Analytical Issues with PFAS

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Collaborative on Health end the Environment (CHE) Webinar

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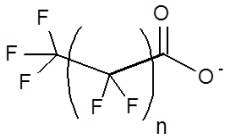
Analysis of PFAS

USEPA Method 537, *Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)*, version 1.1 (September 2009)

- Method 537 is currently the only quantitative published method
- EPA in process of developing method(s) for other matrices and to improve accuracy of measurements
- Beginning in January 2017, Interstate Technology & Regulatory Council (ITRC) will be a developing guidance document on PFAS

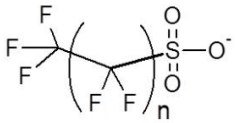
PER AND POLYFLUORINATED COMPOUNDS (PFAS/PFC)

PFCAs incl. PFOA



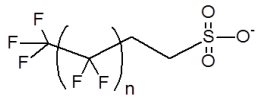
n=2, PFBA; n=3, PFPeA;
n=4, PFHxA; n=5, PFHpA;
n=6, PFOA; n=7, PFNA;
n=8, PFDA; n=9, PFUnDA;
n=10, PFDoDA;

PFSA incl. PFOS



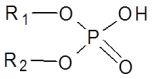
n=3, PFBS
n=5, PFHxS
n=7, PFOS

FTS



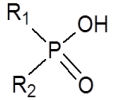
n=3, 4:2 FTS
n=5, 6:2 FTS
n=7, 8:2 FTS

PAP, DiPAP



R_1=$C_2H_4C_6F_{17}$, R_2=$C_2H_4C_8F_{17}$ } 6:2 diPAP
R_1=$C_2H_4C_6F_{13}$, R_2=$C_2H_4C_6F_{13}$ } 8:2 diPAP
R_1=$C_2H_4C_6F_{13}$, R_2=H } 6:2 PAP
R_1=$C_2H_4C_6F_{17}$, R_2=H } 8:2 PAP

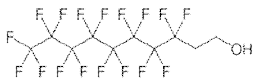
PFPA/PFPiA



R_1=OH, R_2=C_6F_{13} } PFHxPA
R_1=OH, R_2=C_8F_{17} } PFOPA
R_1=OH, R_2=$C_{10}F_{21}$ } PFDPA

R_1=C_6F_{13}, R_2=C_6F_{13} } 6:6 PFPiA
R_1=C_6F_{13}, R_2=C_8F_{17} } 6:8 PFPiA
R_1=C_8F_{17}, R_2=C_8F_{17} } 8:8 PFPiA

FTOH



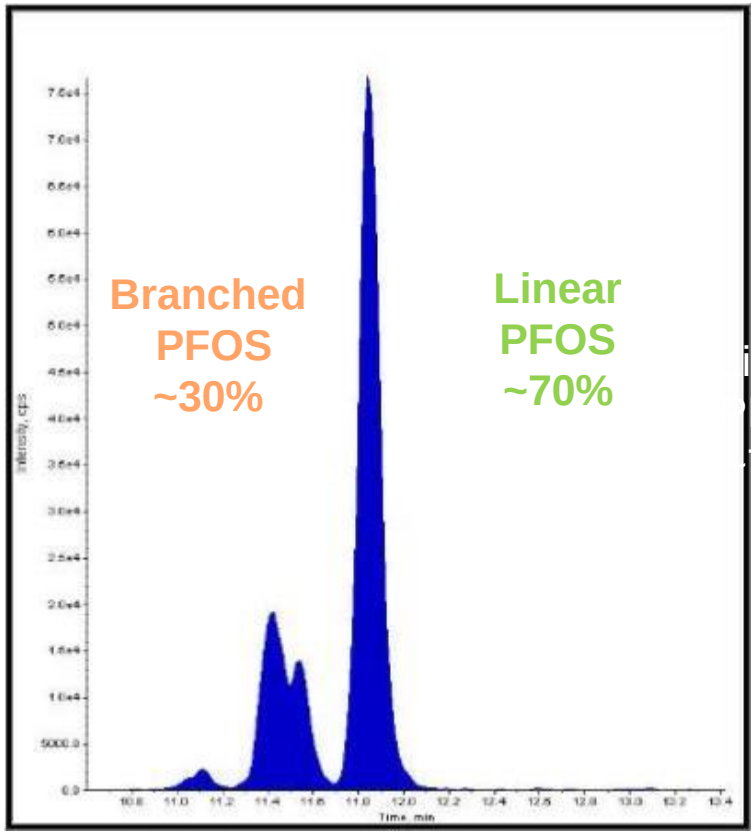
Poly- or perfluorinated alkyl substances (PFAS) or Perfluorocarbons(PFC) – General term for all chemicals formed from carbon chains with fluorine substituting some/all of the hydrogens on the chain

- C-F bond very strong
- Unique properties – repel water and oil, surfactant, stable
- Diverse and complex chemistries based on product use
- Precursors FTS (Fluorotelomer Sulfonate) , PAP (Polyfluorinated Alkyl Phosphate Esters), PFPA (Polyfluorinated phosphonic acid), FTOH (Fluorotelomer alcohol) can all degrade to PFOA

Major Factors Affecting Analytical Accuracy

- Background Contamination
- Not quantitating Branched Isomers along with straight-chain Isomers
- Matrix Interferences causing Enhancement and/or Suppression of Analytical Signal
- Recovery Correction through Isotope Dilution is not routinely performed

LINEAR VS. BRANCHED ISOMERS



- Eleven *known* isomers of PFOS
- 499>80 and 499>99 transitions have different relative response factors for the linear and the branched isomers.
- Quantitative biases possible depending on standard type and MRM transitions used for quantitation
- Distribution/half lives in tissue are different between linear and branched
- Speciation is more important in research applications. Contaminant analysis issues centered around accuracy of quantitation

Riddell, N. et. al, Environ Sci. Technol. 2009 (43) 7902-7908.

Analytical Recommendations

- Validate method of extraction and analysis for each matrix
- Use Isotope Dilution Technique plus recovery-correction for analysis
- Extend List of Analytes to include C4- or C5-alkly acids & Precursors
- Modify LC/MS/MS to eliminate PFCs and minimize PFC background in sampling and analysis
- Include Branched Isomers in Reporting
- Perform rigorous QC: e.g., Field Duplicates, Blank Spikes, Blanks analyzed between each sample