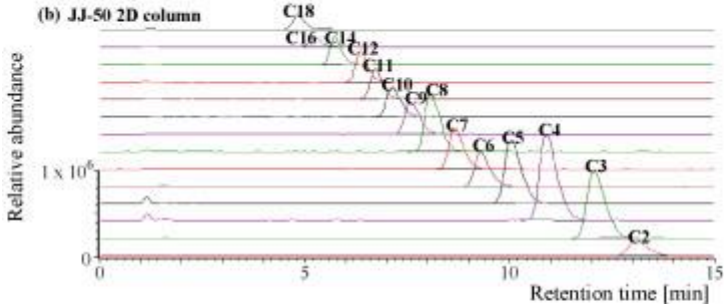
Derivatization for GC-MS

Ye *et al. Anal. Chem.* **2023**.



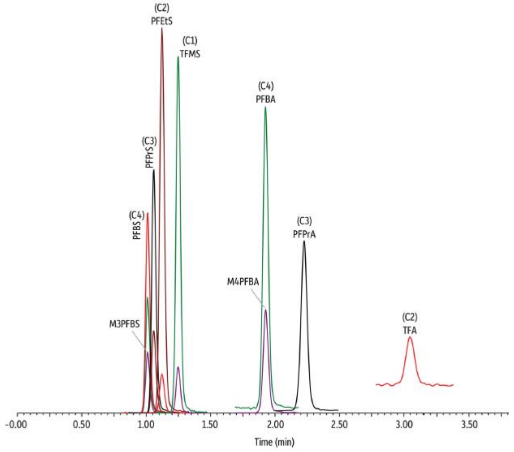
IC-MS

Cloutier *et al.* in prep.



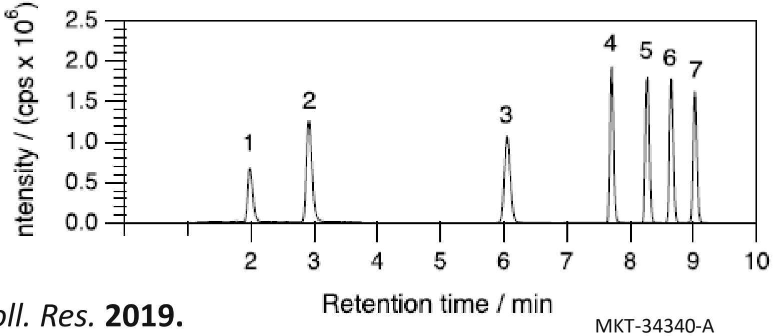
Mixed mode ion-exchange/C18 LC

Taniyasu *et al. Anal. Chim. Acta.* **2008**.



Hybrid HILIC/ion exchange

Liang *et al. J. Chrom. Open.* **2023**.

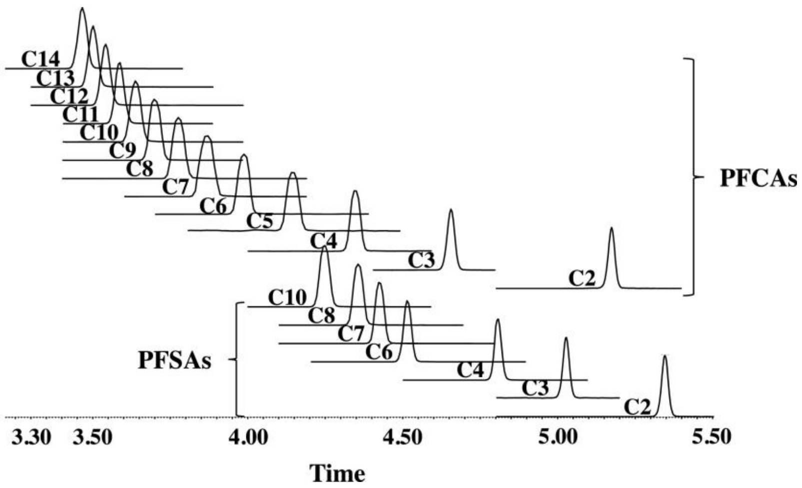


Reverse phase C18

Janda *et al. Environ. Sci. Poll. Res.* **2019**.

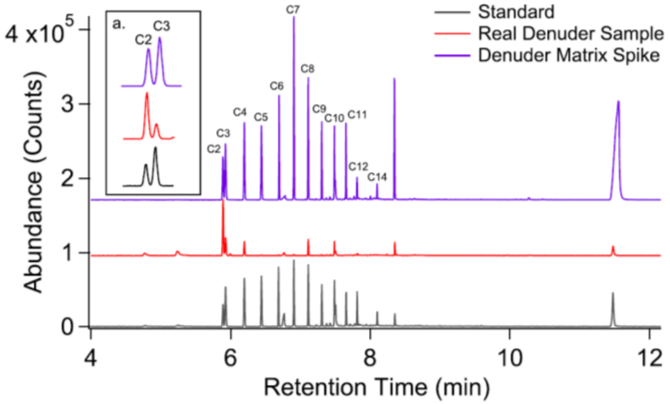
MKT-34340-A

Chromatographic techniques for ultrashort-chain PFAS in the literature



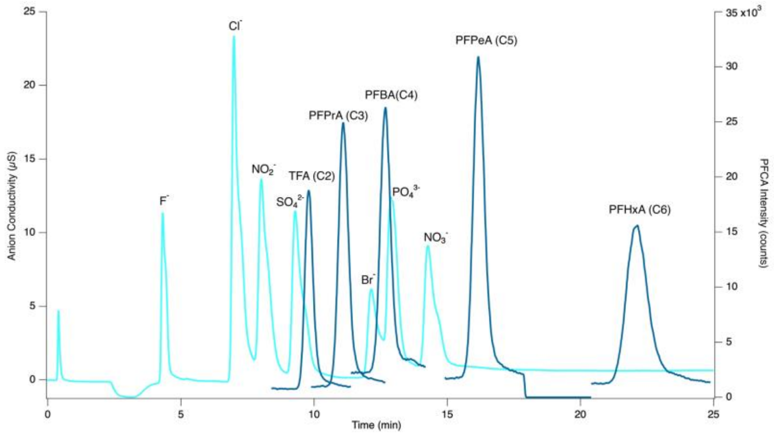
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



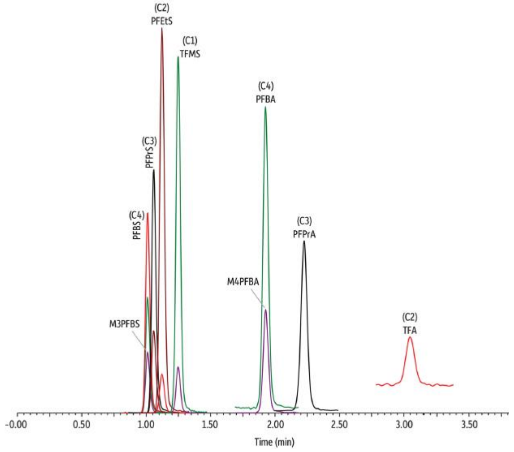
Derivatization for GC-MS

Ye *et al. Anal. Chem.* **2023**.



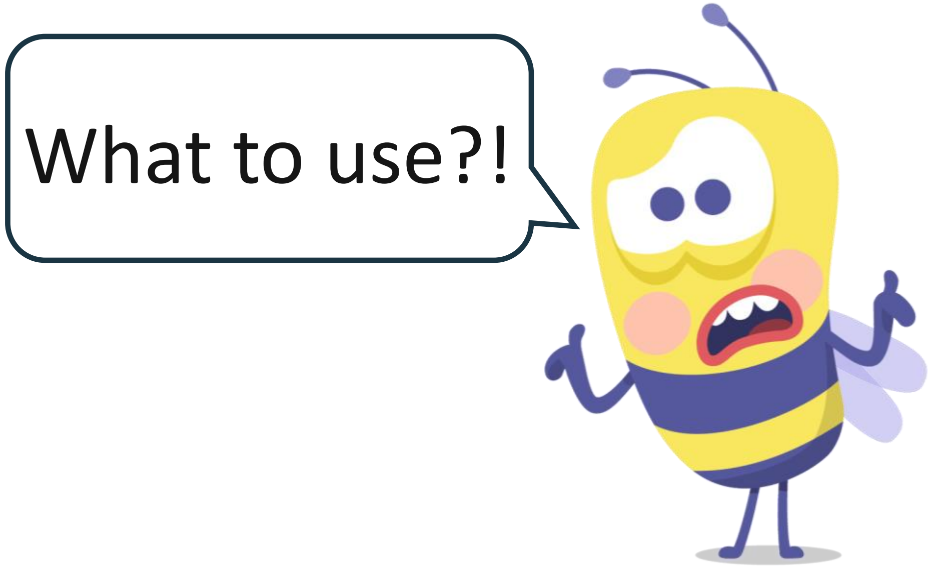
IC-MS

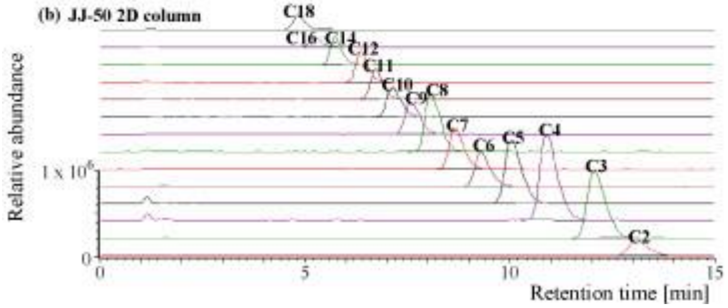
Cloutier *et al.* in prep.



Hybrid HILIC/ion exchange

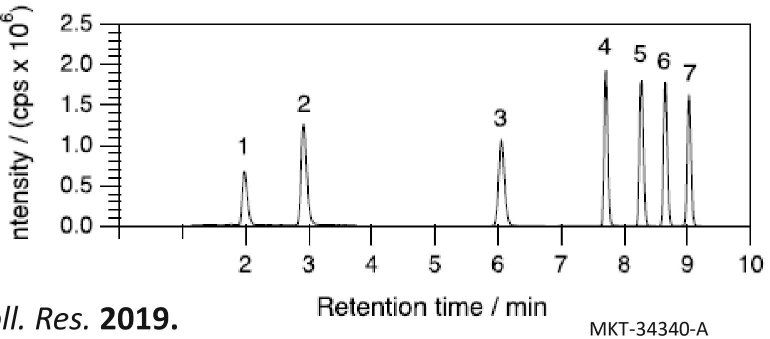
Liang *et al. J. Chrom. Open.* **2023**.





Mixed mode ion-exchange/C18 LC

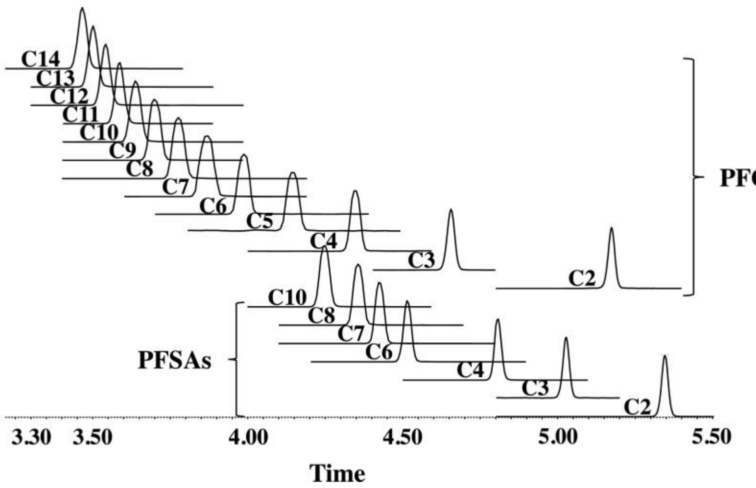
Taniyasu *et al. Anal. Chim. Acta.* **2008**.



Reverse phase C18

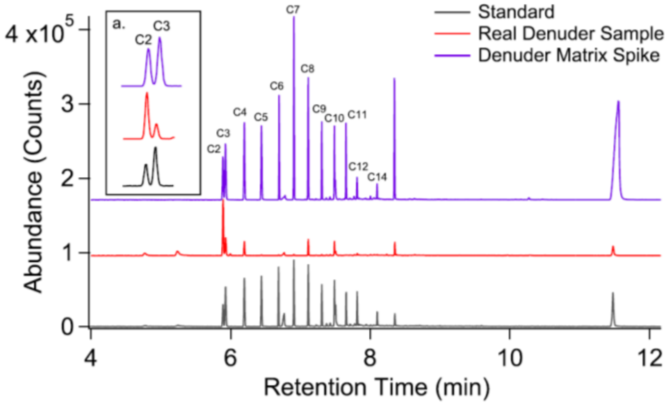
Janda *et al. Environ. Sci. Poll. Res.* **2019**.

Chromatographic techniques for ultrashort-chain PFAS in the literature



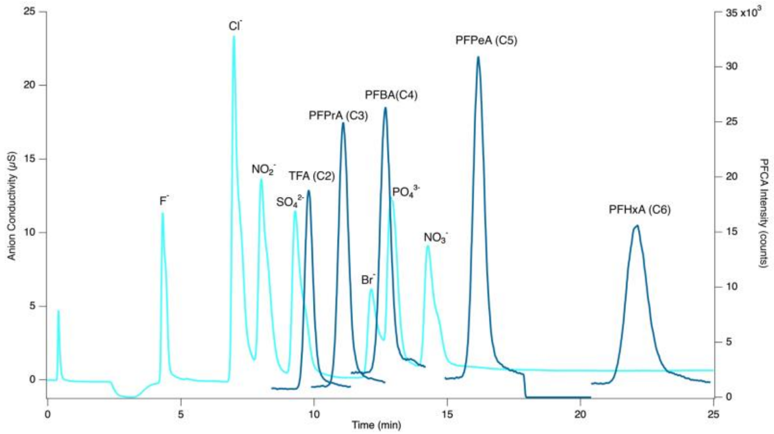
Supercritical fluid chromatography

Yeung *et al. J. Chrom. A.* **2017**.



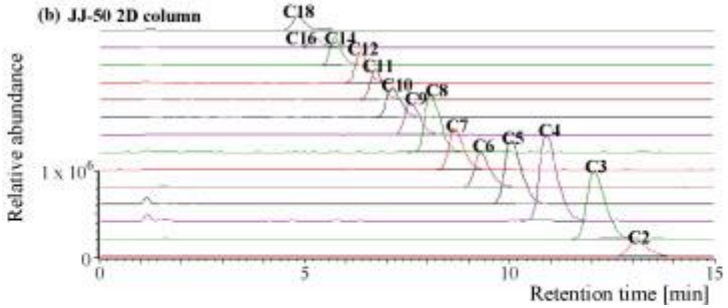
Derivatization for GC-MS

Ye *et al. Anal. Chem.* **2023**.



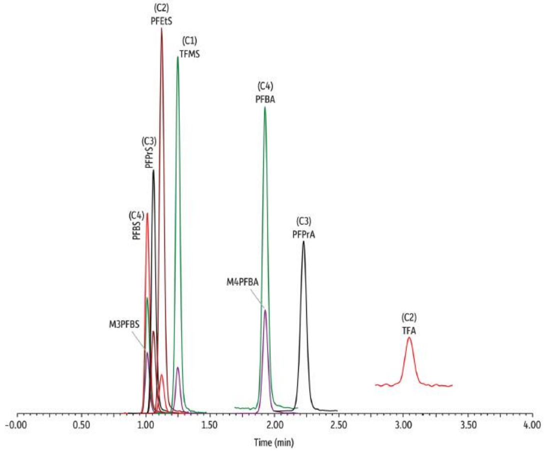
IC-MS

Cloutier *et al.* in prep.



Mixed mode ion-exchange/C18 LC

Taniyasu *et al. Anal. Chim. Acta.* **2008**.



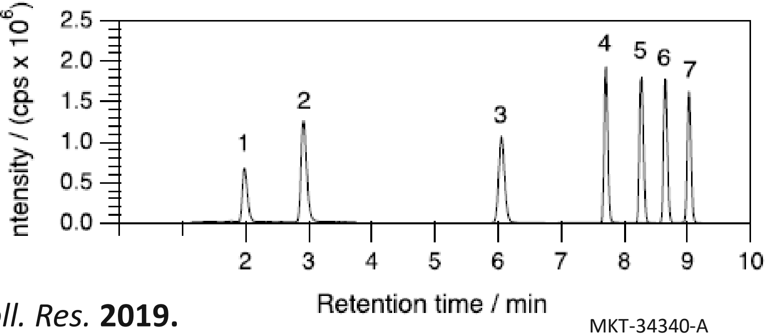
Hybrid HILIC/ion exchange

Liang *et al. J. Chrom. Open.* **2023**.

What to use?!

That depends on…

- analyte needs
- matrix type
- sensitivity needs



Reverse phase C18

Janda *et al. Environ. Sci. Poll. Res.* **2019**.

SCIEX

MKT-34340-A

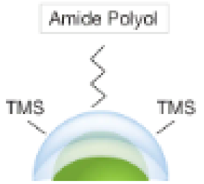
Different chromatographic strategies

HILIC
Reverse phase C18
Stacked columns

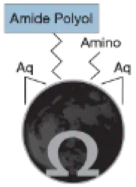
Method development journey

Columns

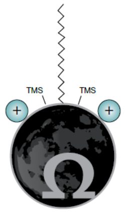
Biozen Glycan



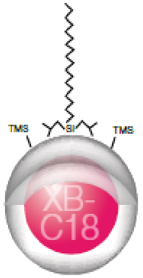
Luna Omega Sugar



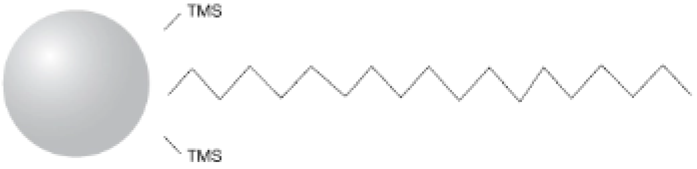
Luna Omega PS C18



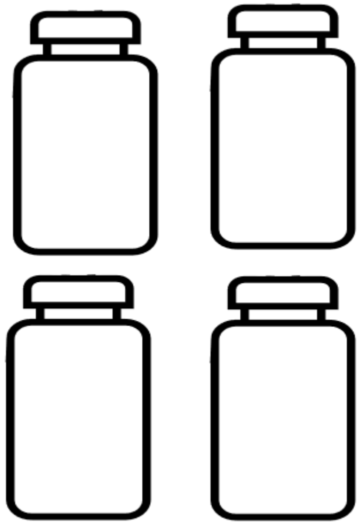
Kinetex NX-C18



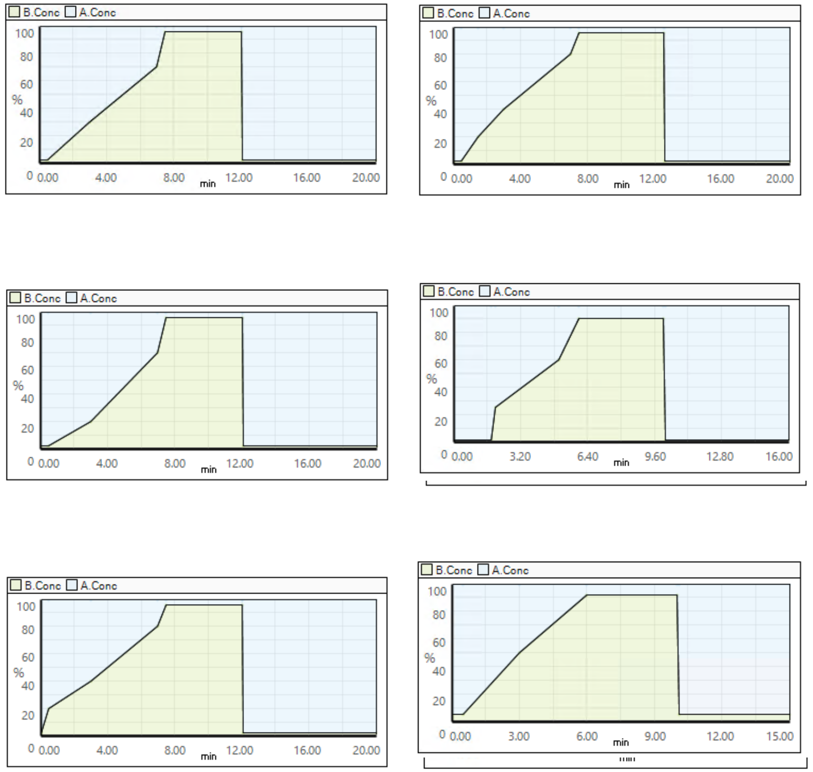
Gemini C18 and Gemini-NX C18



Mobile phases

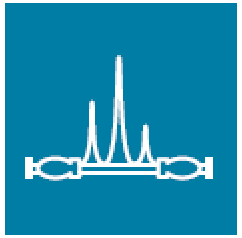


Gradients

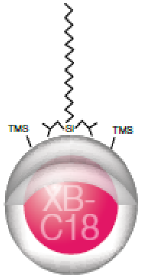


Different chromatographic strategies

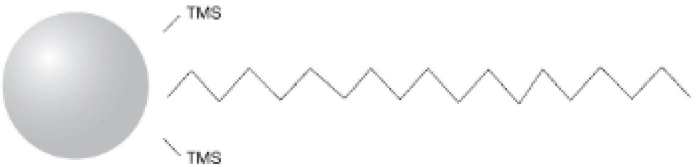
Columns



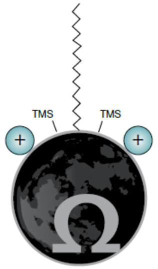
Kinetex NX-C18



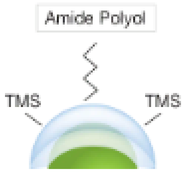
Gemini C18 and Gemini-NX C18



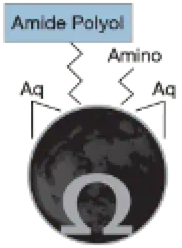
Luna Omega PS C18



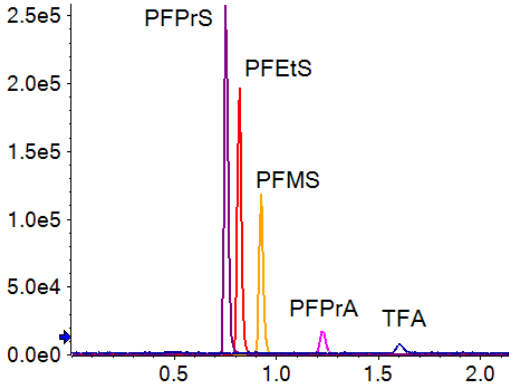
Biozen Glycan



Luna Omega Sugar



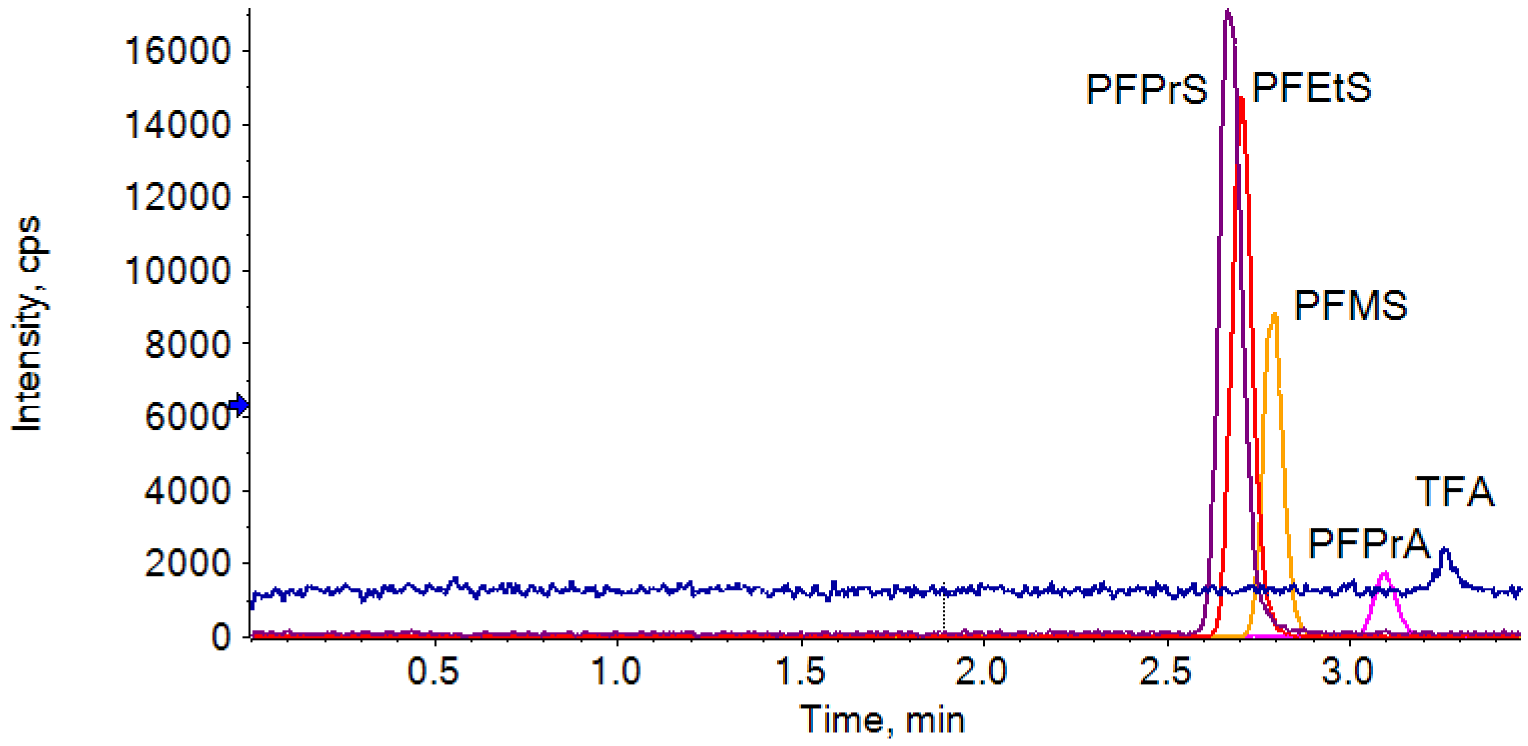
HILIC



Ultra-short chain PFAS

100x3 mm 3 µm Luna Omega Sugar

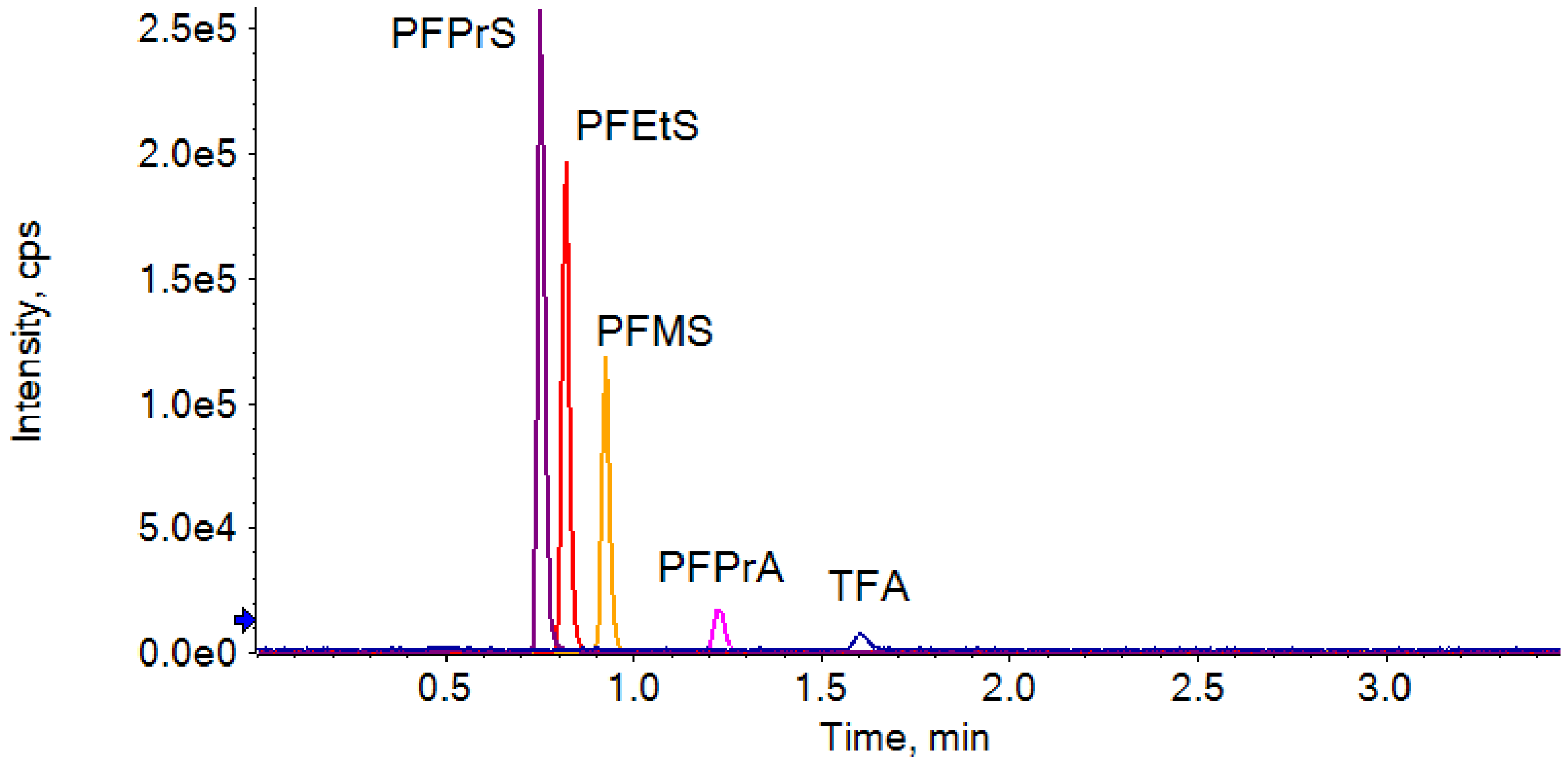
10%B Isocratic
A=10 mM Ammonium acetate+0.01% acetic acid
B=Acetonitrile + 5% water



Ultra-short chain PFAS

100x3 mm 3 µm Luna Omega Sugar

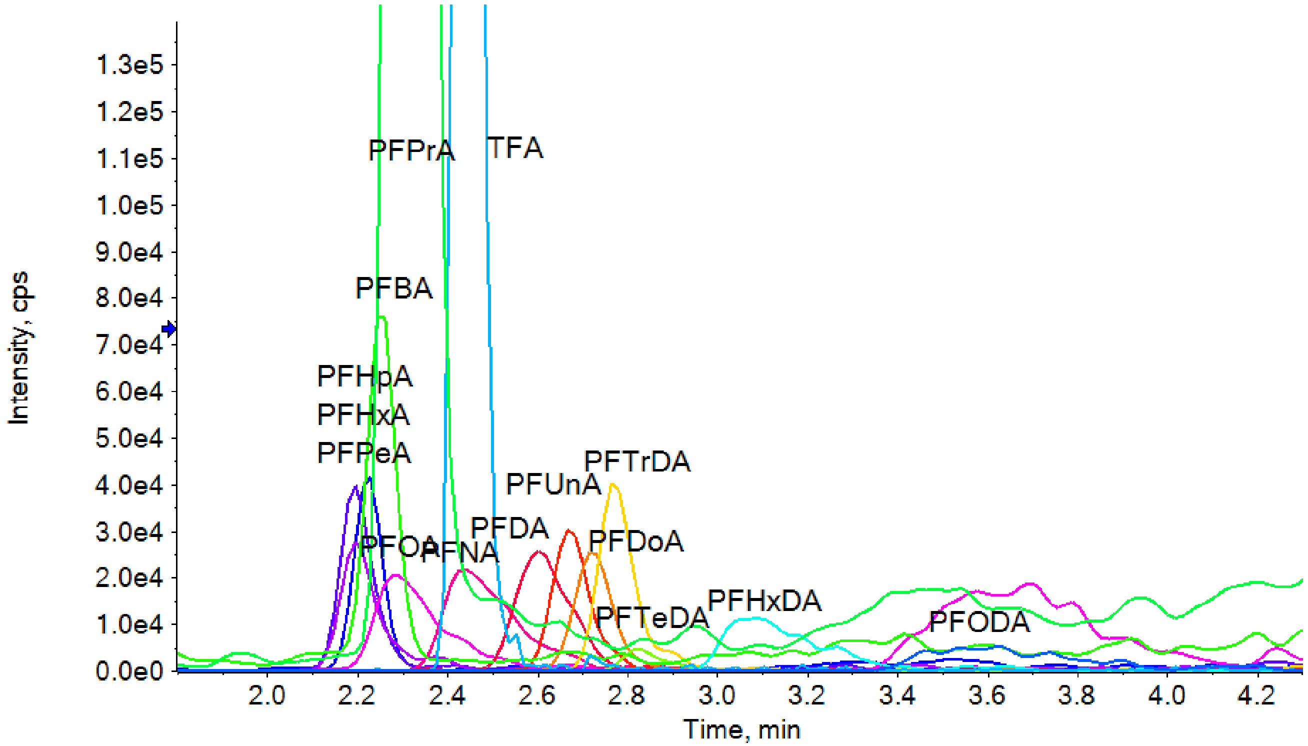
70%B Isocratic
A=10 mM Ammonium acetate+0.01% acetic acid
B=Acetonitrile + 5% water



Ultra-short chain PFAS

100x3 mm 3 µm Luna Omega Sugar

Gradient
A=10 mM Ammonium acetate+0.01% acetic acid
B=Acetonitrile + 5% water



SCIEX phenomenex

Ultra-short chain PFAS

Pros

- Great retention of TFA
- Good separation of ultra-short chains
- Uses the same mobile phases as reverse-phase techniques

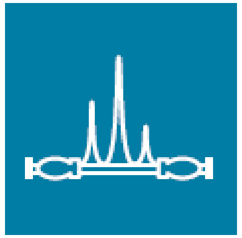
Cons

- HILIC columns can only separate ultra-short chain PFAS
- Peak shape can be impaired by high ionic strength samples
- Injection volume may be limited to 2 µL or less to maintain peak shape

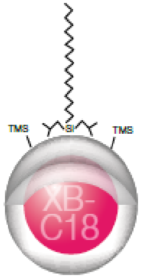
What are the pros and cons of using a HILIC column?

Different chromatographic strategies

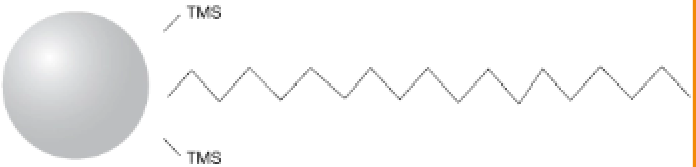
Columns



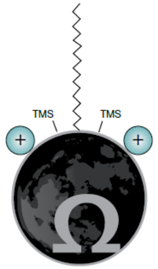
Kinetex NX-C18



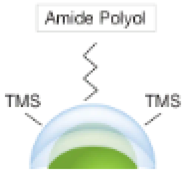
Gemini C18 and Gemini-NX C18



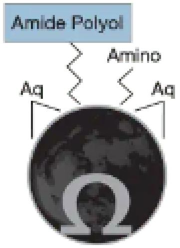
Luna Omega PS C18



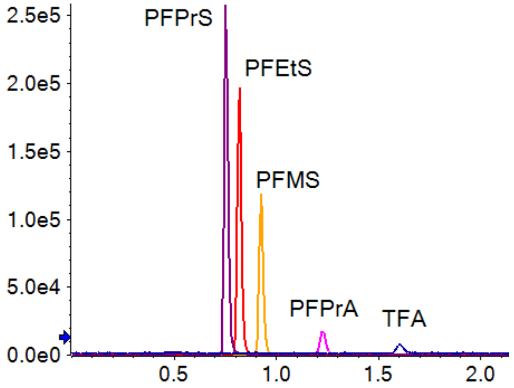
Biozen Glycan



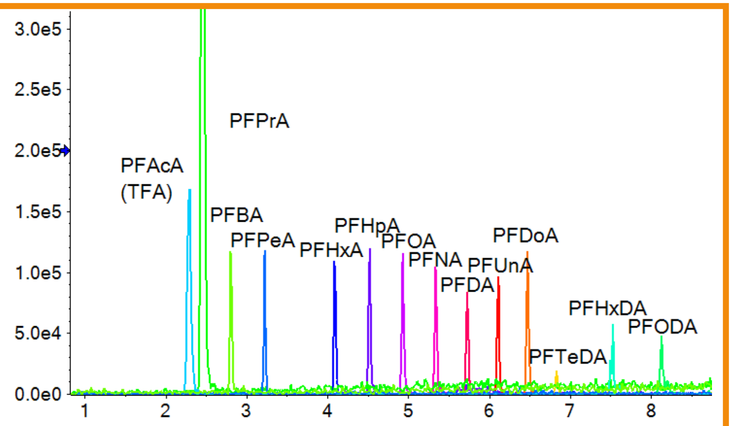
Luna Omega Sugar



HILIC



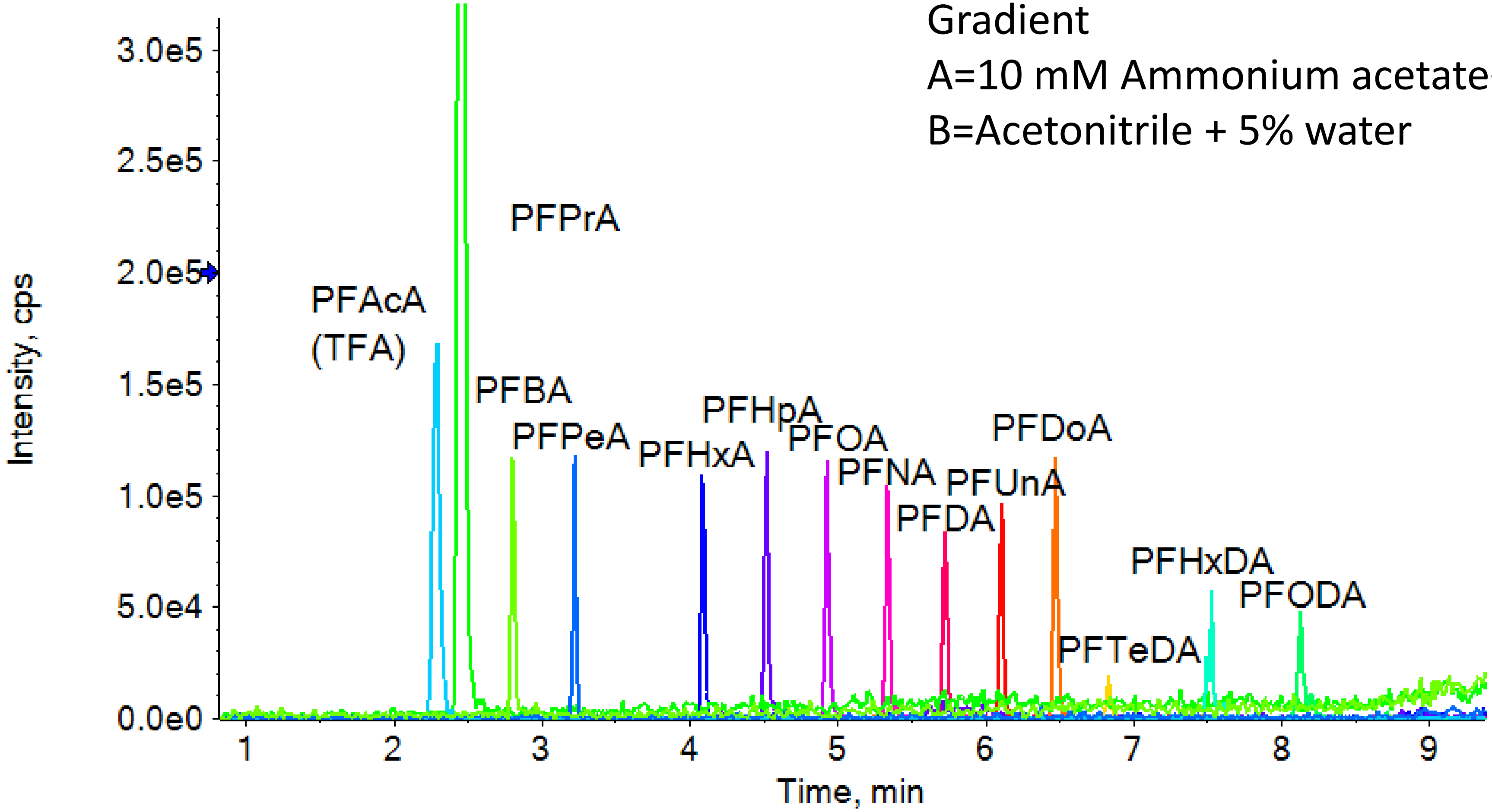
Stacked column



SCIEX phenomenex

Ultra-short chain PFAS

100 x 3 mm 3 µm Luna Omega Sugar with 50 x 3mm 3um Gemini NXC18



Gradient

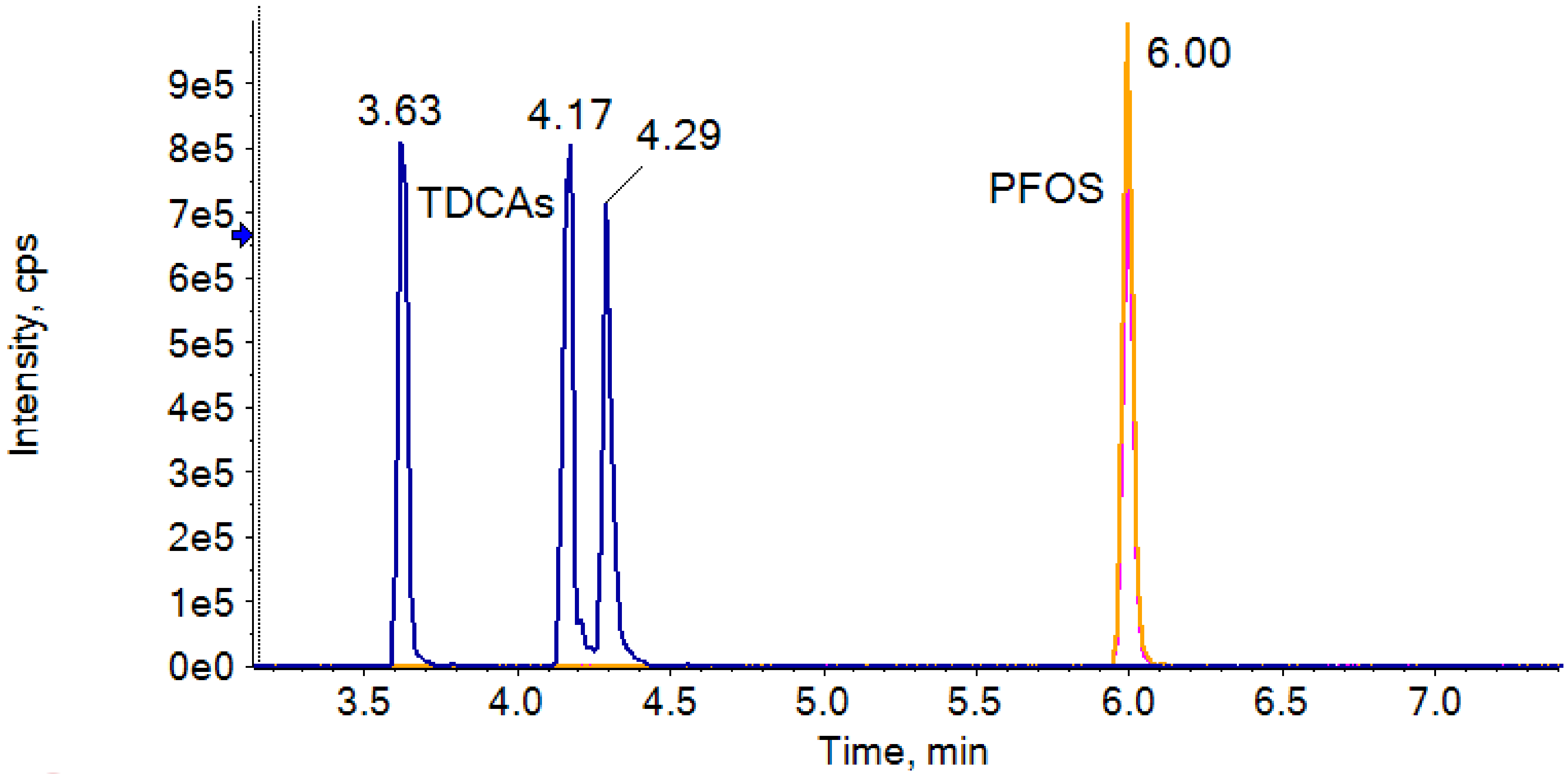
A=10 mM Ammonium acetate+0.01% acetic acid

B=Acetonitrile + 5% water

Ultra-short chain PFAS

100 x 3 mm 3 µm Luna Omega Sugar with 50 x 3mm 3 µm Gemini NXC18

Gradient
A=10 mM Ammonium acetate+0.01% acetic acid
B=Acetonitrile + 5% water



SCIEX

Ultra-short chain PFAS

Pros

- Great retention and separation of all PFAS
- Shorter runtime than reverse-phase only approach
- Can handle very high injection volumes and organic solvent content

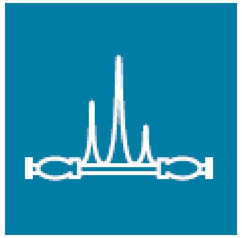
Cons

- Backpressure increases so flow rate must be limited
- Difficult to design a delay column setup

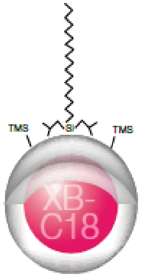
What are the pros and cons of using 2-column approach?

Different chromatographic strategies

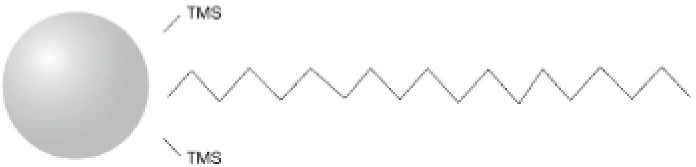
Columns



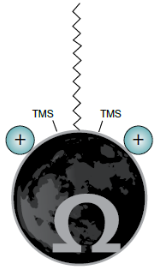
Kinetex NX-C18



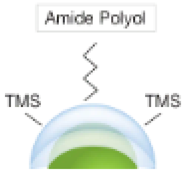
Gemini C18 and Gemini-NX C18



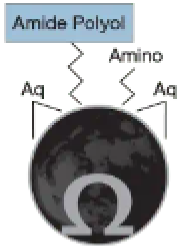
Luna Omega PS C18



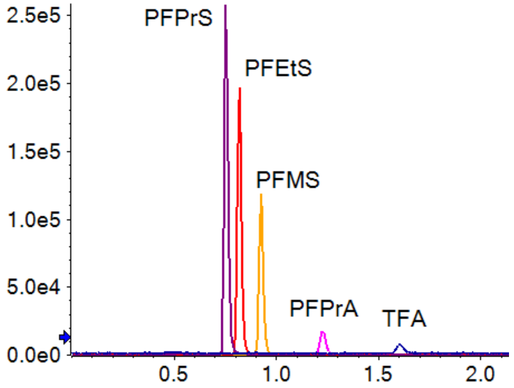
Biozen Glycan



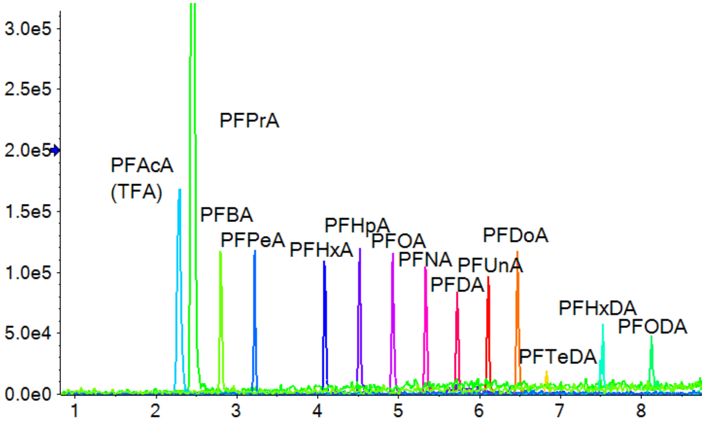
Luna Omega Sugar



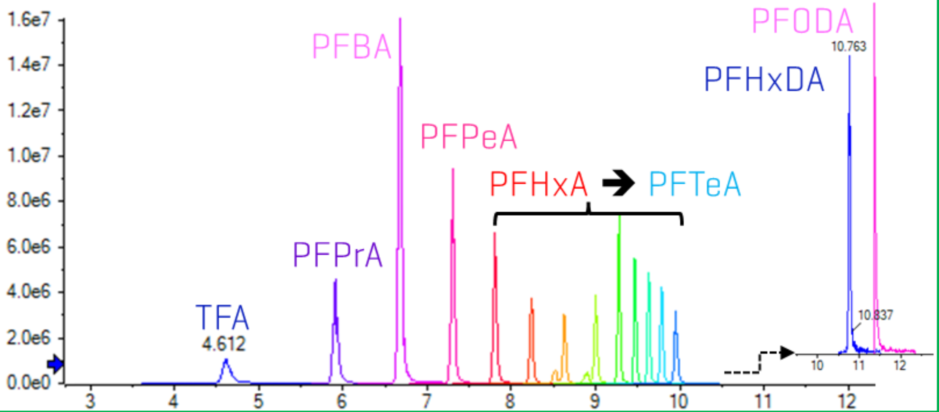
HILIC



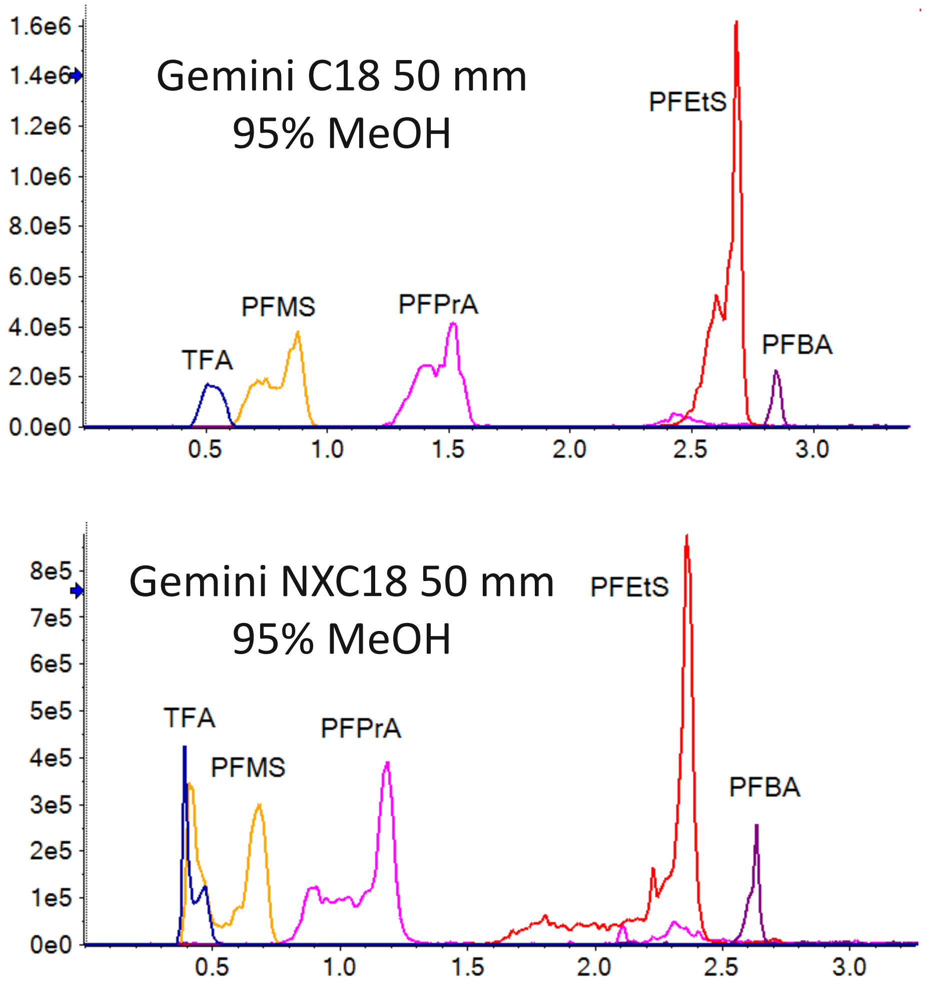
Stacked column

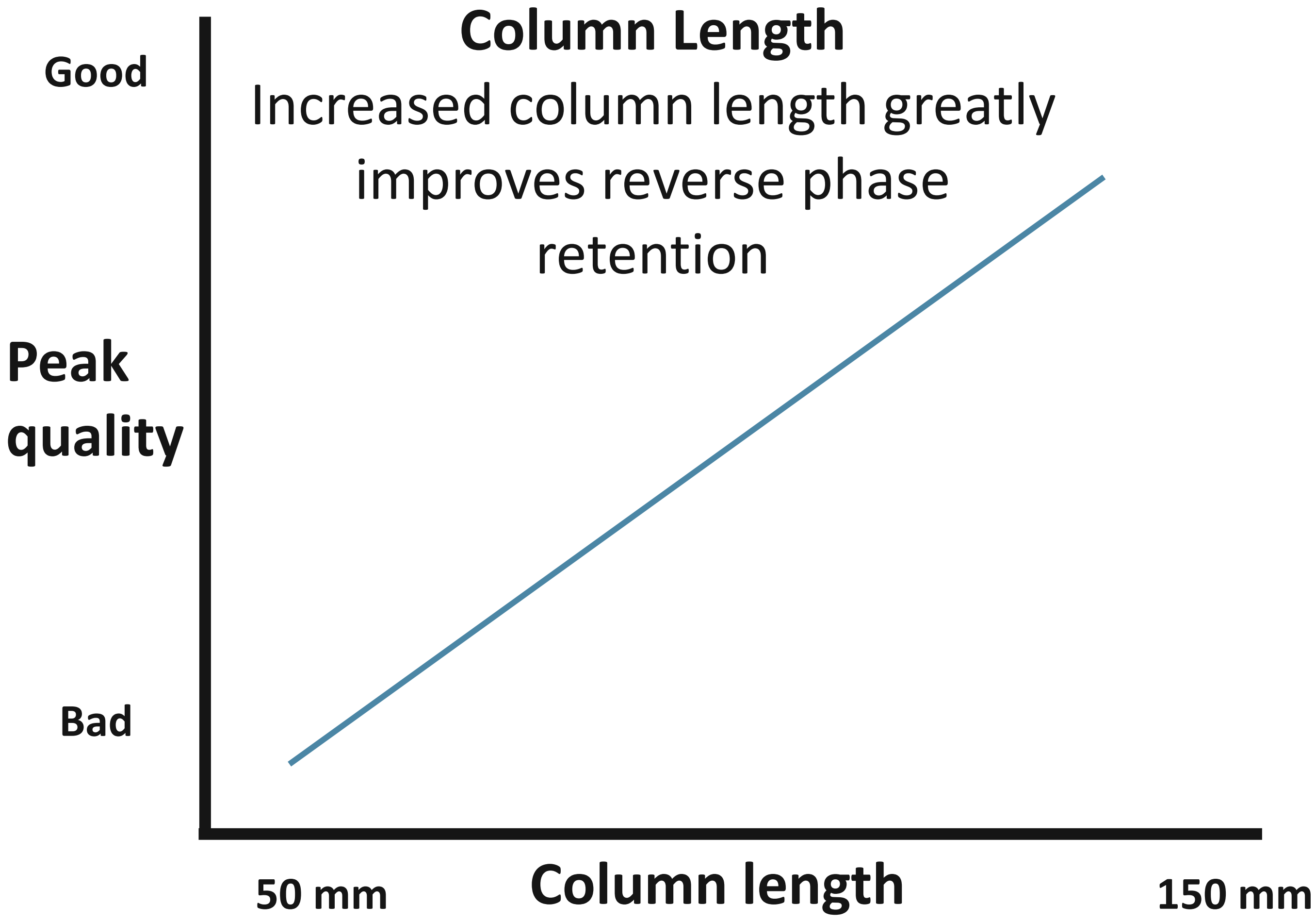


Mixed mode reverse C18



Impact of column length on peak quality





Testing different 150 mm columns, all 3 µm particle size, 2 or 3 mm ID

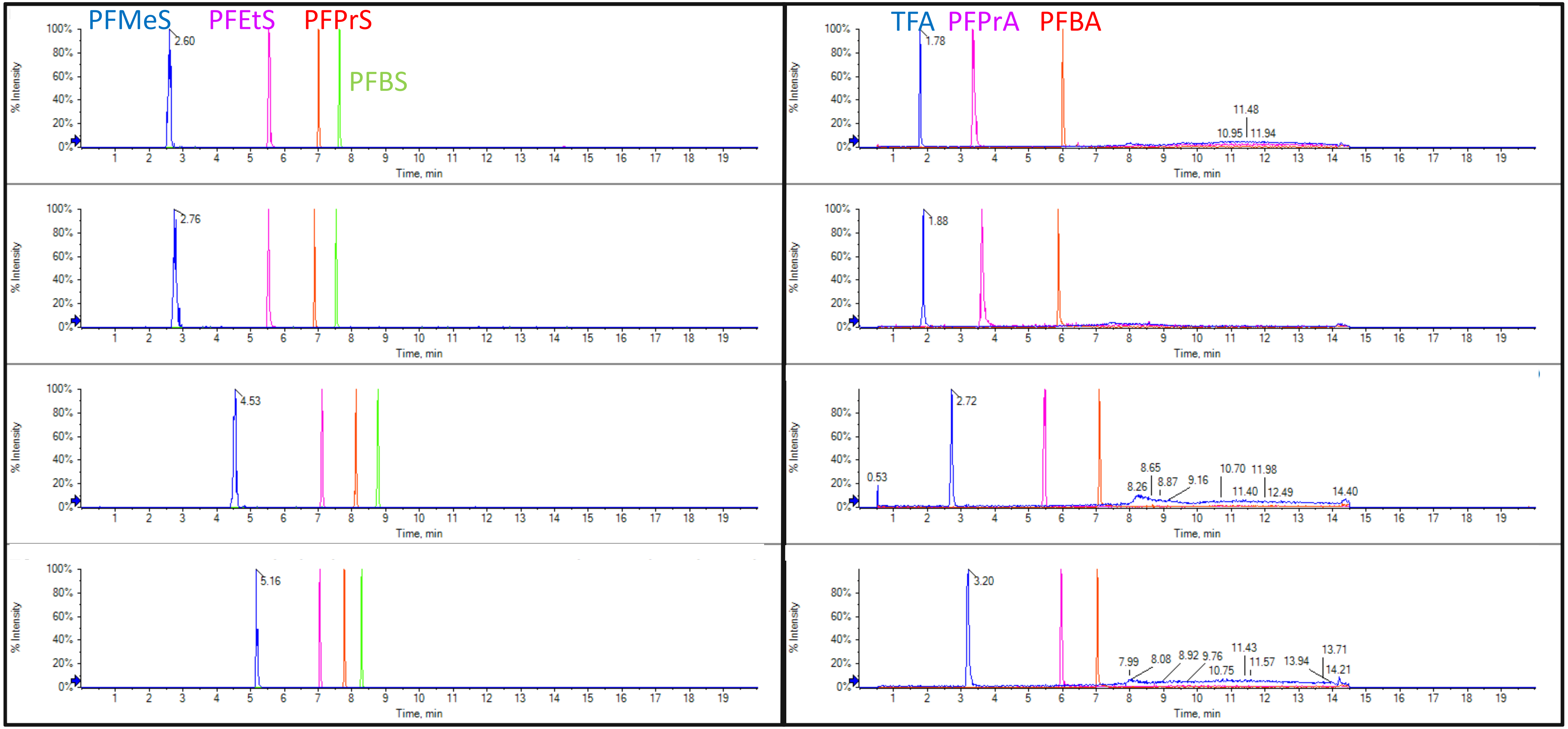
Injection volume: 2 µL
Flow rate: 0.4 mL/min
Instrument: QTRAP 6500+ system

Gemini NX C18

Kinetex NX C18

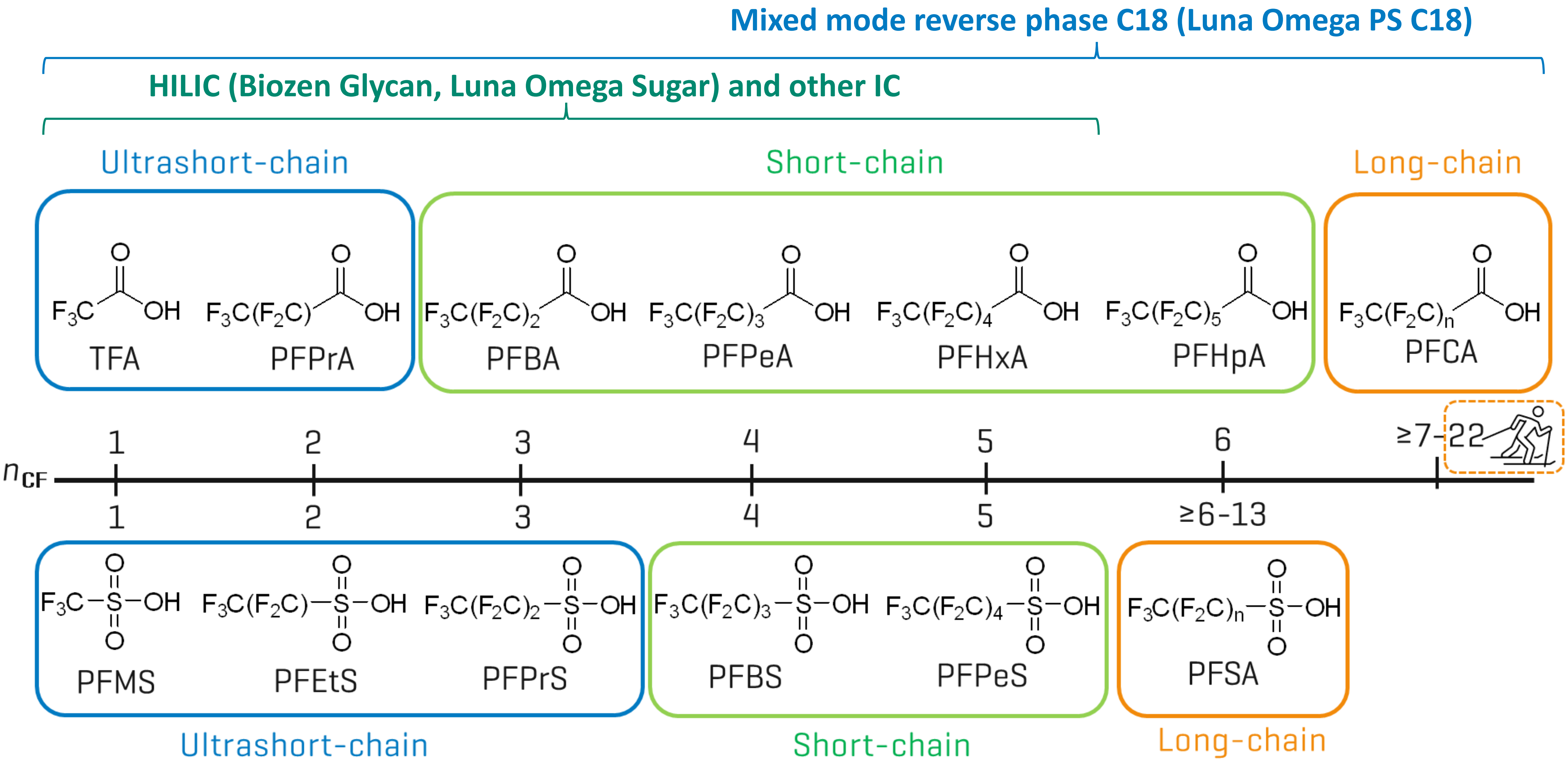
Gemini C18

Luna Omega PS C18



SCIEX

The right column for the right analyte(s)



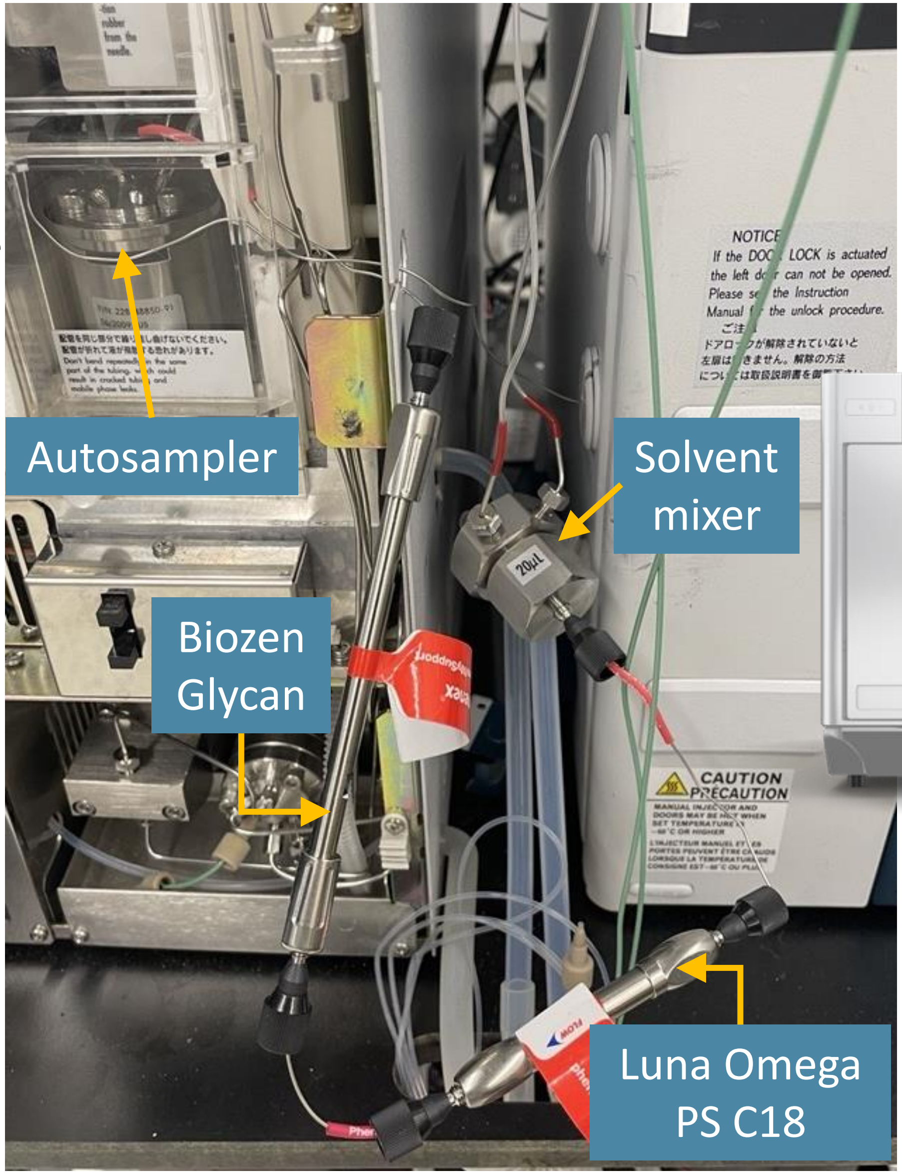
Final optimized LC-MS/MS method

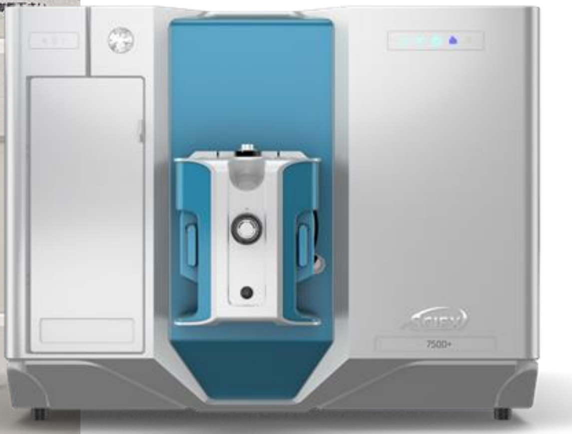
Goal

- Ultra-short chain, short chain and long chain PFAS (C2-C18) in one method

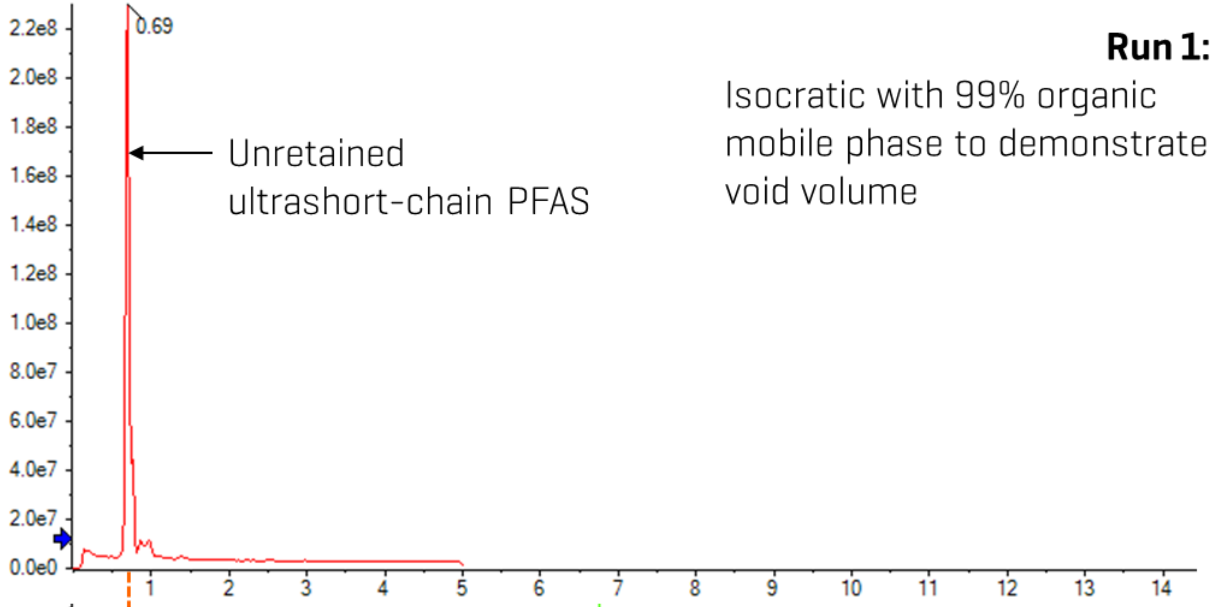
Method

- **Sample preparation:** Direct injection in 50:50 methanol:water
- **Analytical column:** Luna Omega PS C18 (150x2.1 mm, 3 um)
- **Delay column:** (1) Luna Omega PS C18 (50 x 3 mm, 3 µm)
  (2) Biozen Glycan (100 x 2.1 mm, 2.6 µm)
- **Mobile phase A:** 0.1% acetic acid
- **Mobile phase B:** 10mM ammonium acetate in 90:10 ACN:water
- **Injection volume:** 1-45 uL tested (final used 45 uL)
- **Instrument:** SCIEX 7500 system
- **Runtime:** 20 min (needed to stabilize TFA RT)



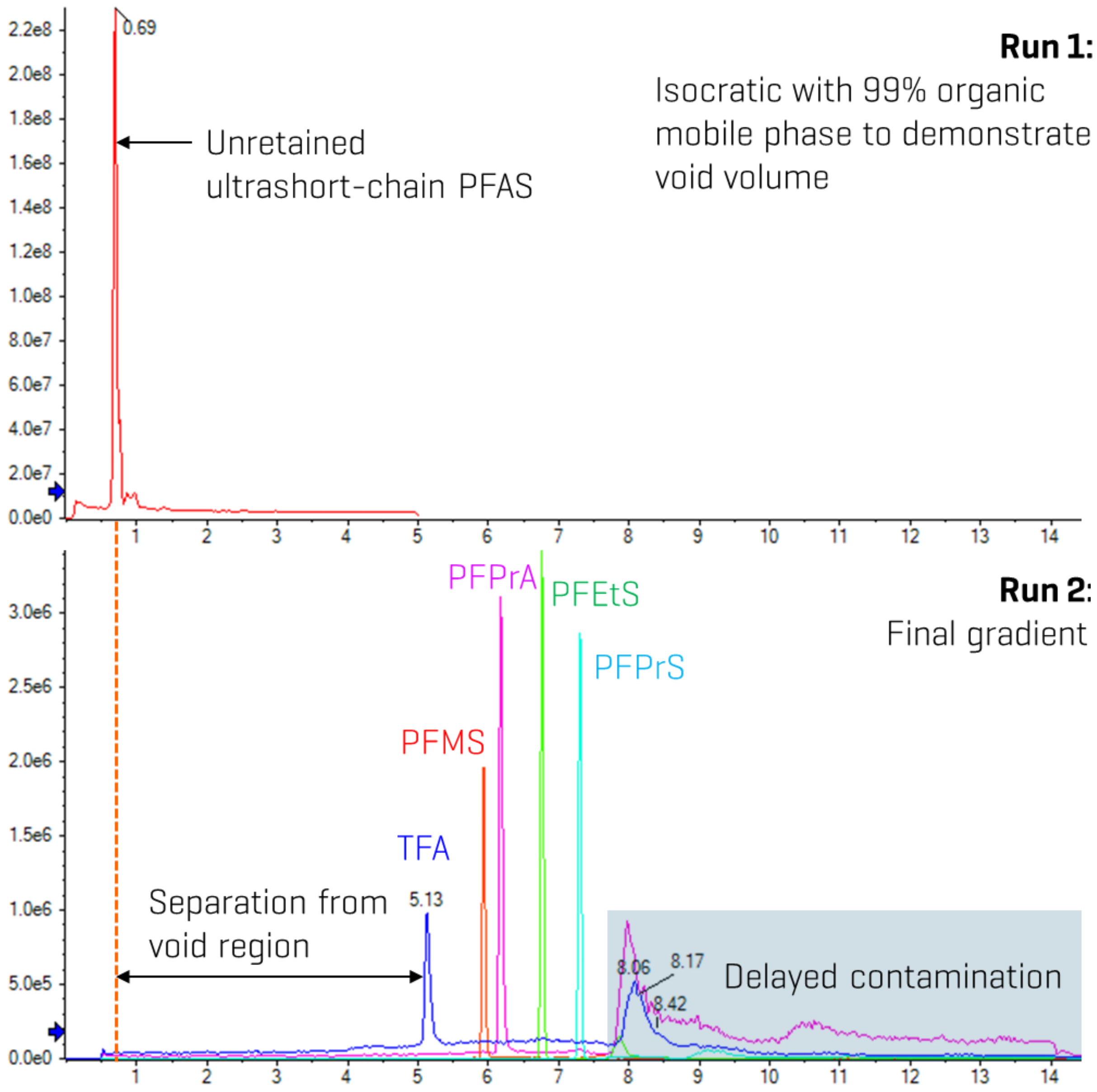


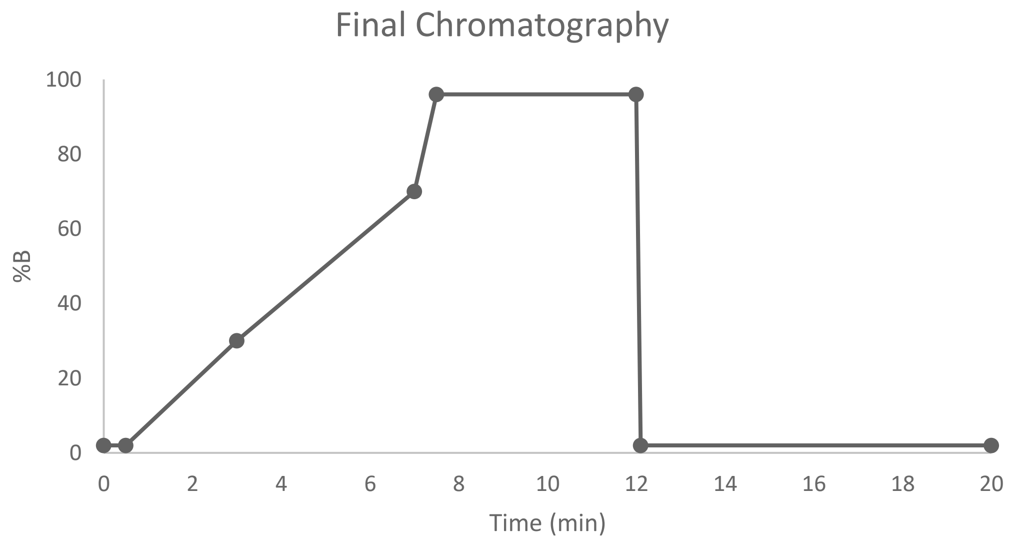
Extensive chromatographic development to optimize retention and separation



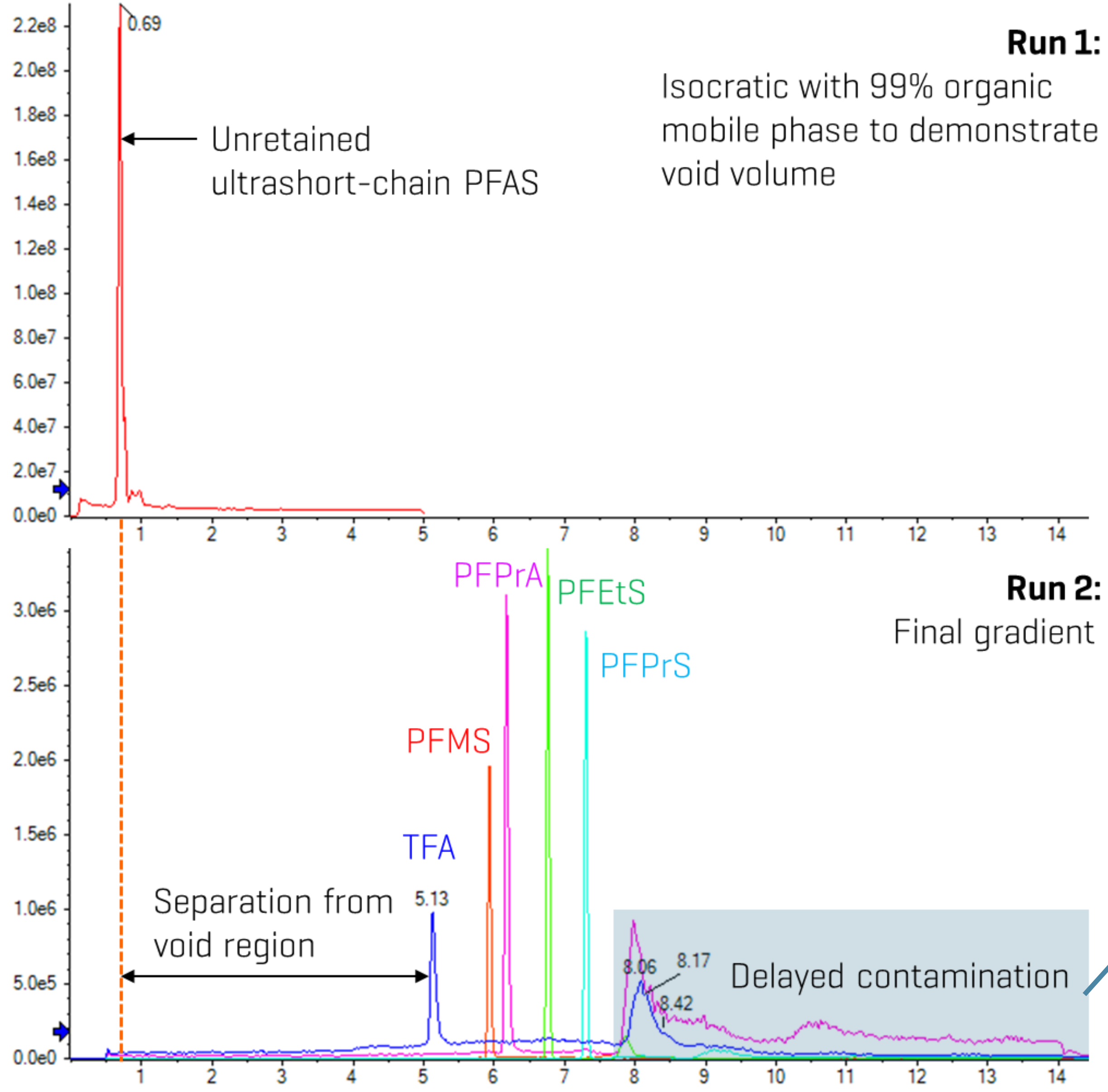
Run 1:
Isocratic with 99% organic mobile phase to demonstrate void volume

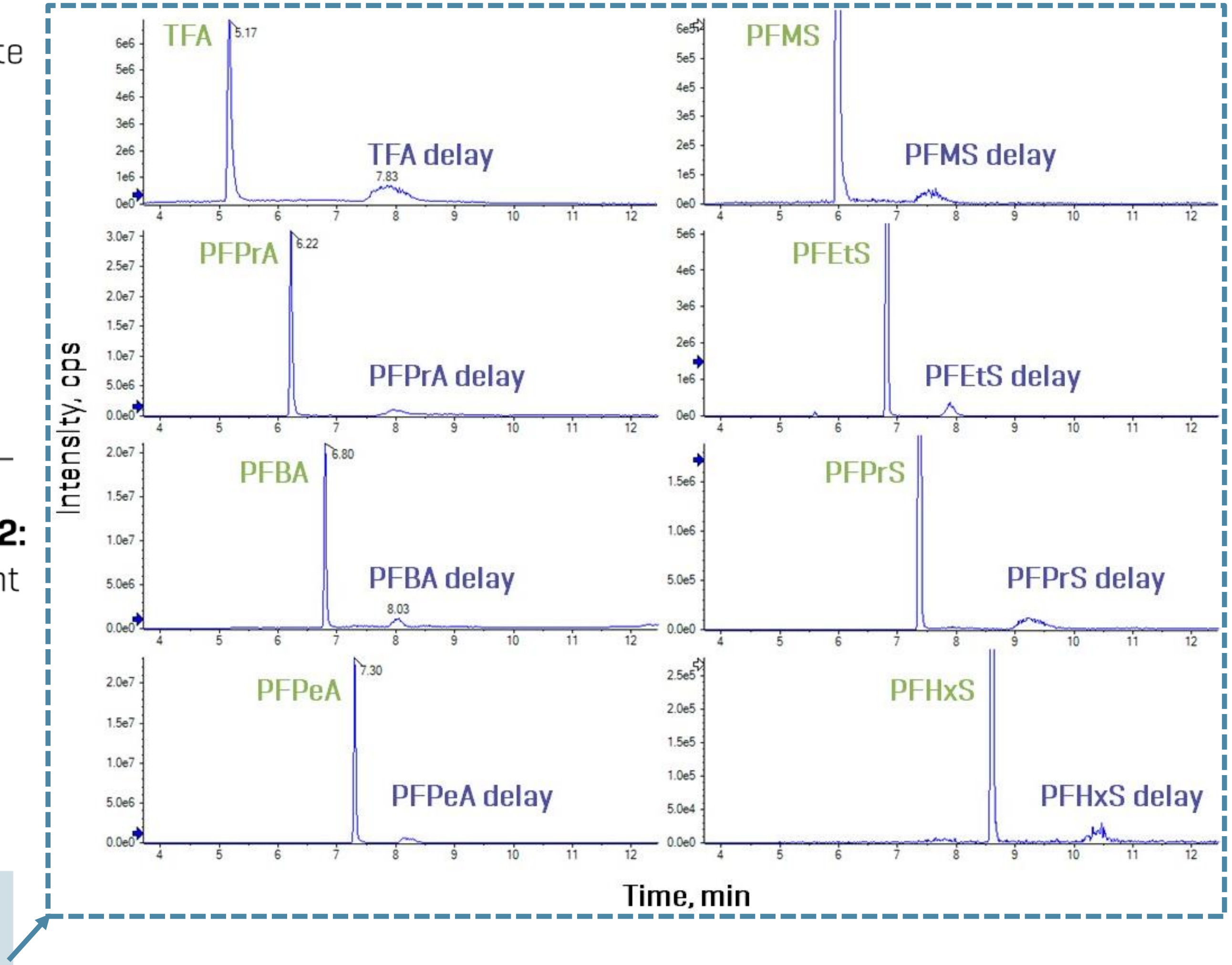
Extensive chromatographic development to optimize retention and separation



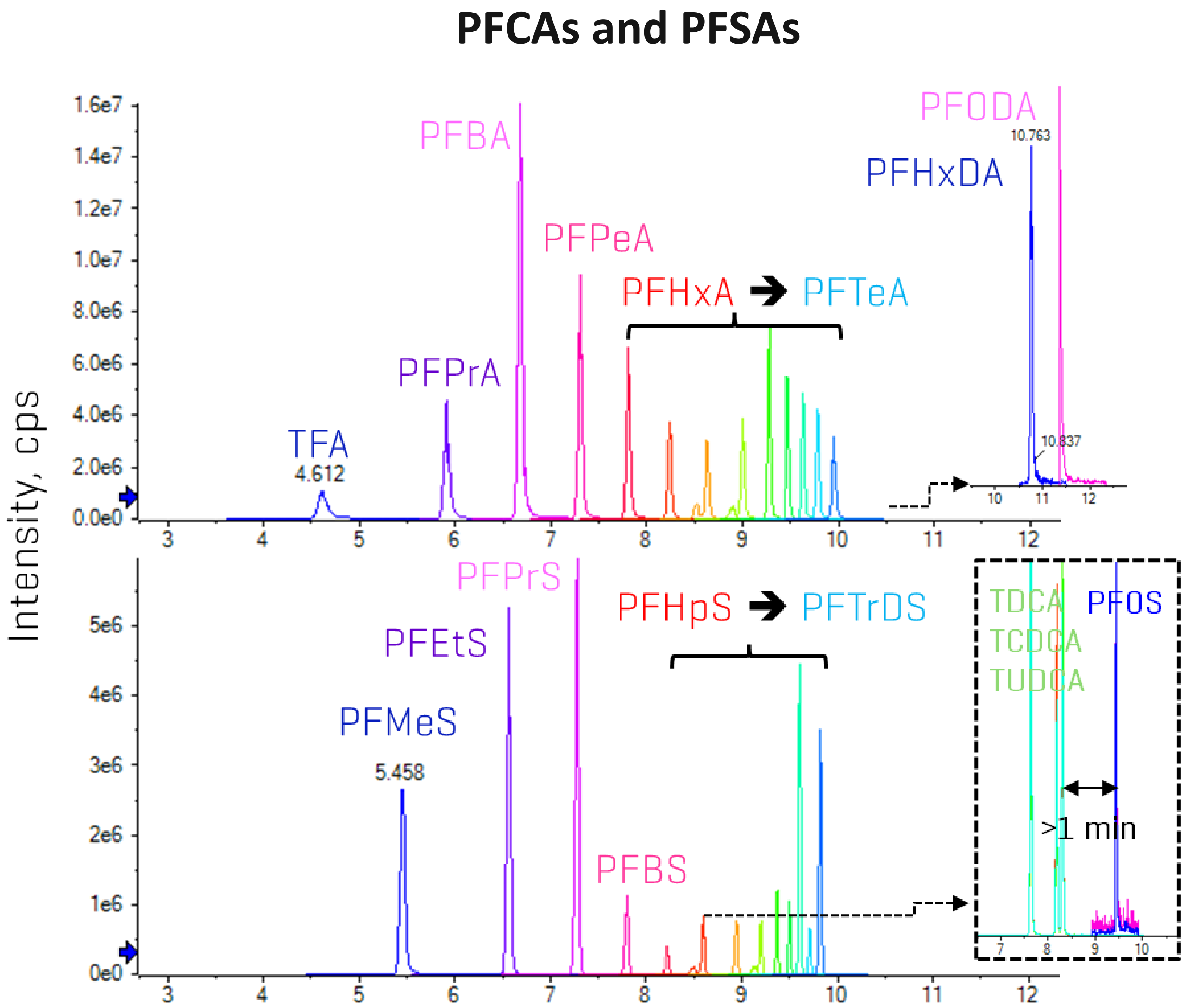


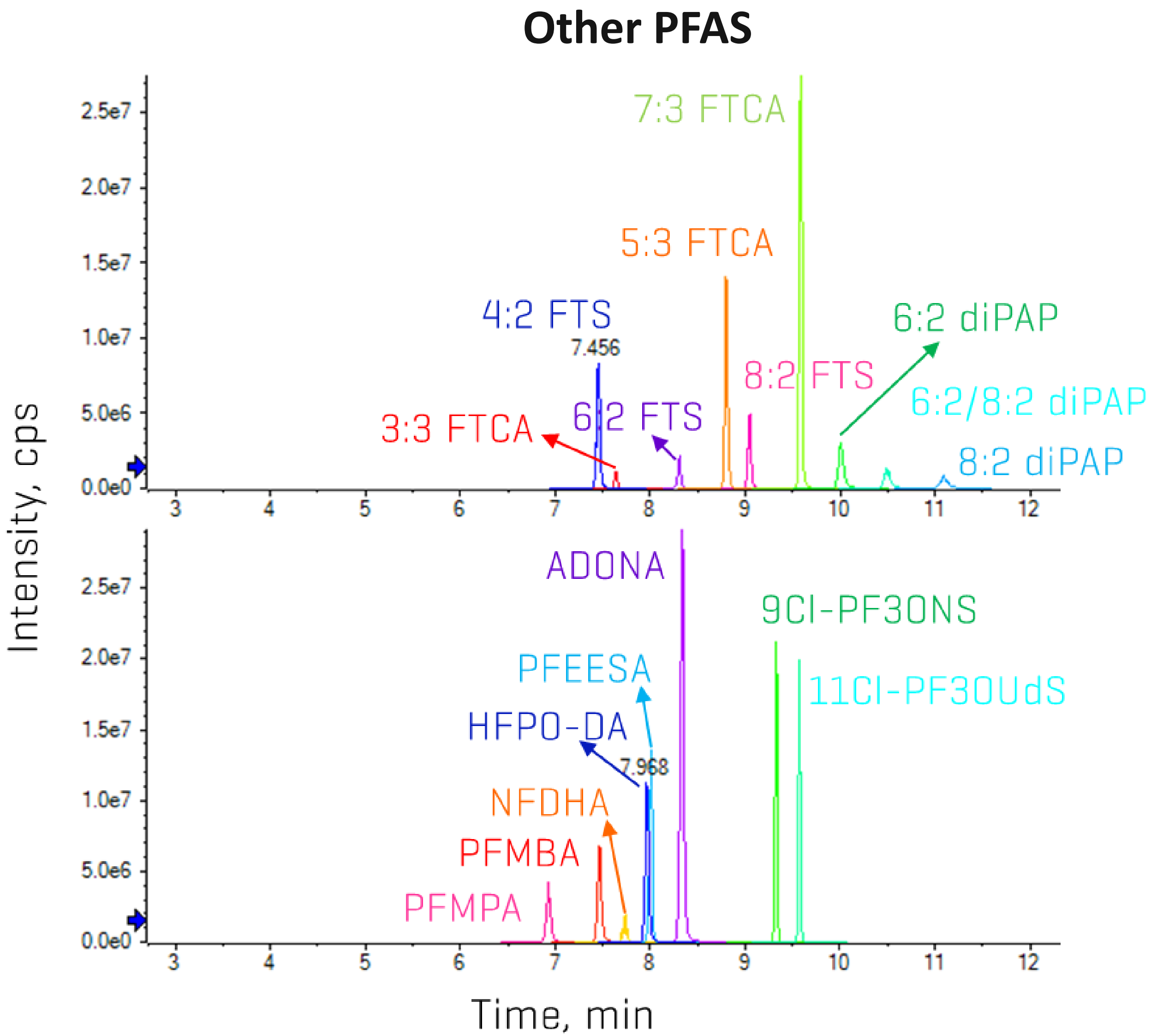
Extensive chromatographic development to optimize retention and separation





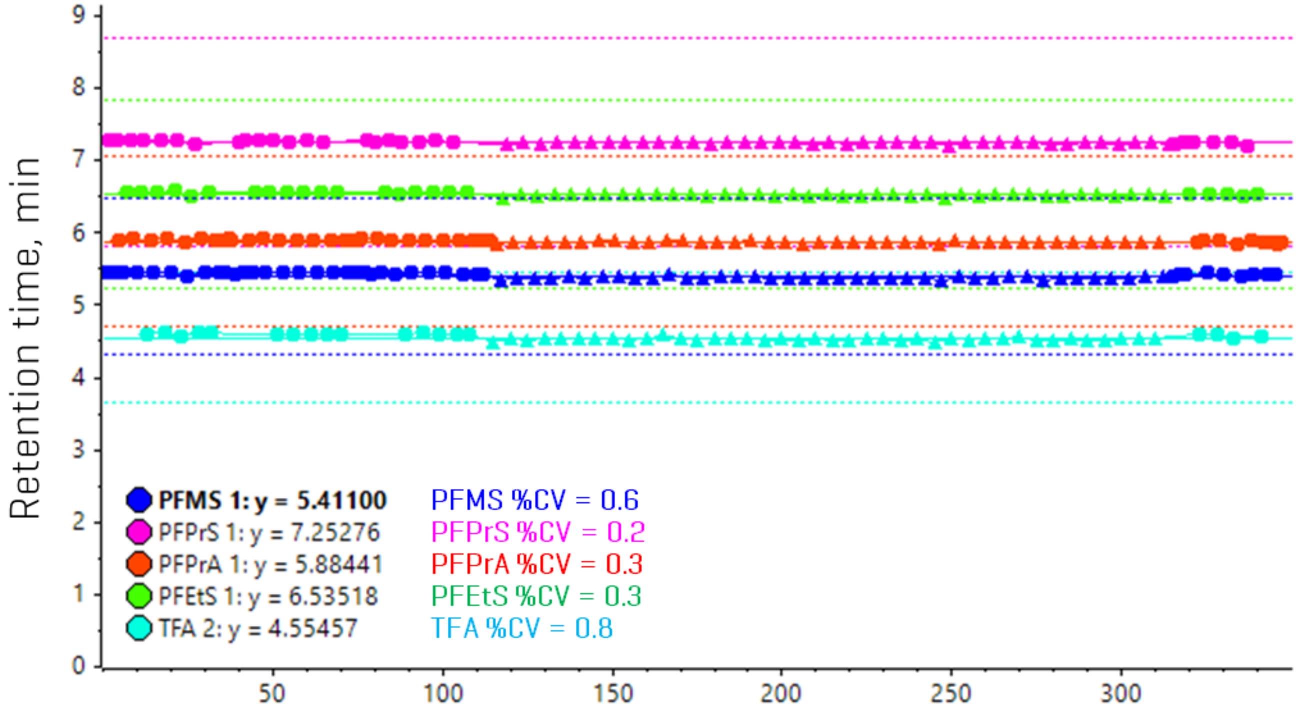
Final optimized chromatography





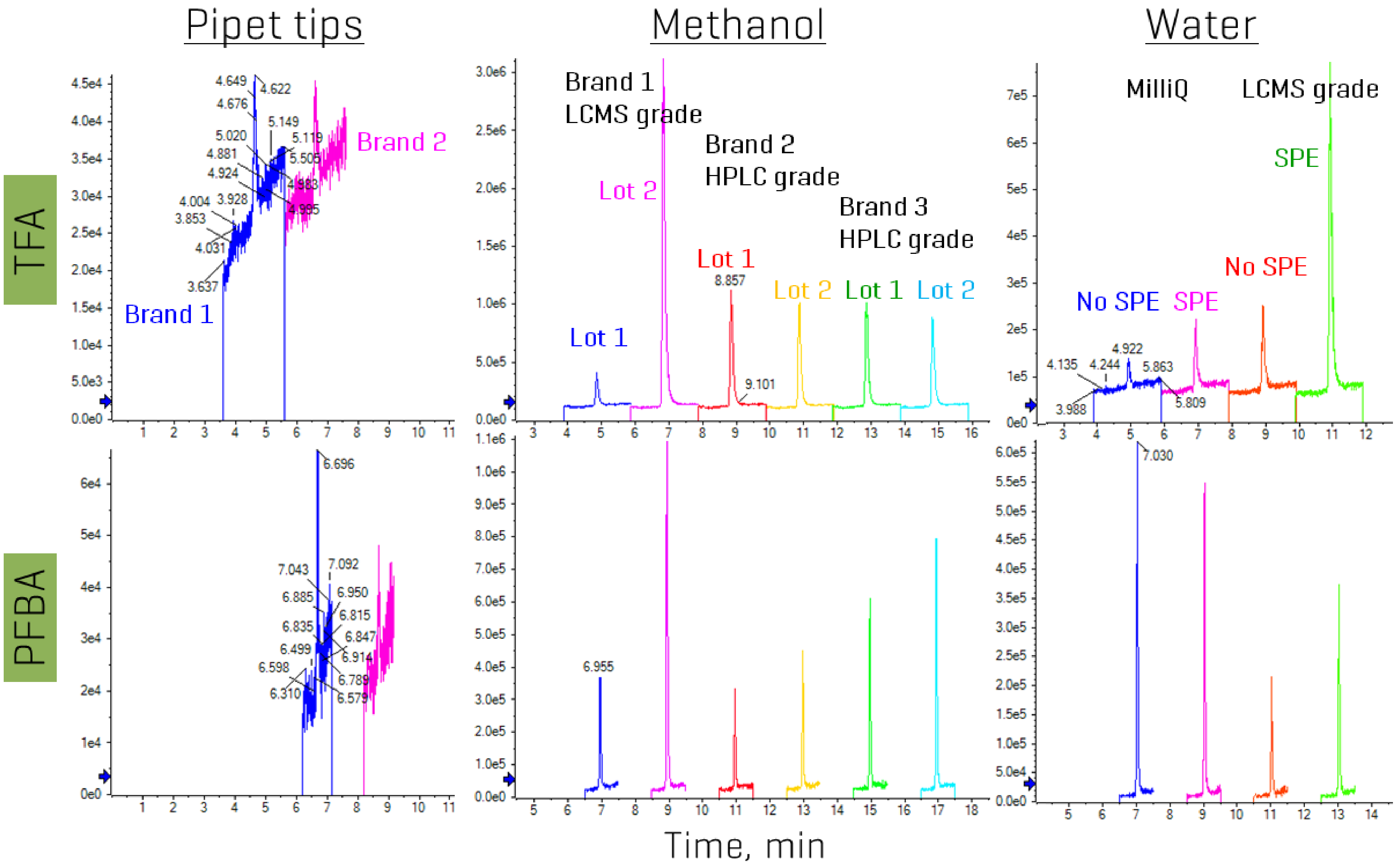
Demonstrated reproducibility of RTs of ultrashort-chain PFAS

- Analysis of batch comprised of >170 injections of solvent blanks, standards, spikes and 15 different real-world water samples
- Excellent RT reproducibility
- %CVs <1 %

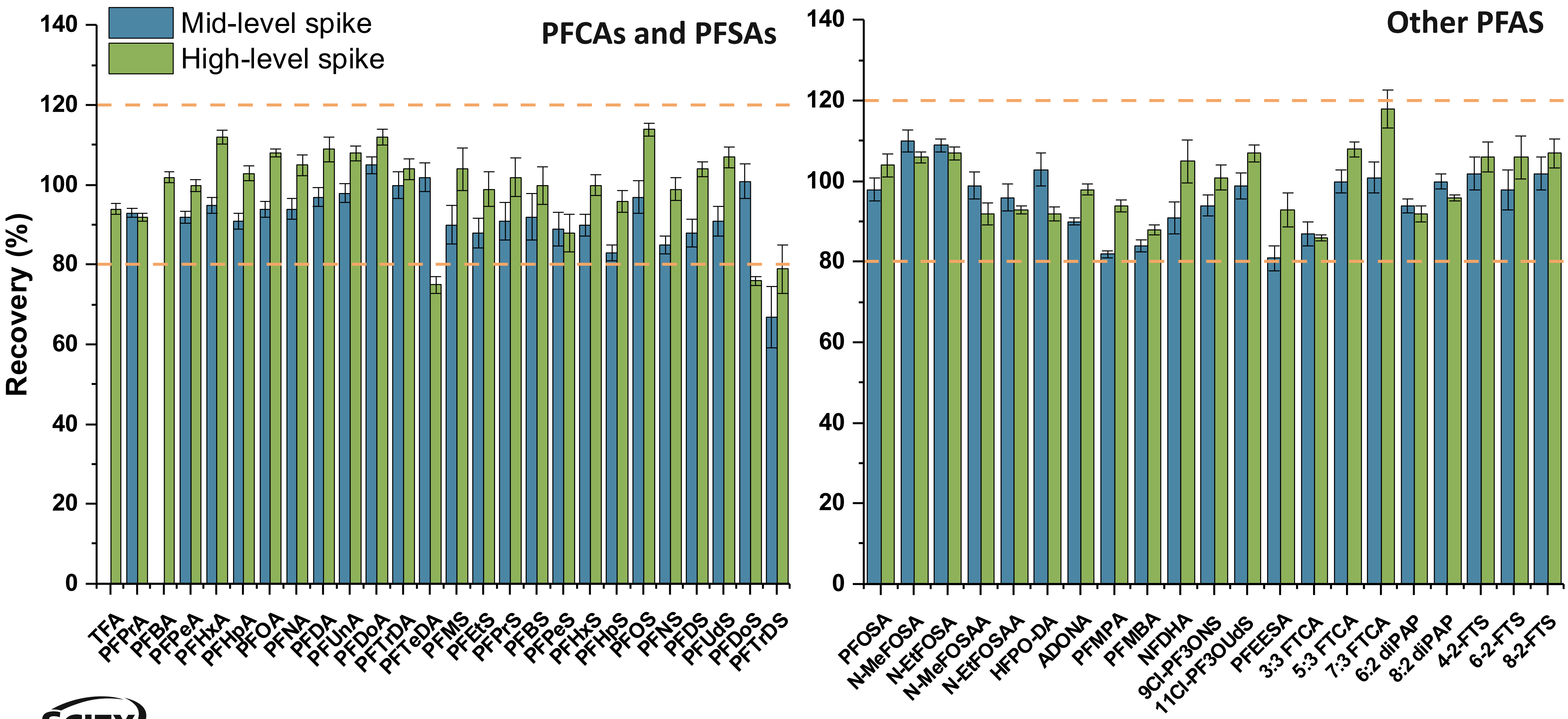


SCIEX

Background contamination in solvents and lab consumables

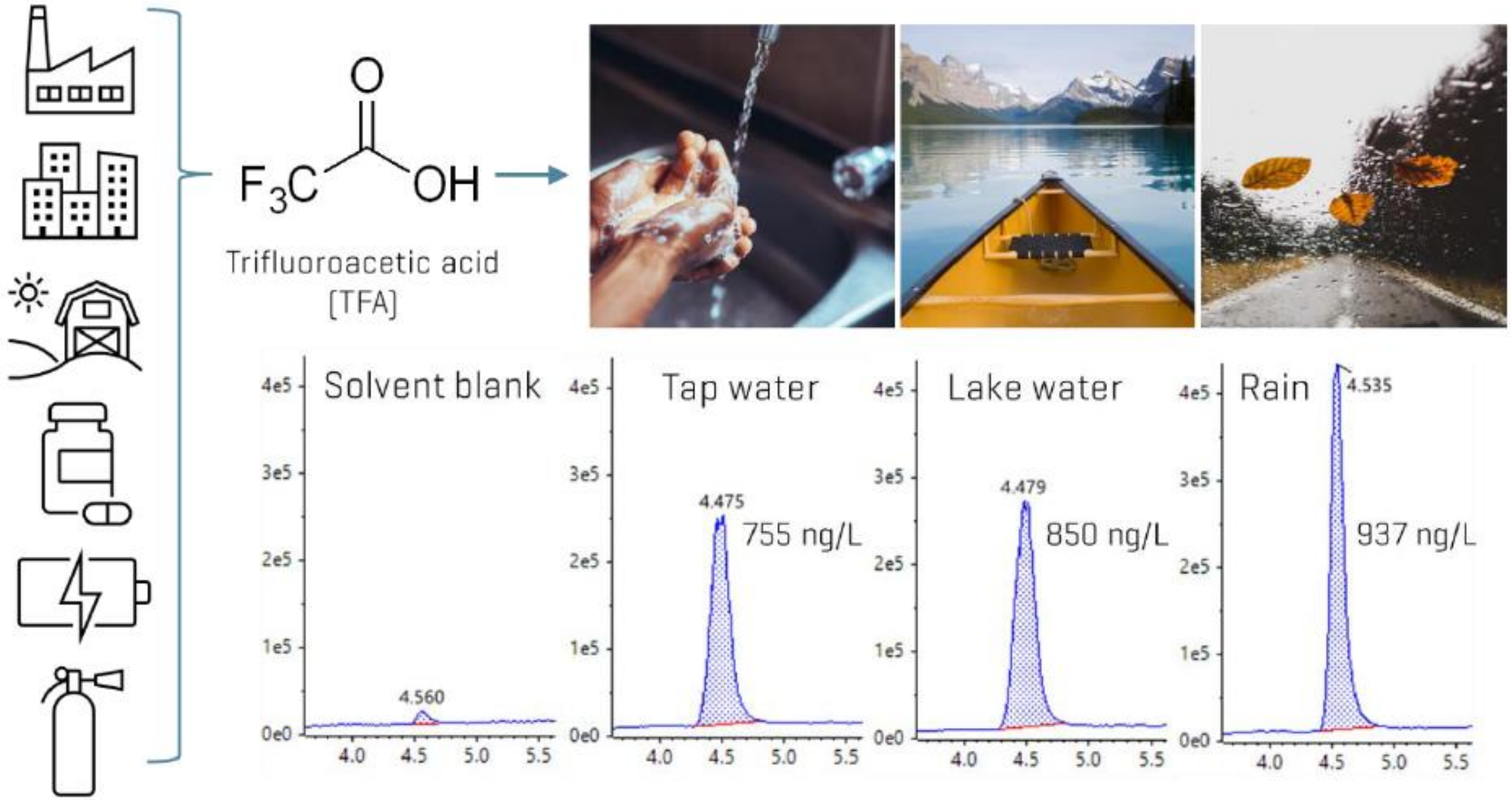


Tap water spikes at 2 concentration levels (5–500 ng/L and 10–5000 ng/L)



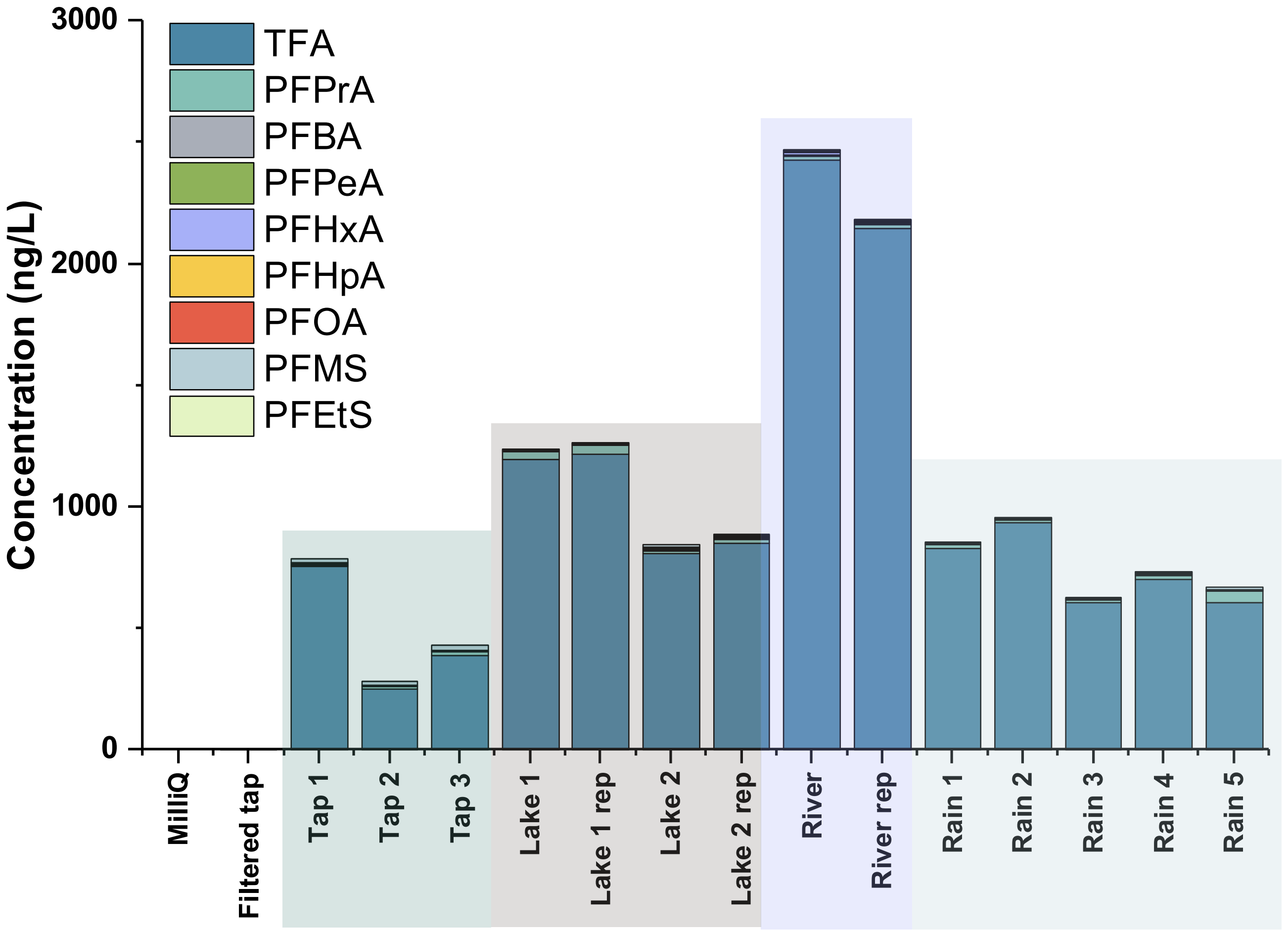
SCIEX

Quantitation of TFA in aqueous matrices



TFA demonstrates its ubiquity at sub µg/L levels in tap water, surface water and rainwater

Sensitive quantitation in different water matrices on the SCIEX 7500 system



- Method applied to drinking, surface and rainwater
- Dominant presence of TFA
- Excellent RT reproducibility of ultrashort-chain PFAS in a long batch (>2.5 days and >170 injections)

Demonstrated reproducibility of RTs of ultrashort-chain PFAS

Link to technical note
with additional details

- **In-sample LOQs:**
  - Most analytes
    - 0.2–10 ng/L
  - TFA, PFBA, 5:3 and 7:3 FTCA, 6:2 and 8:2 diPAP
    - 10–100 ng/L (blank contamination)
  - Accuracy ±30%, %CV <30%

- **In-sample MDLs in tap water:**
  - Most analytes
    - 0.1–13 ng/L
  - TFA, PFBA
    - 63–190 ng/L (blank contamination)
  - Accuracy ±30%, %CV <30%

Thank you

Trademarks/ Licensing

The power of precision