

Introduction

Perfluoroalkyl and polyfluoroalkyl compounds (PFAS) are a structurally diverse class of manmade chemicals utilized in a variety of manufacturing processes since the 1960s. Due to their hydrophobic and lipophobic moieties, these compounds have high mobility in water and soil allowing their proliferation throughout the environment; further, the high bond strength of the C-F bond renders many PFAS indestructible in common environmental conditions and in human bodies, leading to bioaccumulation. Ultra-short chain PFAS compounds (C1-C4) also accumulate in aquatic environments and can be the dead-end product of various remediation technologies*. Due to their links with adverse health effects, recalcitrance, and widespread occurrence in the environment, attention is focused on the ability to detect PFAS at low concentrations. Reversed phase methods generally target long-chain PFAS (ex. PFOS) and do not simultaneously retain polar 1-3 chain carbons species, while a multimodal method showed retention of C2-C18 compounds by incorporating ion exchange*. Utilizing the Shodex VT-50 2D, a sensitive and repeatable assay of PFAS including ultra-short chain (C1-C4) though long chain (C8-C10) compounds was developed to explore the retention mechanism and MS sensitivity. The chromatographic separation utilized a polyvinyl alcohol solid support with quaternary ammonium surface functional groups, the VT-50 series, capable of multi-modal retention capabilities in buffered acetonitrile eluents. * Sachi Taniyasu., Analytica Chimica Acta, 2008

Shodex HILICpak™ VT-50 Series Columns

< Features >

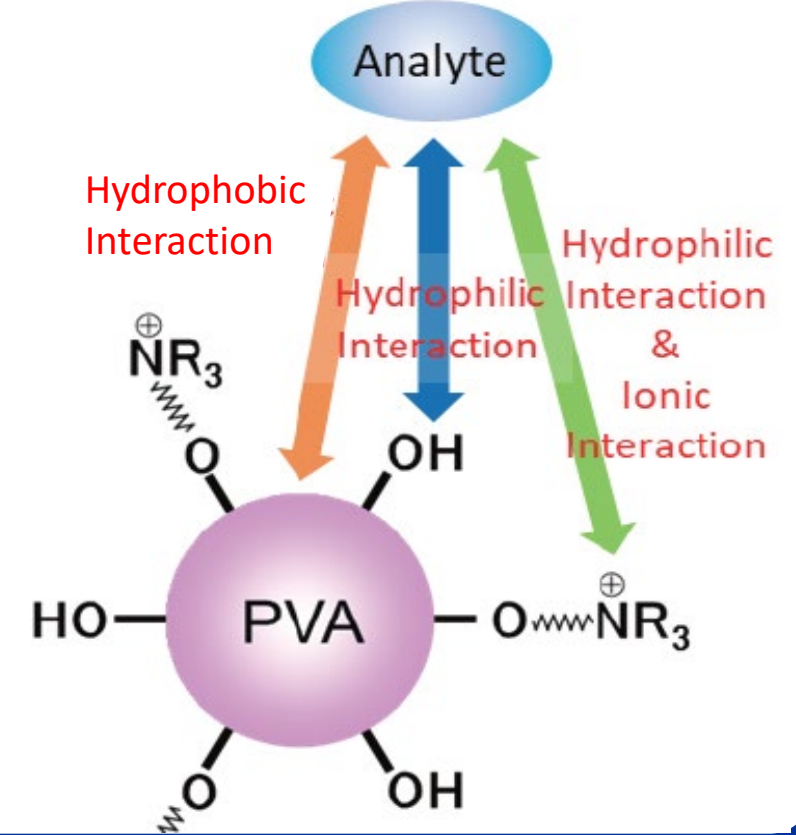
- Retains anions without the use of ion-pair reagents
- Operates under HILIC and Anion Exchange mode under high organic solvent conditions

< Specifications >

- Base Material: Spherical porous particles of polyvinyl alcohol modified with Quat. Ammonium functional group
- Particle Size: 5 µm
- Pore Size: 100 Å
- Column Housing: PEEK
- Usable pH: 2 - 13
- Usable temperature: 4 - 60 °C
- Applicable solvents: Mixture of water and acetonitrile or water and methanol of any ratio. Up to 100 % water, acetonitrile, or methanol.

Product name	Column size (mm) I.D. x Length
HILICpak VT-50 2D	2.0 x 150
HILICpak VT-50G 2A	2.0 x 10 (Guard)

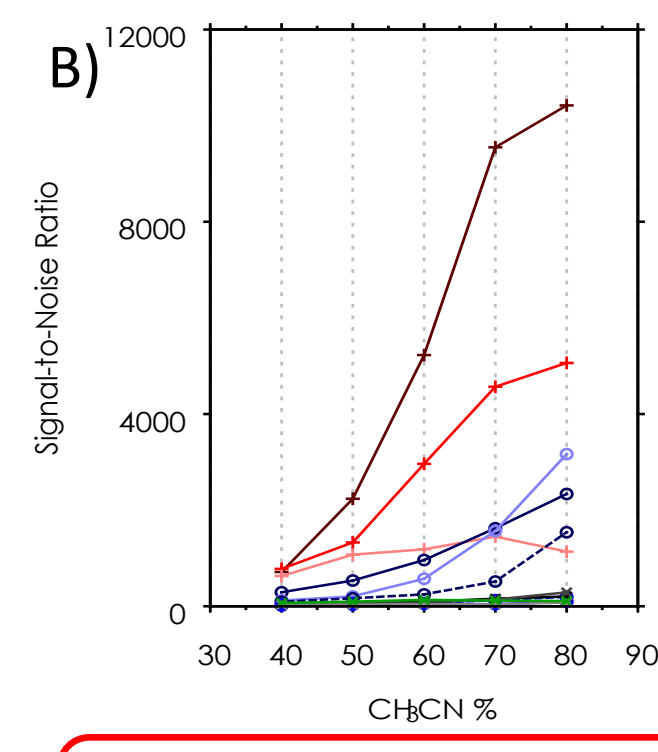
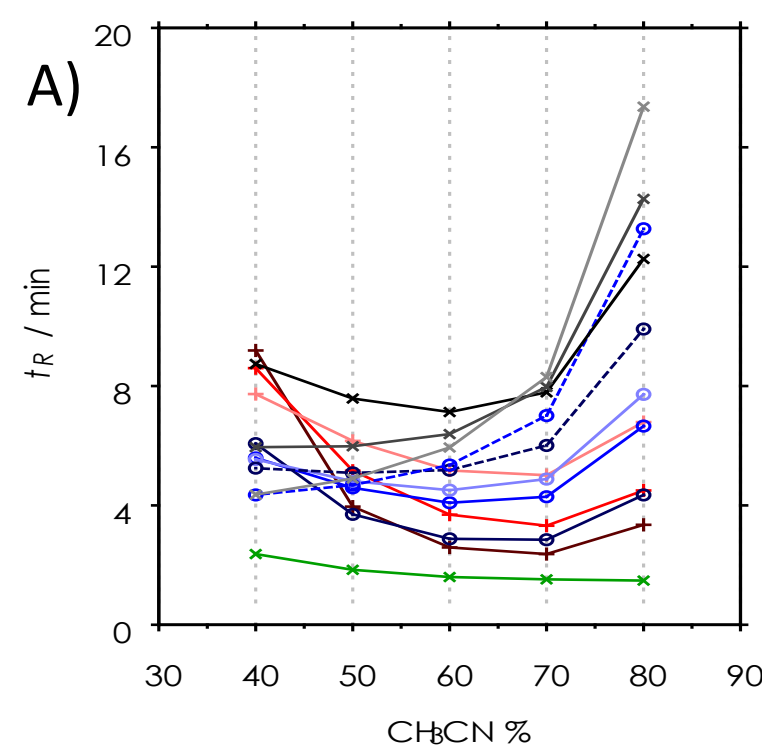
*PEEK housing



[Optimization of Method Parameters] Buffer Type and Acetonitrile Ratio

50 mmol/L Ammonium Bicarbonate

Method development Instruments: Waters ACQUITY UPLC H-Class / SQD2 (above) Shimadzu i-Series 2050 (below)



50 mmol/L Ammonium Acetate

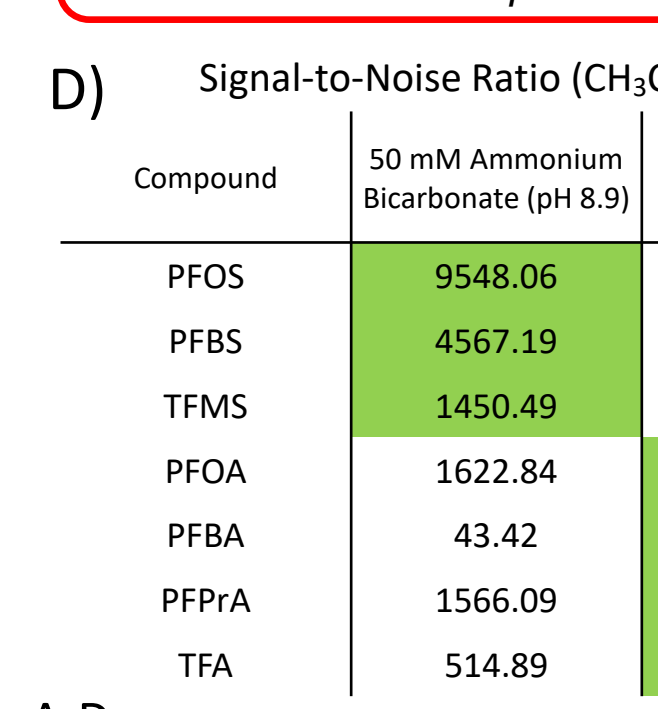
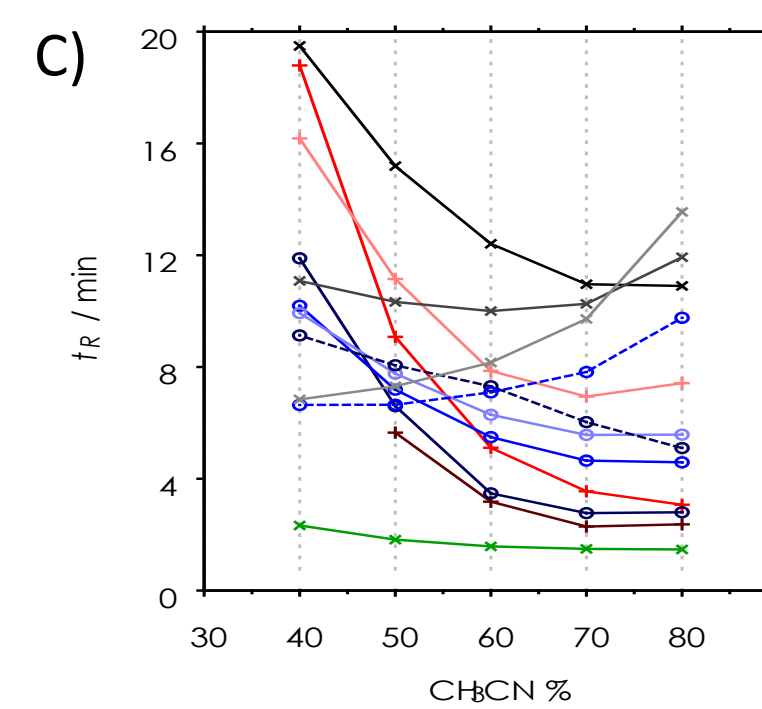


Figure 1: A-D

Method Parameters (pH, Temp, Buffer Conc.)

Reference Mobile Phase: A: 50 mM AMAC, pH 6.8 B: 74% Acetonitrile, 40 C

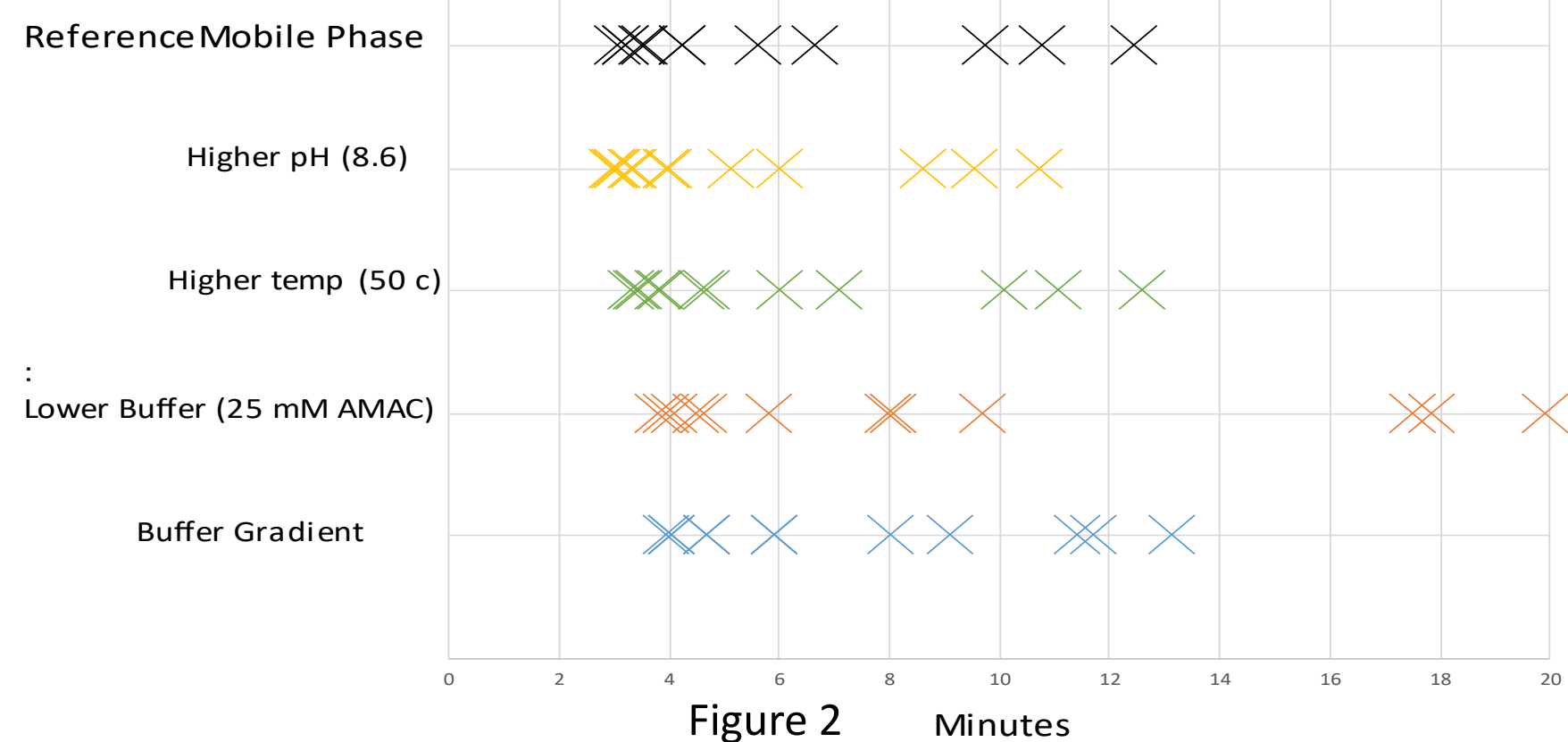


Figure 2

Optimized Method : 50 mM Ammonium Acetate

< Analytical Condition >

Instrument: Agilent 1200/ Sciex 5500 Qtrap
Column: Shodex HILICpak VT-50 2D (2.0 mm I.D. x 150 mm)
Eluent: (A) 50mM CH₃CO₂NH₄ aq.(pH 6.8) / (B) CH₃CN (A) 26% / (B) 74%
Flow rate: 0.2 mL/min
Detector: ESI-MS MRM(-)
Column temp.: 40 °C
Injection vol: 10 µL

< Sample with (m/z, Cone Voltage) >

- Cal Curve (0, 1, 10, 20, 50, 100 ppb)
In 50/50 H₂O/Methanol
- Ultra-Short Chain
- TFMS (149, -45), TFA (113, -30), PFPrA (163, -55), TRiFBA (141, -80), PFBS (299, -50), PFBA (213, -35)
 - Not Detected – DFA, MFA
- Short Chain
- PFHxS (399, -60), PFHxA (313, -25)
- Long Chain
- PFOS (499, -65), PFOA (413, -25), PFDA (513, -25)

Discussion

Two buffer systems, Ammonium Bicarbonate and Ammonium Acetate, were studied for sensitivity during method development. Sulfonate PFAS species sensitivity was consistent with both buffers, however, sensitivity of carboxylic acid PFAS species improves significantly by using acetate buffer (Figure 1D). Therefore, ammonium acetate buffer was selected. The optimized Ammonium Acetate method was able to simultaneously retain most ultra short chain through long chain compounds and showed linear calibration curves for TFA, PFPrA, PFBS, through long chain compounds from 1 – 100 ppb (Figure 3). The PFAS were separated and eluted in the order of larger to smaller chain length, showing multimodal retention characteristics including anion exchange, with the highest S/N ratios in 70-80% acetonitrile conditions (Figure 1, C & D). The method was unable to detect DFA on all instruments but was detected during method development by LC/MS. Although MFA was not detected under the current method conditions, it is possible that further optimization the ionization may allow detection of the remaining ultra-short compounds to be detected and increase sensitivity. Chloroacetic acid species had similar retention characteristics to corresponding organofluoride acetic acids during method development.

Conclusions

The Shodex™ HILICpak™ VT-50 series, polymer-based quaternary ammonium type HILIC columns, demonstrated highly selective LC/ESI-MS measurements. The simple isocratic mixture of 50-mM aqueous ammonium acetate solution and acetonitrile enabled the simultaneous analysis of ultra short through long chain PFAS which cannot be simultaneously retained using reversed phase methods.

Further method development and cross instrument validation, including optimization of ionization parameters for ultra-short chain compounds, is recommended for future work.

Results

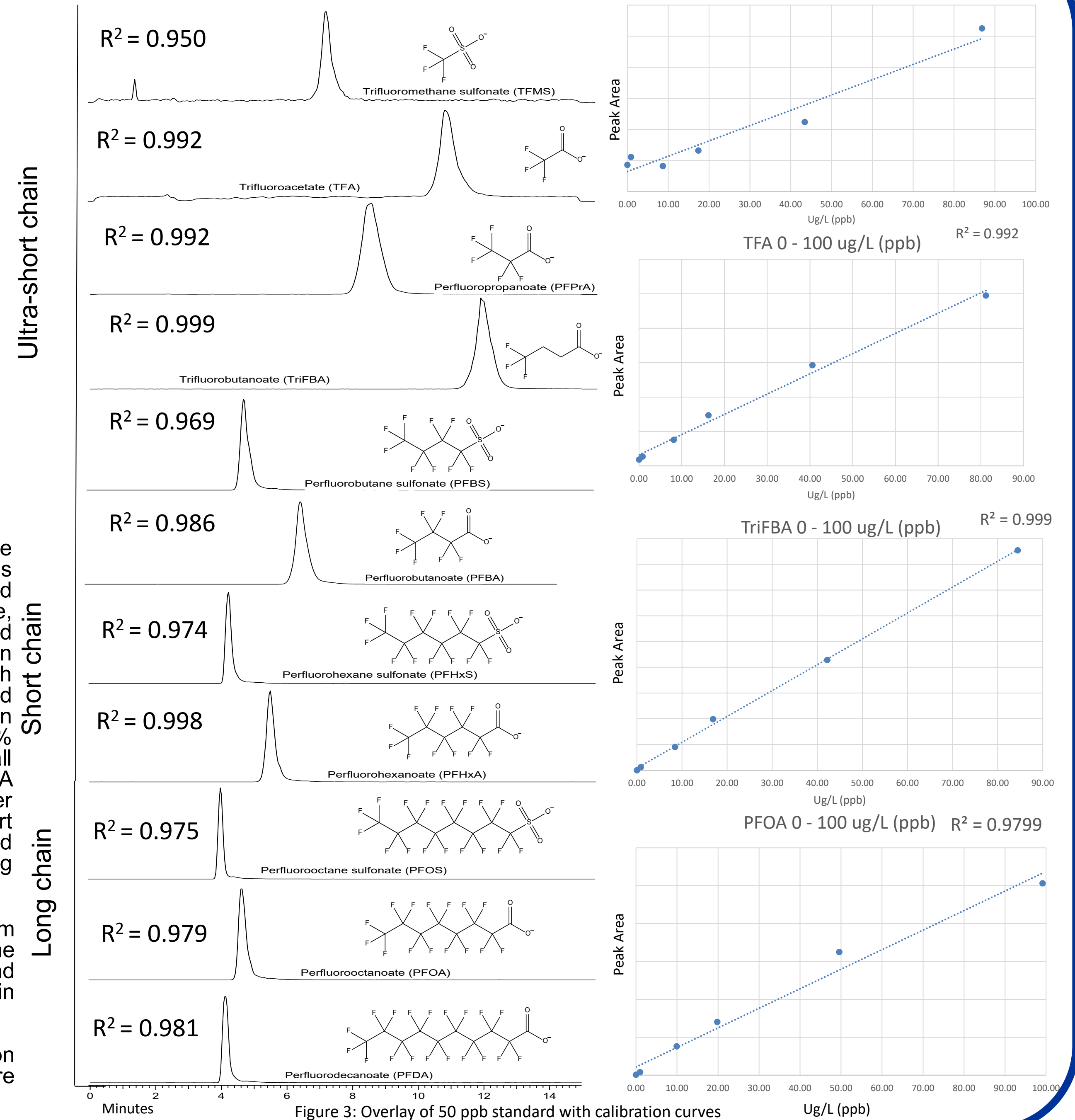


Figure 3: Overlay of 50 ppb standard with calibration curves