

Non-targeted analysis of PFAS using two-dimensional gas chromatography (GC×GC)

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What is a PBX?

- Plastic-bonded explosives (PBXs): powdered explosives coated in polymeric binders
 - Increases safety of explosives
 - ~5-10 wt% polymer
 - May also contain plasticizer
- Allows for pressing and machining of explosives
- Process developed at LANL in the 1950s
 - In 1954 LANL started using fluoropolymers in some PBXs
 - From 1959-2003 LANL processed ~91,000 kg of fluoropolymer-containing PBXs



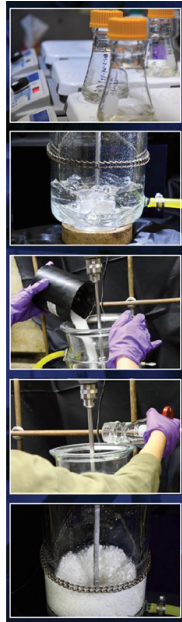
PBX #2: 95 wt% Explosive and 5 wt% binder

PFAS Contamination in PBXs

PBXs are made using a wet-slurry process

1. Suspend explosives in a controlled temperature water bath which is rapidly stirred
2. Add lacquer (**polymer**, additives dissolved in an organic solvent)
3. **Polymer** crashes out of solvent and coats explosive to create **explosives prills**
4. Then quench with water to separate out **PBX prills**
5. Dispose of **liquids** to recover **PBX**

Red = PFAS



High Explosives Areas at LANL

Red = PFAS

- High Explosive R&D
- Formulation
- Pressing
- Machining
- Disposal



Targeted (EPA Regulated) vs. Non-targeted PFAS

- 40 EPA regulated PFAS compounds for which a method exists
 - The list is expanding as of 2024 to ~150 compounds
- Gold standard for targeted analysis is UHPLC-QQQ
- There are over ~12,000 PFAS compounds
- Types of PFAS used in fluoropolymer production has changed over the years
- LANL is lucky to have standards of 1950s and 1960s fluoropolymers
 - But only have a limited amount of material
- Ongoing research by many groups use UHPLC-QTOF and other MS detectors

Our goals are to:

1. Develop a non-targeted method(s) for *all* PFAS
2. Evaluate fluoropolymers / PBXs to fingerprint material based on PFAS content
3. Apply a methods and fingerprinting for environmental samples

Detection of PFAS using LC or GC (or Both)?

UHPLC

- *Almost* universal for all PFAS
- QQQ/QTOF is the gold standard
 - QQQ is extremely sensitive
 - QTOF is “simple” expansion of QQQ



GC (GC×GC)

- Ideal for volatile PFAS (alcohol and ether derivatives)
- Does not work for ionic PFAS (e.g. sulfonic acids) without derivatization
- GC×GC allows for unique selectivity



Sample Preparation Method Development for UHPLC-QTOF

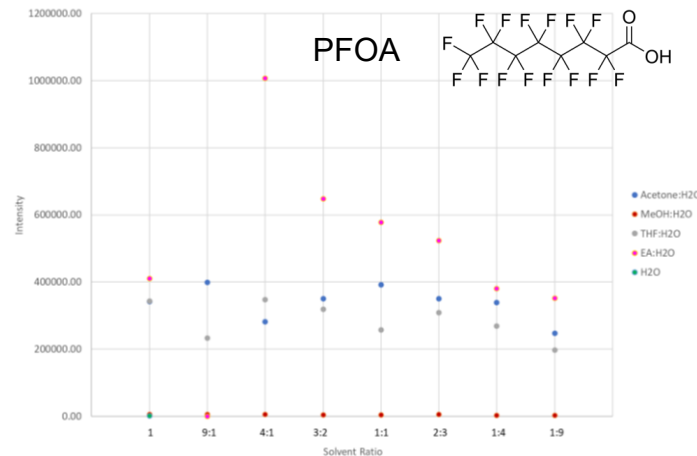
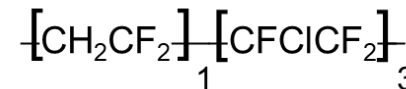
- 4 Organic solvents (OS) were used at various ratios with water for multiple fluoropolymers

- 100% OS
- 9:1 OS:H2O
- 4:1 OS:H2O
- 3:2 OS:H2O
- 1:1 OS:H2O
- 2:3 OS:H2O
- 1:4 OS:H2O
- 1:9 OS:H2O
- 100% H2O

- Organic Solvents:

- Acetone
- MeOH
- THF
- EA

Kel-F 800

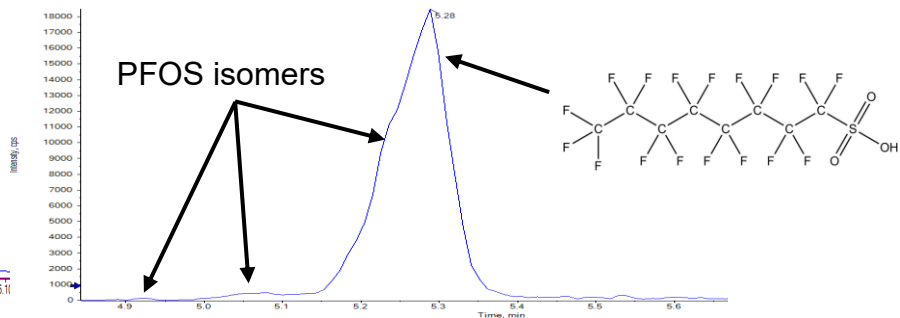
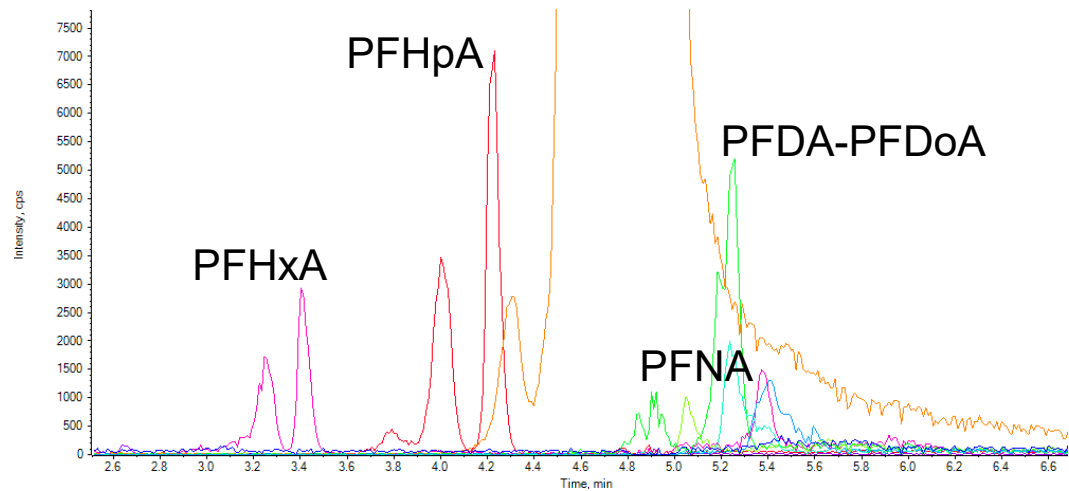
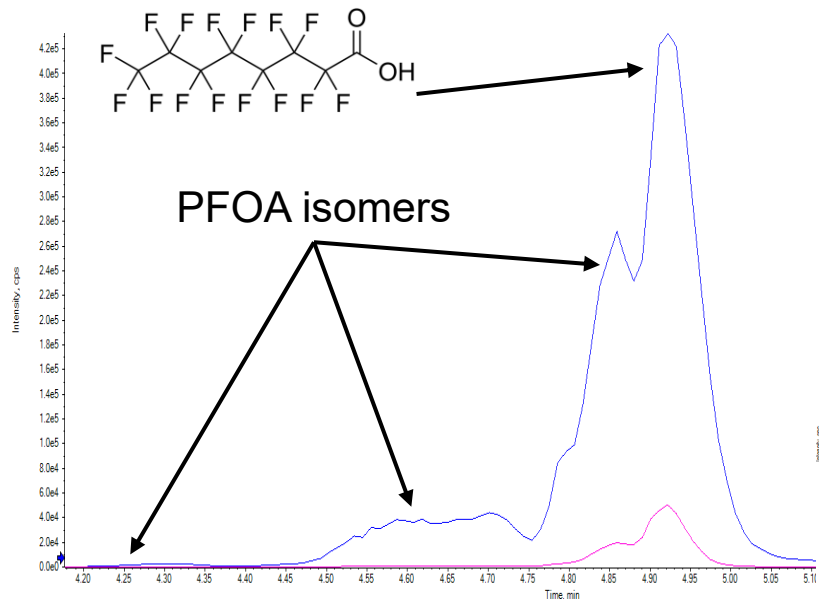


Strong OS solvent (THF, EA) required to dissolve fluoropolymer and free PFAS from matrix

Perfluorooctanoic Acid (PFOA) and PFAS using EPA Method

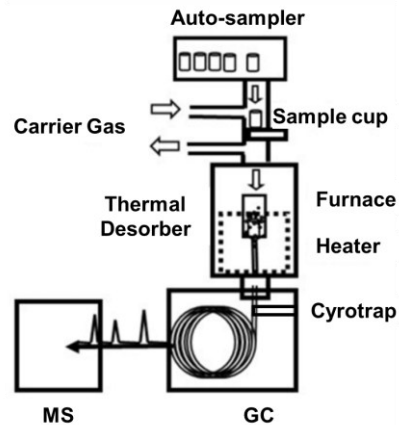
Kel-F 800 Lot 576

PBX #1 (Kel-F 800 Lot 603)

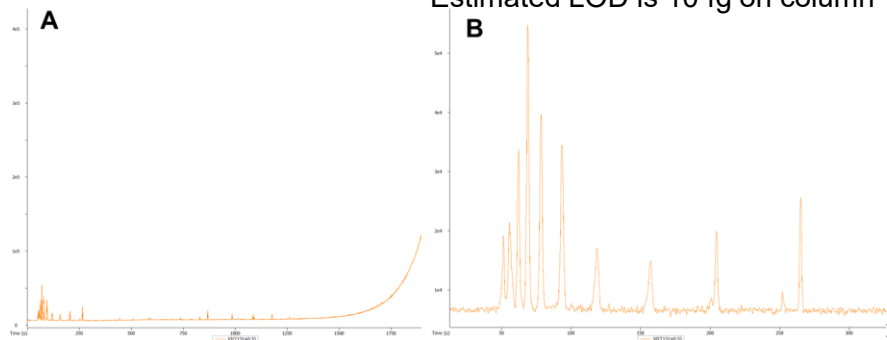


GC-TOFMS Analysis of 28 Standard PFAS Mix

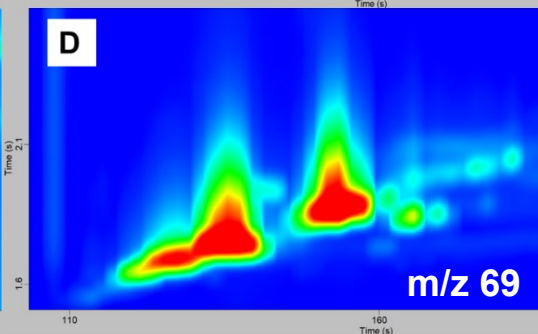
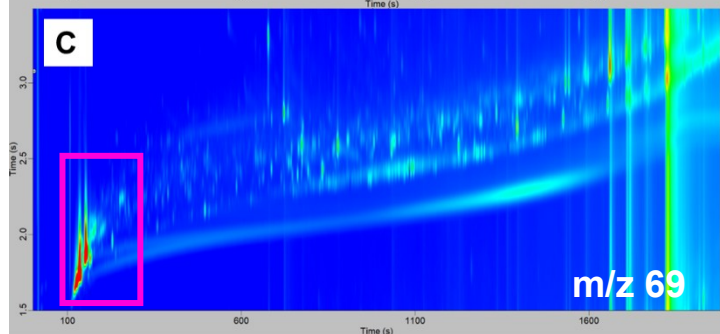
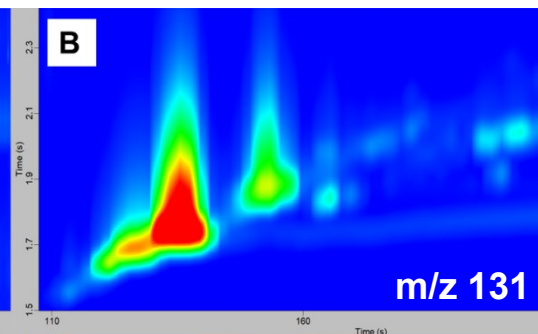
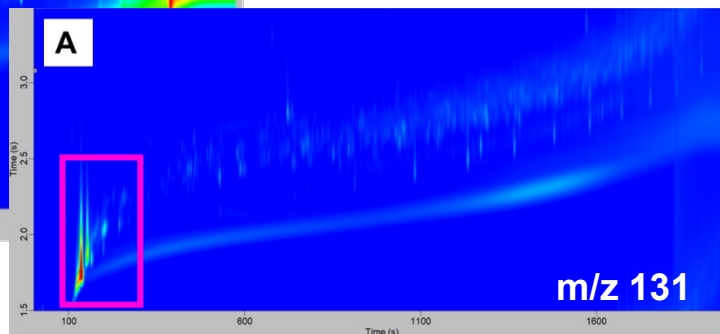
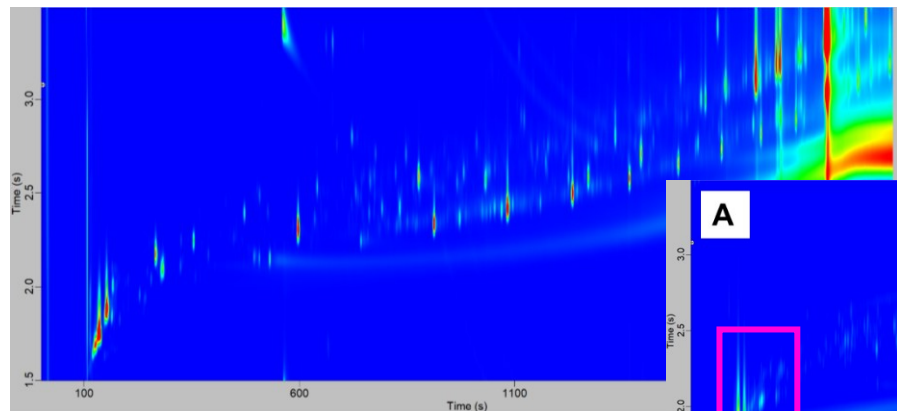
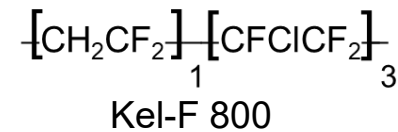
- GC *should* be an ideal technique for environmental samples due to reduced background matrix
- GC-MS was the preferred technique before LC-QQQ
- Perfluorocarboxylic acids (PFCAs) elute at the same time as solvent and exhibit poor focusing on column
 - Overcome using a solvent-free injection technique, thermal desorption combined with cryotrap → added bonus of being able to inject large volumes of sample



Perfluorocarboxylic acids (PFCAs) C₅ to C₁₄
Estimated LOD is 10 fg on column

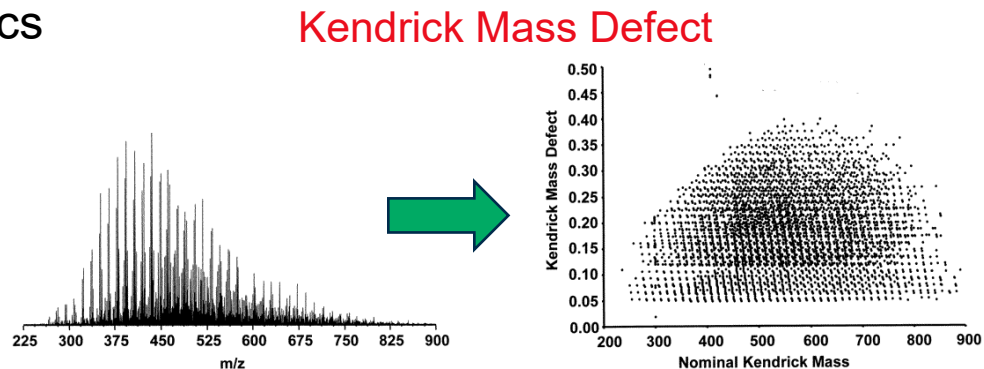
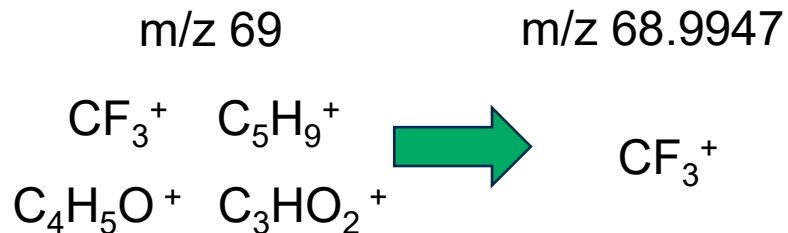


TD-GC×GC-TOFMS of Kel-F 800

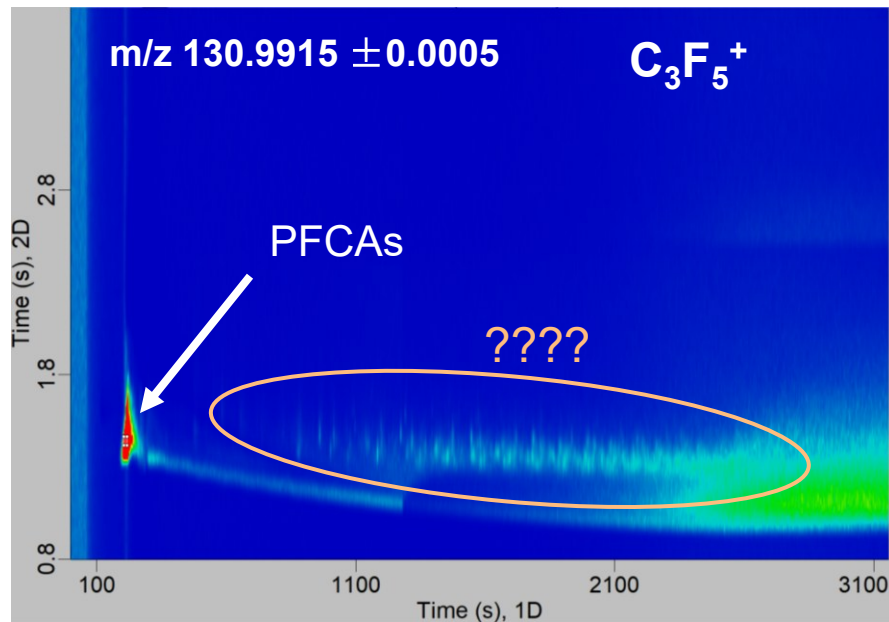
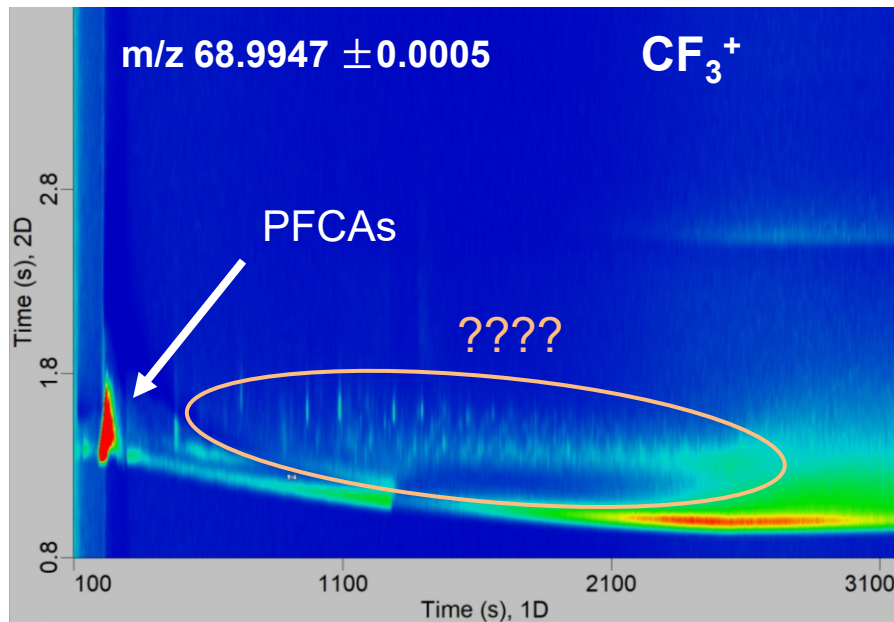
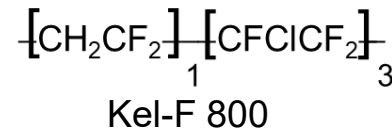


Transitioning from MS to HRMS

- High selectivity in mass spectral dimension improves specificity
- Slight loss in sensitivity (~3x)
- HRMS allows for unique data analytics
 - AI/ML for fingerprinting
 - Kendrick Mass Defect

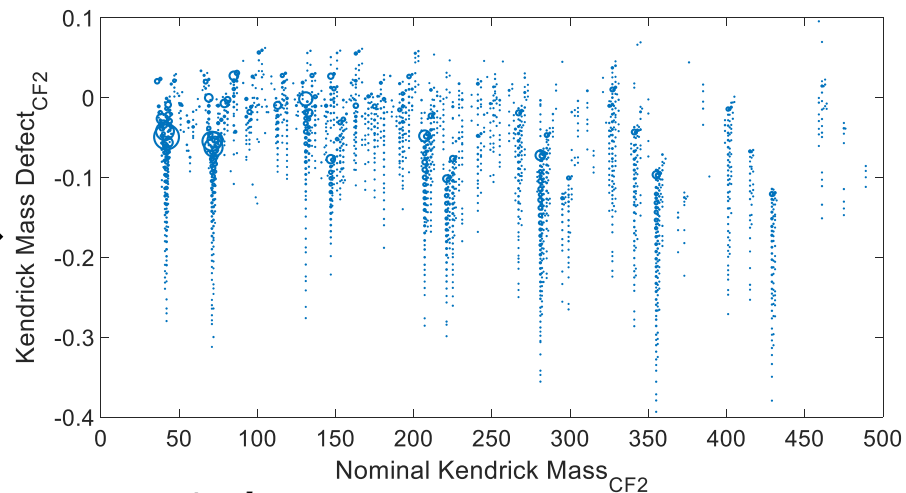
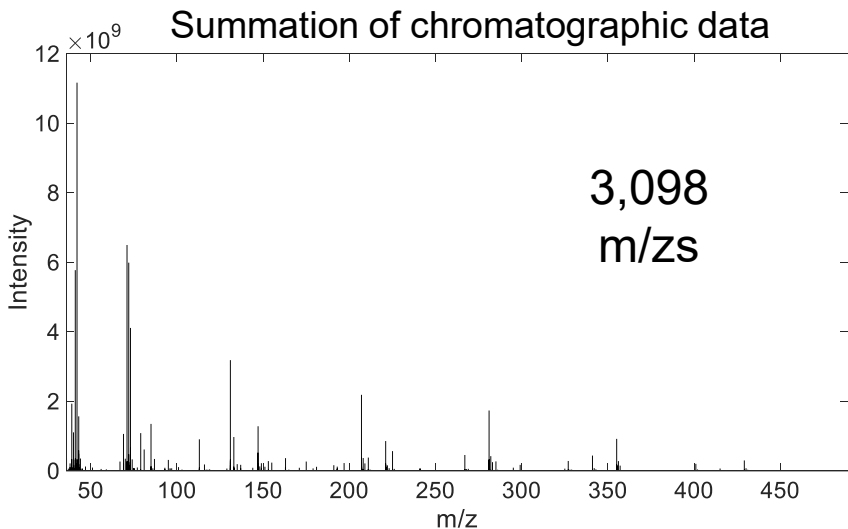


GC×GC-HRMS of Kel-F 800



Targeted evaluation of GC×GC-HRMS lead to discovery of numerous other compounds.
What else could be present?

Kendrick Mass Defect on GC×GC-HRMS

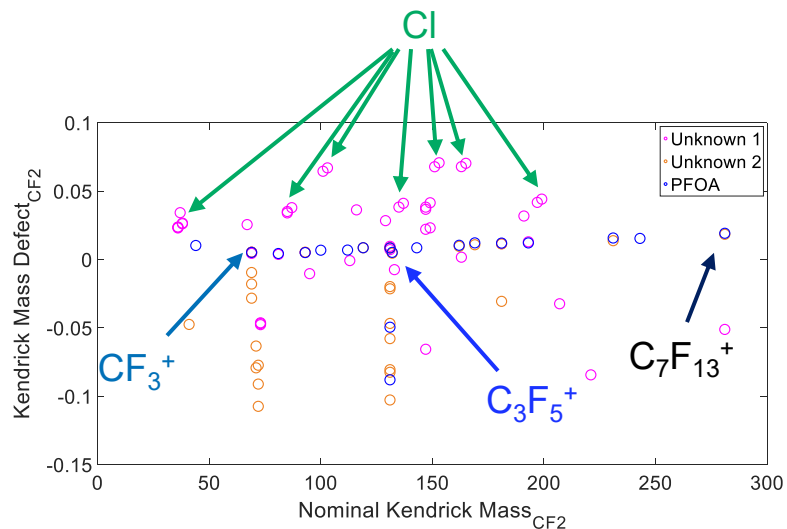
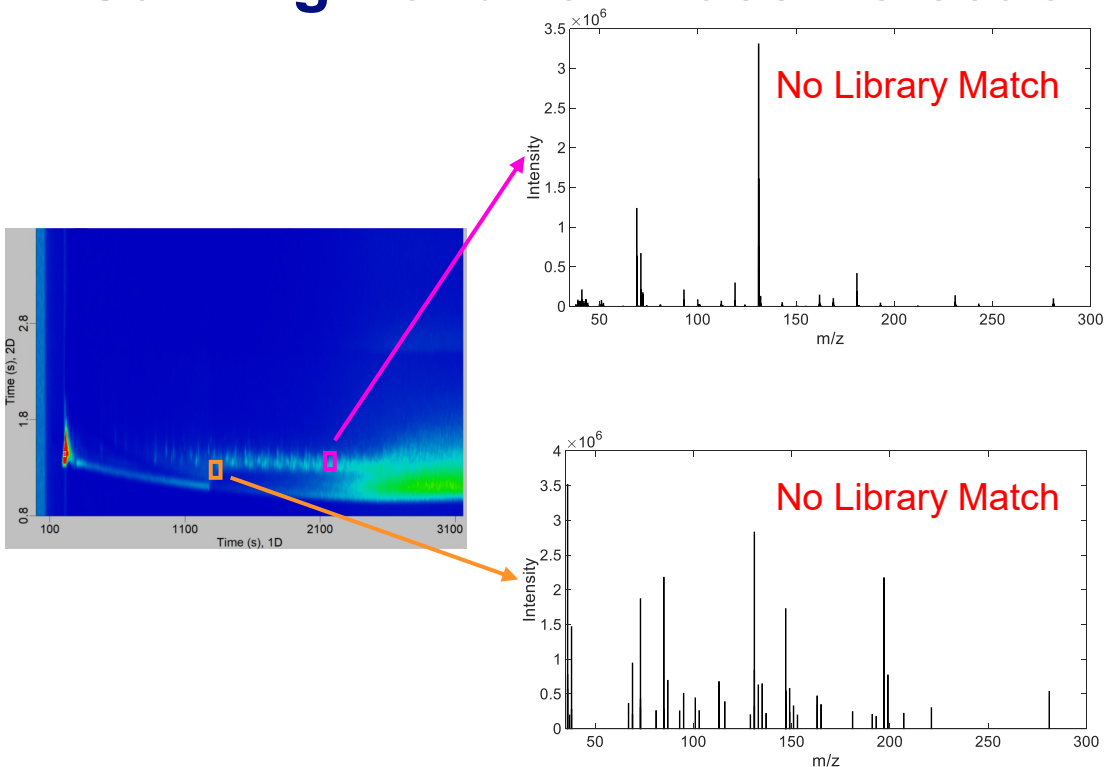


$$\text{Kendrick Mass} = \text{Observed Mass} * \frac{\text{nominal mass}}{\text{exact mass}}$$

$$\text{Kendrick Mass Defect} = \text{nominal KM} - \text{exact KM}$$

Kendrick mass defect for electron impact ionization is informative, but dismisses important chromatographic information

Utilizing Kendrick Mass Defect on per compound basis



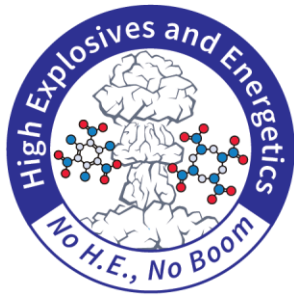
Kendrick mass defect can be used to uncover PFAS and "PFAS like" substances

Future Work

- Improvements to GC×GC-HRMS separations for fluoropolymers
- Modification of KMD for non-targeted analyses
- AI/ML for fingerprinting different fluoropolymers and lots of fluoropolymers based on PFAS content
 - Application to environmental samples
- Emissions from disposal of PFAS containing PBXs
- Decomposition of PFAS in the environment

Acknowledgements

- **Pollution Prevention (P2)**
 - Michael Moss and Sarah Gould
- **High Explosives and Energetics Program**
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Questions?