Past, Present, and Future of PFAS Analysis in the Field

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2018 | Enhancing DoD's Mission Effectiveness

Outline

- Background and intro to mass spec
- Approaches to overcome mass spec pitfalls
- Rapid Site Profiling of Organofluorine: Quantification of PFASs by Combustion Gas Analysis (ER19-C2-1214)

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Background

- Thermally stability of CFCs (late 1930s) - Teflon
- Chemical stability usually translates to environmentally persistent
- "Evidence that there are Two Forms of Fluoride in Human Serum"
  - *Nature,* 1968
- 1970's discovery of organfluorine in blood with speculation that it is PFOA (Guy *et al*. 1974)
  - 26 ng/L organofluorine
- 2001 speciation and quantitation of organfluorine in human serum by 3M researchers (Hansen et al., 2001)
  - LC/MS/MS gaining popularity
  - Sum of four measured PFASs = 27 ng/L

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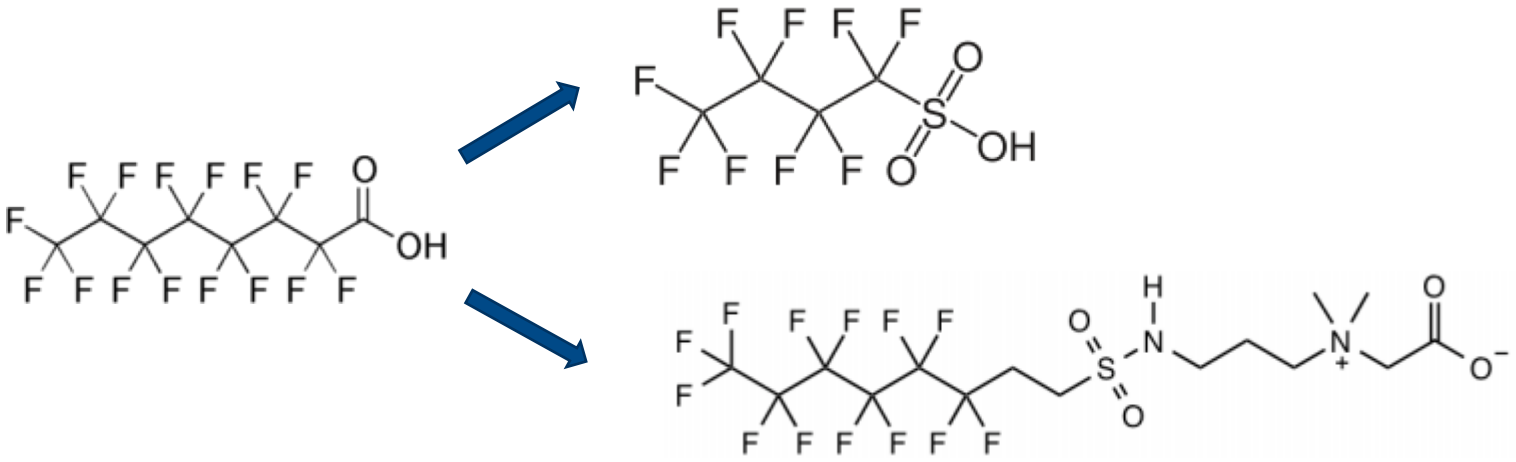
Chemical Substitutes

- 3M voluntary phase out of PFOS and PFOA (2002-2005)
- Recognition that shorter alkyl chain results in faster renal clearance
- Inclusion of abstractable hydrogens decreases environmental (and probably blood serum) persistence of parent compounds



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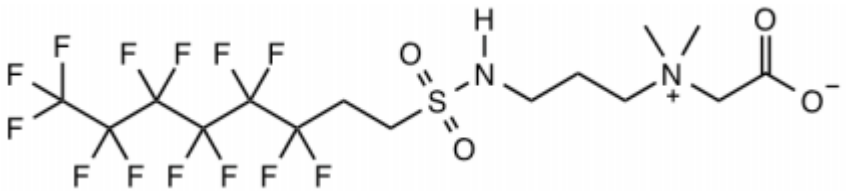
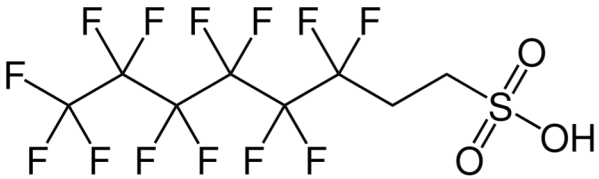
New Chemistry, Old Problems

Sunlight photolysis causes *N*-dealkylation

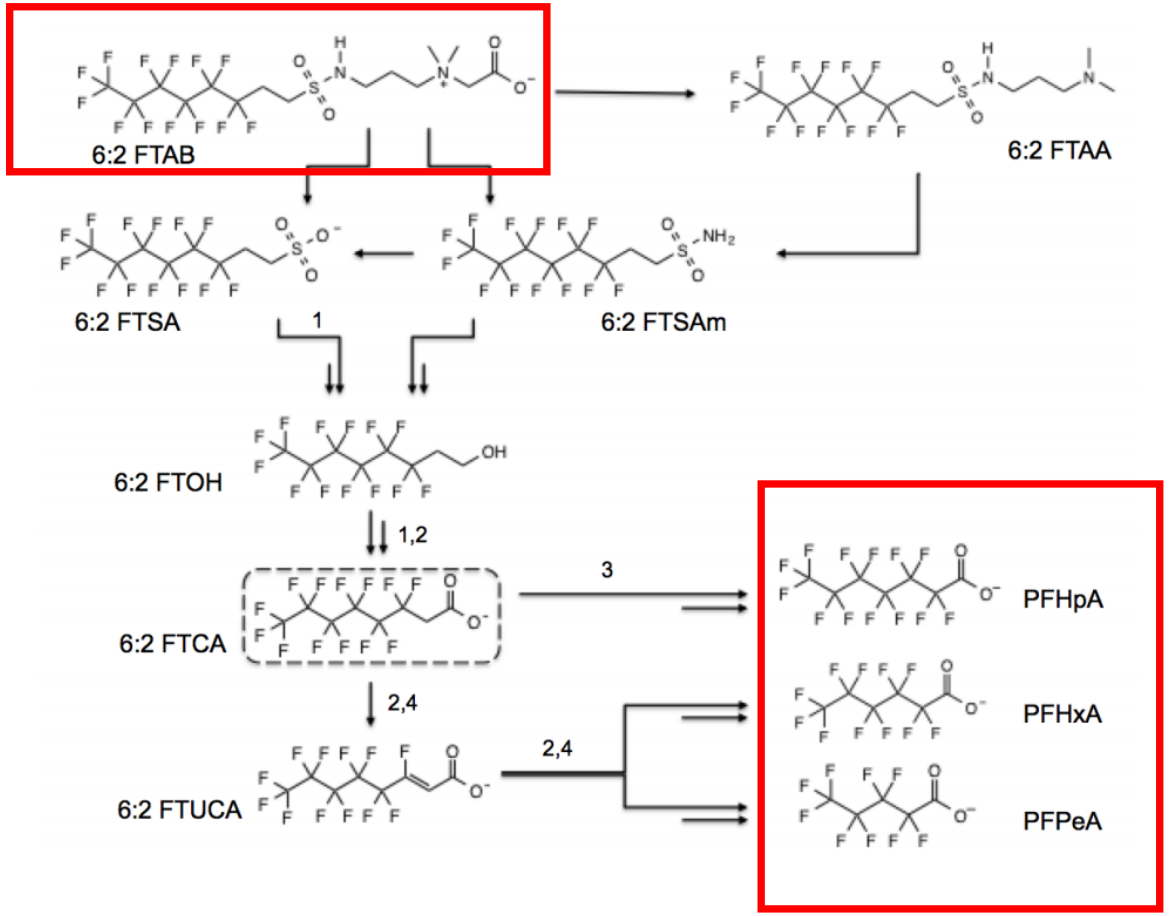


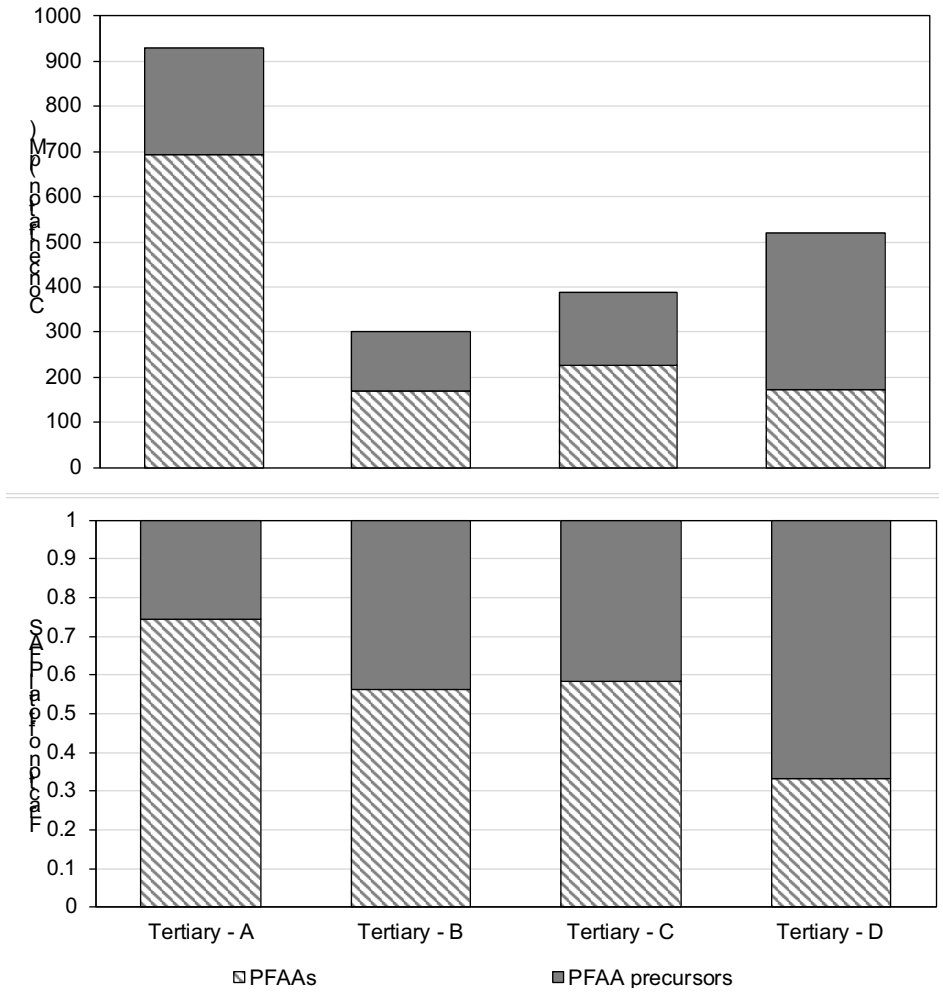
6:2 FTAB (Florafac 1157)



6:2 FTSA

Precursors





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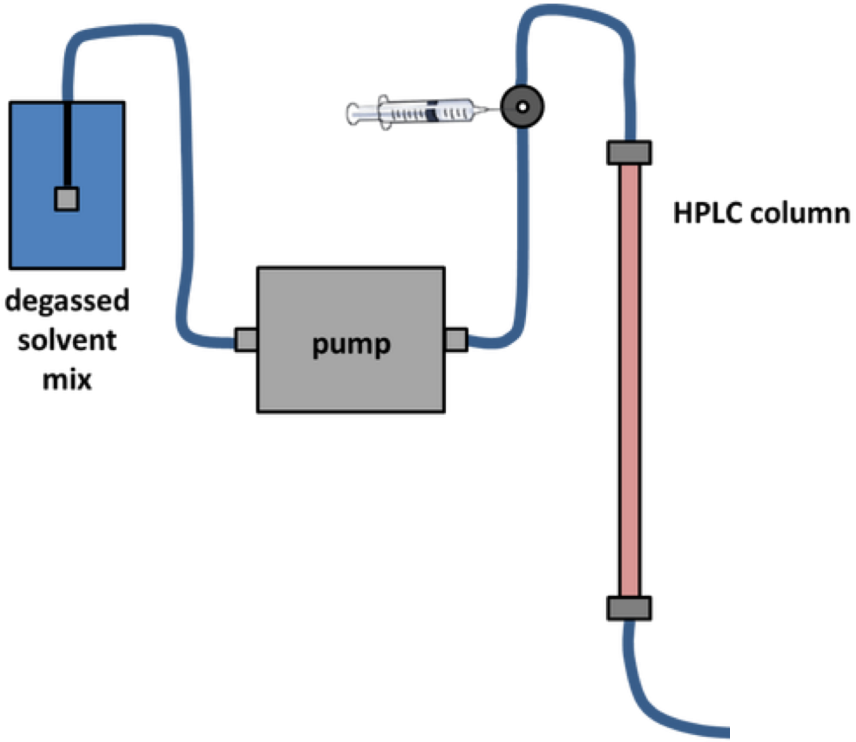
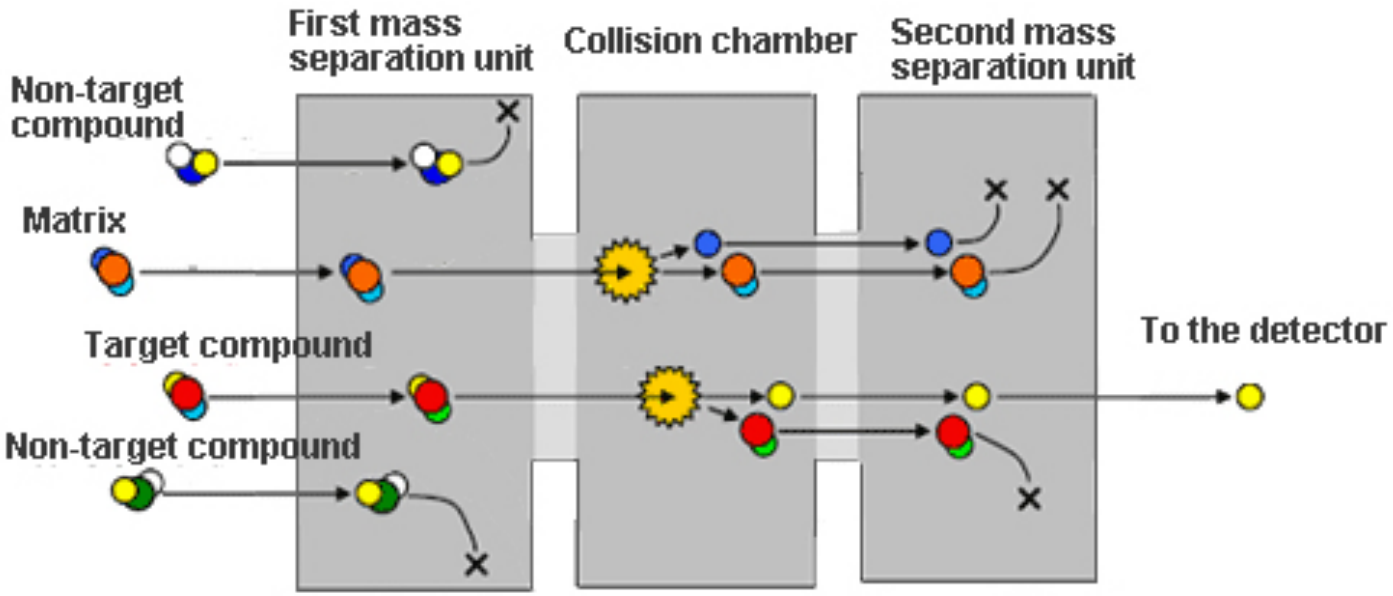
Chromatography and Mass Spectrometry

Liquid Chromatography



Tandem Mass Spectrometry (mass filters)



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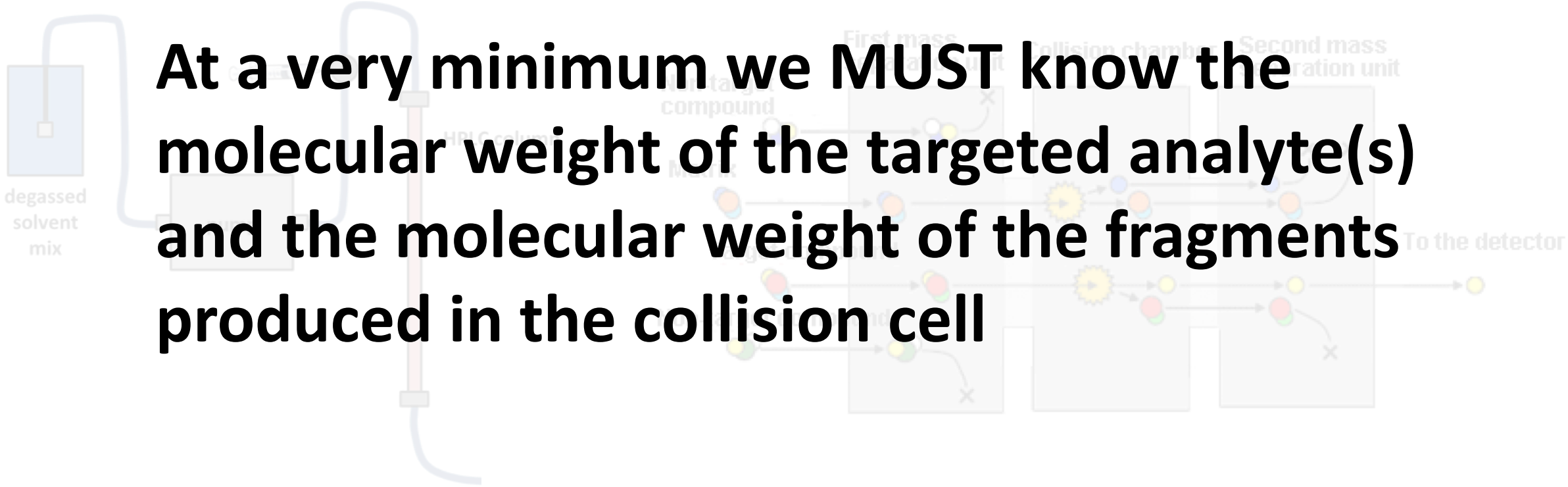

At a very minimum we MUST know the molecular weight of the targeted analyte(s) and the molecular weight of the fragments produced in the collision cell

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Implications of MS/MS

- Environmental/engineered processes alter the mass of the analyte (analyte is “gone”) but unclear if toxicological profile of product is changed
- Need standards of individual analytes to conduct instrument calibration and quantification – not always available
- Expensive instrumentation, not well suited for field use, and highly specialized technical expertise required

Subsurface PFOS and ? AFFF compounds → Environmental or engineered transformation → Unidentified/unknown organofluorine with potential health risk →

Expensive and difficult to use tool intended to measure specific, known compounds (expensive paperweight)

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Non-target Mass Spectrometry

- High resolution MS – look at as many compounds as possible and identify
- Orbitrap or Time-of-flight instruments typical (>$600k). Field?
- Not quantitative without analytical standards

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WILEY-VCH

COMMUNICATION

Hundreds of Unrecognized Halogenated Contaminants Discovered in Polar Bear Serum

Yanna Liu,[a] Evan S. Richardson,[b] Andrew E. Derocher,[c] Nicholas J. Lunn,[d] Hans-Joachim Lehmler,[e] Xueshu Li,[e] Yifeng Zhang,[a] Julia Yue Cui,[f] Lihua Cheng[f] and Jonathan W. Martin*[a][g]

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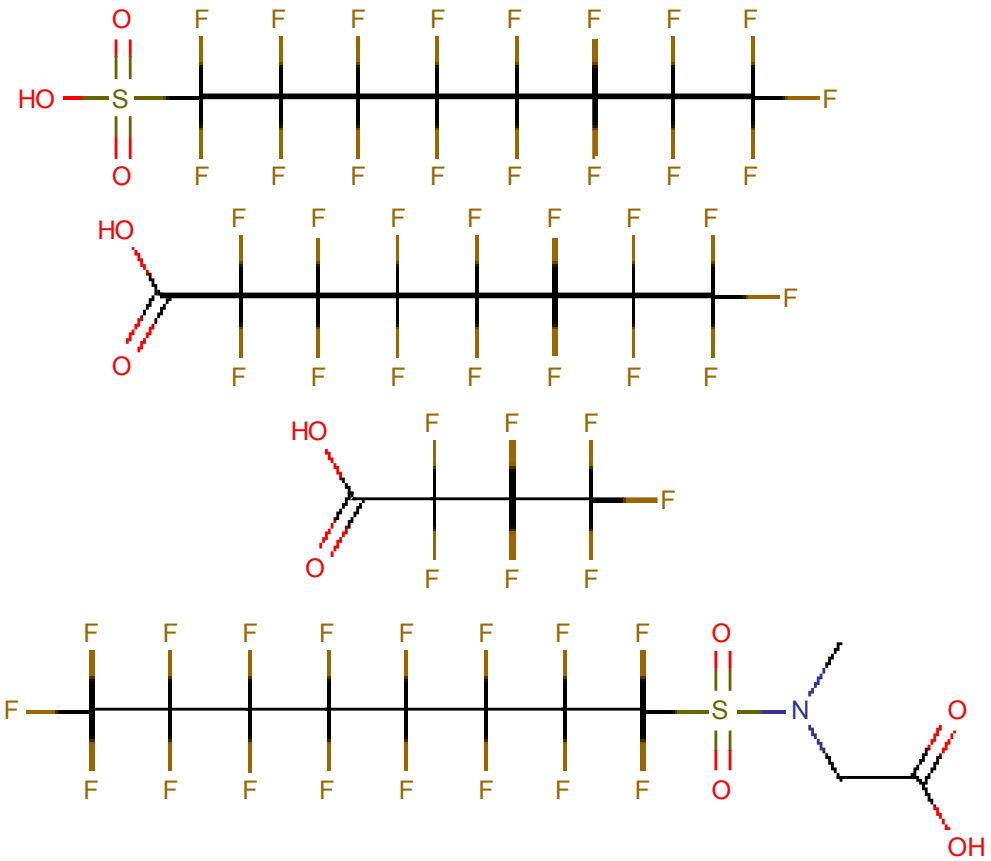
Organofluorine

Why measure all of these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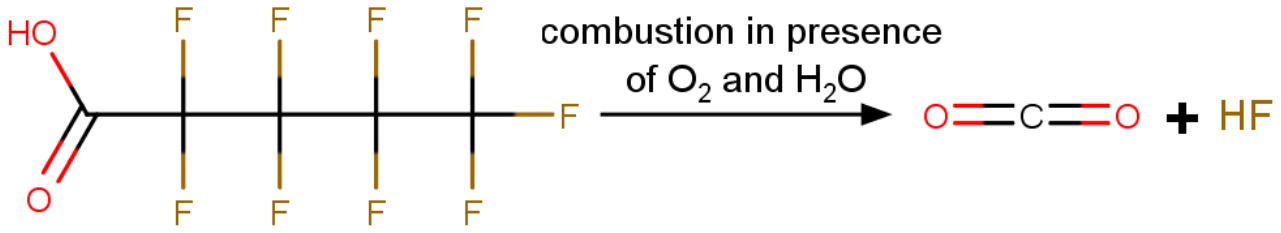
Measurements of Organohalogens

- Combustion of organohalogens (CCl_3, CBr_3, R-Cl, R-X) results in release of gas phase hydrogen halides (HCl, HBr, HF) and CO_2.



- Measurements of unknown/unidentified disinfection by-products has taken advantage of this for many years.
  - Microcoulometric titration – no halogen specificity, captures all organohalogens

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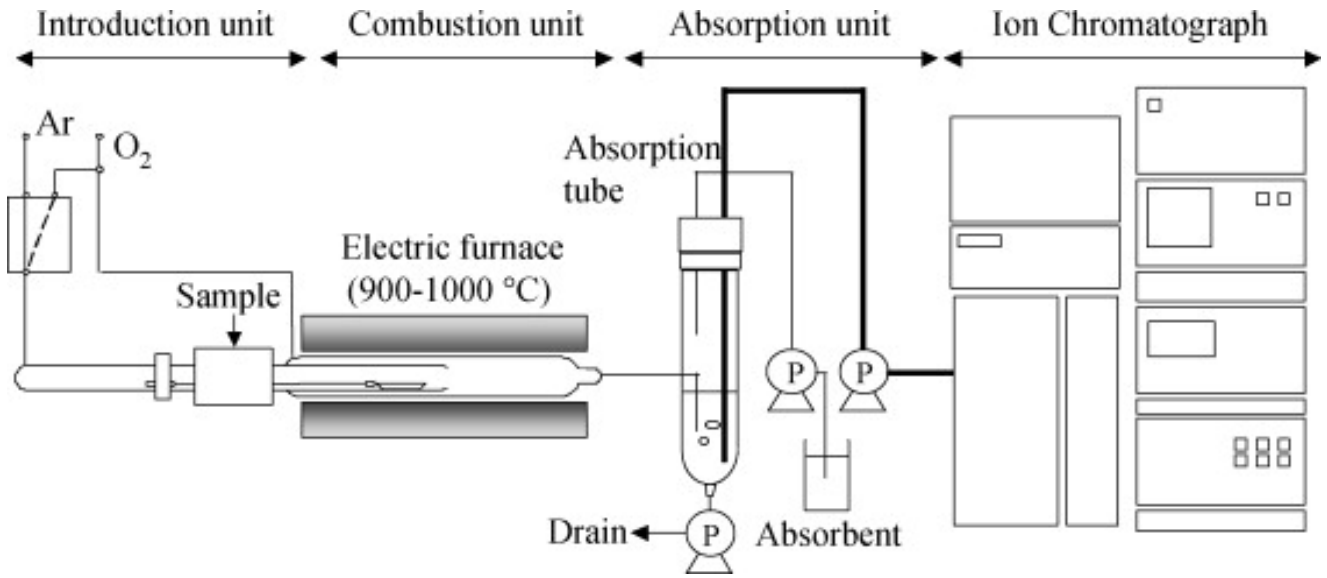
Measurements of Organofluorine

- Organohalogen combustion methods adapted in 2007 to measure organofluorine in human blood
- Combustion gasses bubbled through alkaline trap
  - $HF + NaOH_{(aq)} \rightarrow H_2O + F^- + Na^+$
- Measure fluoride with ion chromatography



Miyake, Y., So, M., Rostkowski, P., Taniyasu, S., Lam, P., Kurunthachalam, K., and Yamashita, N., Trace Analysis of Organic Fluorine in Human Blood Using Combustion Ion Chromatography for Fluorine (Cic-F). *Organohalogen Compounds*, **2006**. 68: p. 519-522.

Measurements of Organofluorine

- Shortcomings of combustion ion chromatography
  - No speciation of fluorinated compounds
  - Environmental F^- interference
  - Detection limit of ion chromatography ~µg/L PFOA as F^-
  - Field deployable?

- Particle-induced gamma ray emission spectroscopy (PIGE) also has been used to measure organofluorine
  - Currently applicable to paper and textile samples (250 µm beam penetration)
  - Need SPE for aqueous samples
  - Authors also working to field deploy but large and immobile for right now

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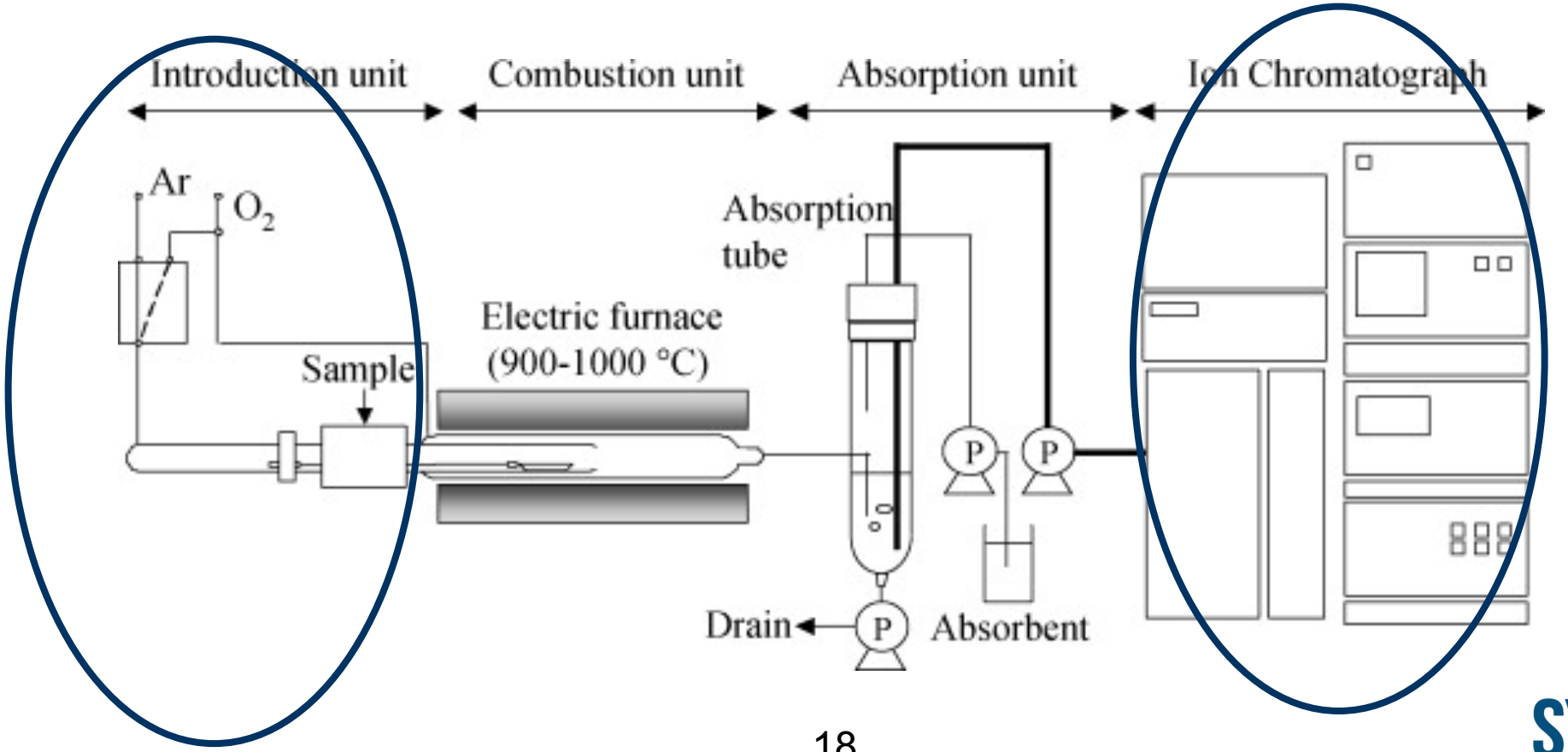
Rapid Site Profiling of Organofluorine: Quantification of PFASs by Combustion Gas Analysis (ER19-C2-1214)

Objective: Develop and validate robust, field-ready instrumentation and methods to quantify total organofluorine.



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HF Quantification in the Gas Phase

- Industrial safety equipment
- Mature technology – laser spectroscopy
- Relatively low detection limits (5pptv)
- Robust and field deployable
- Picarro willing to collaborate

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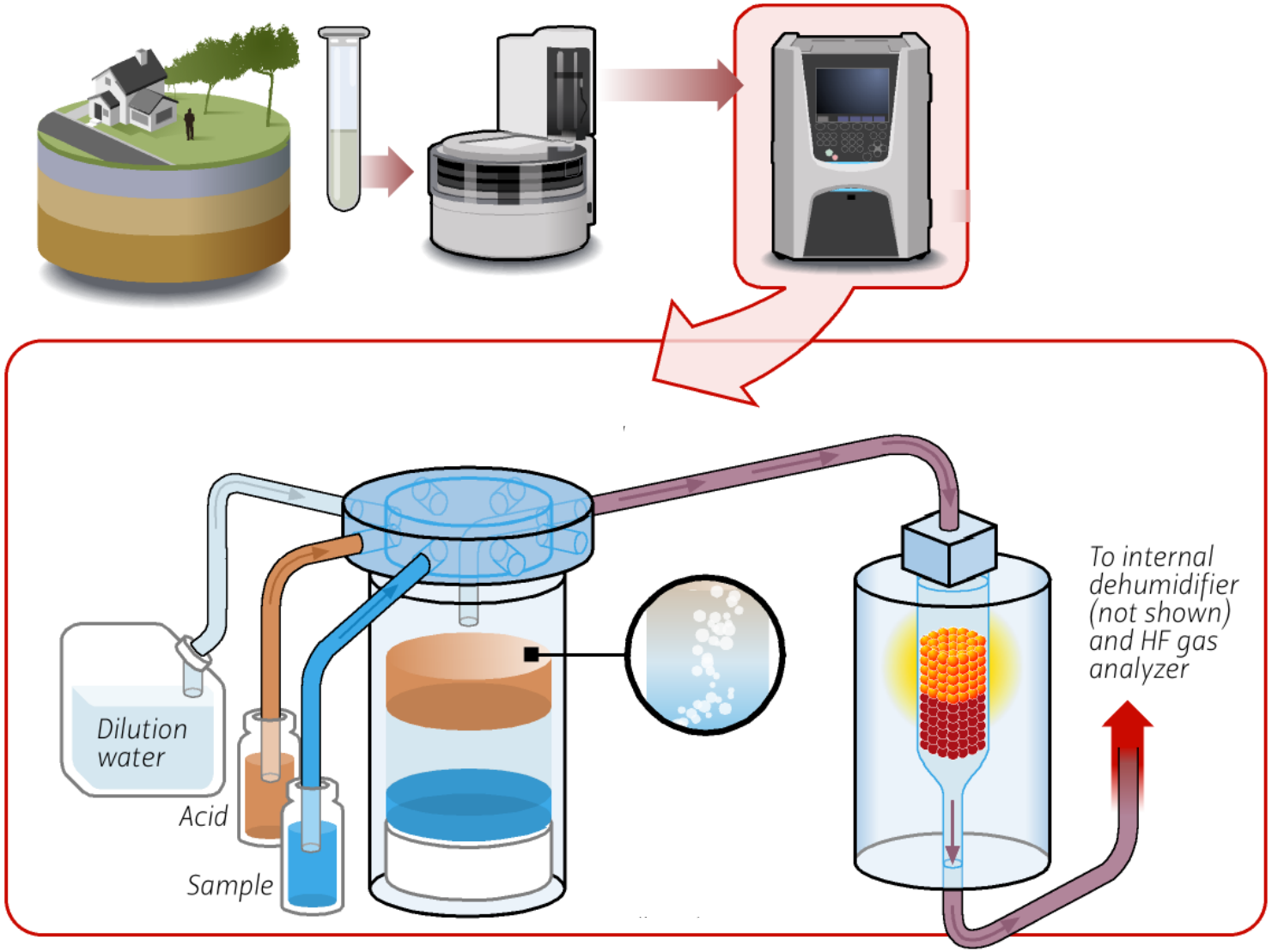
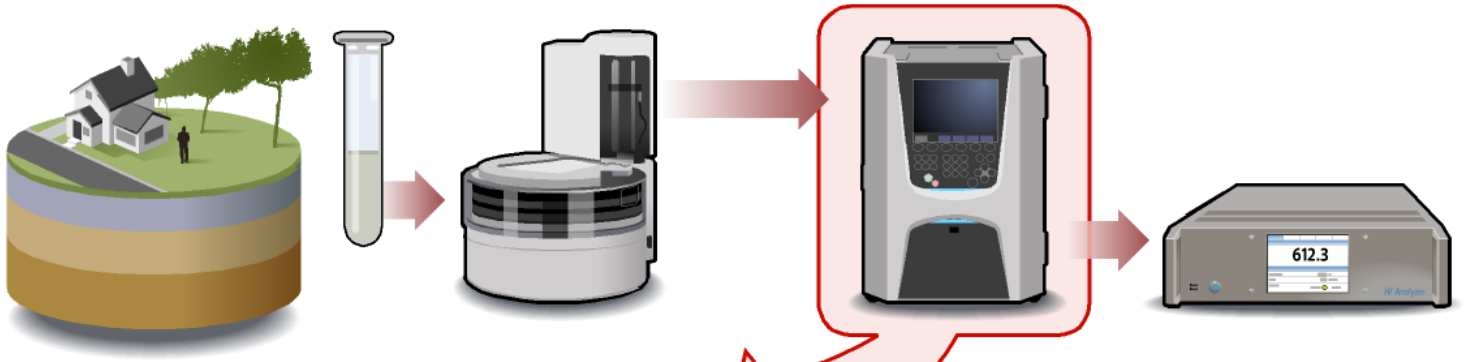
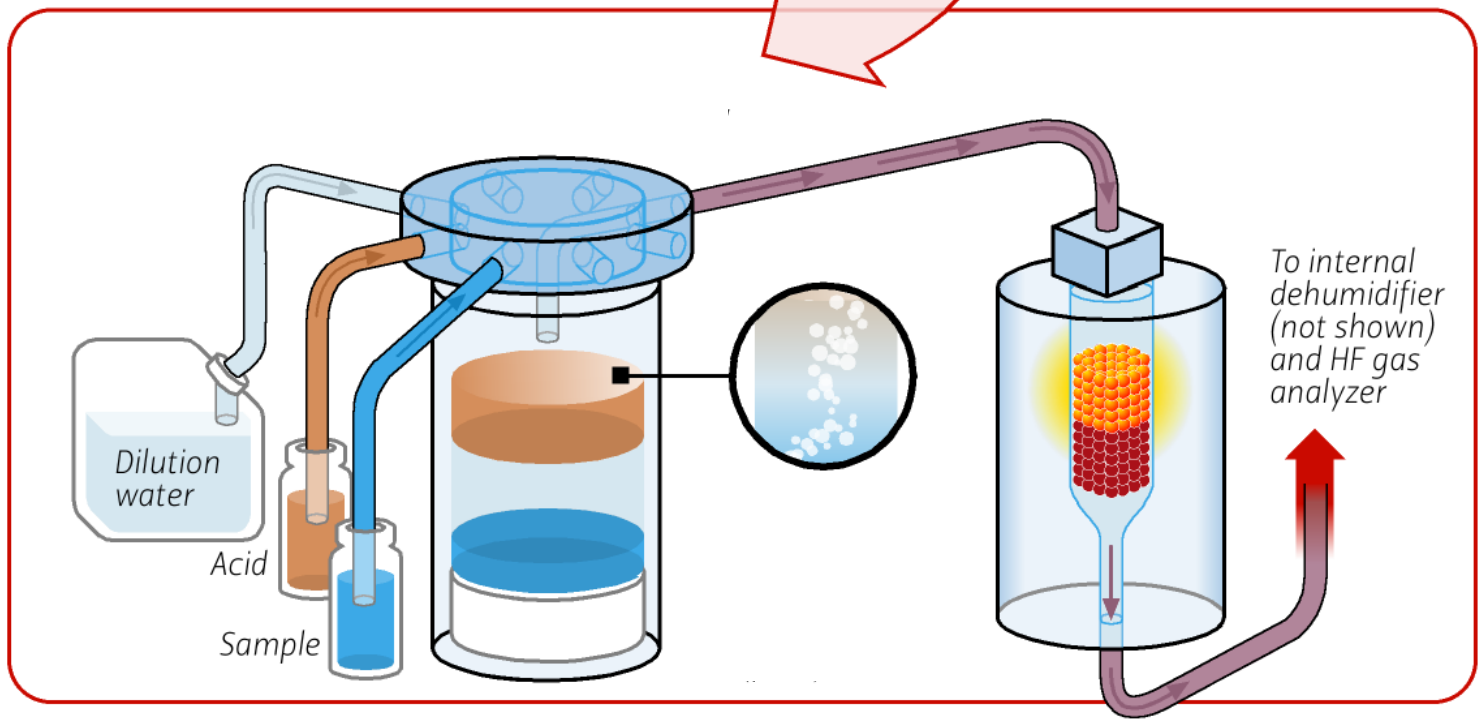
Automation and Removal of F^-

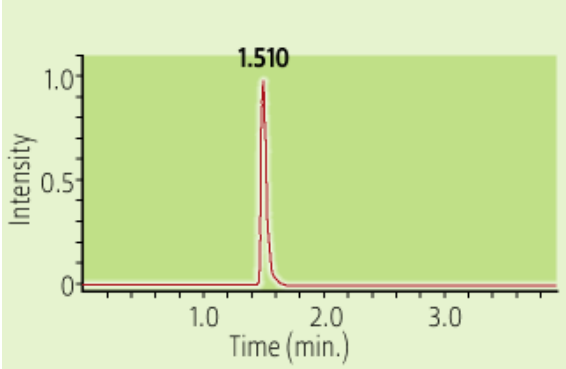


Organofluorine measurements as a single peak



Calibrate with a single organofluorine standard





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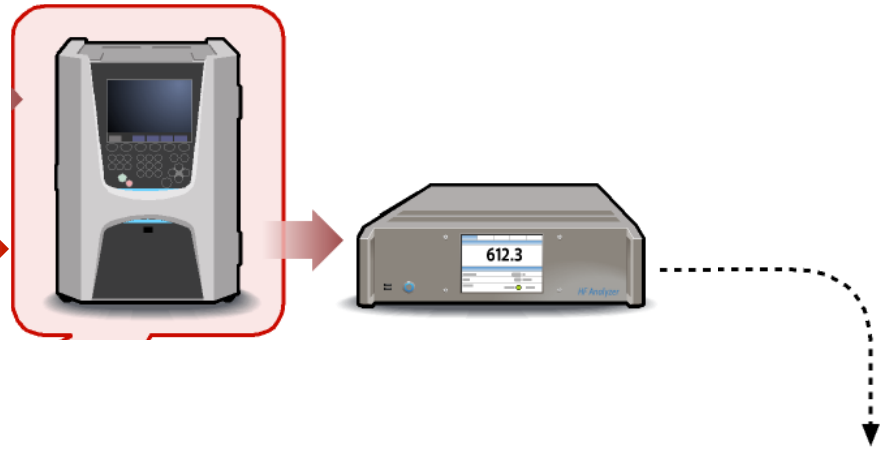
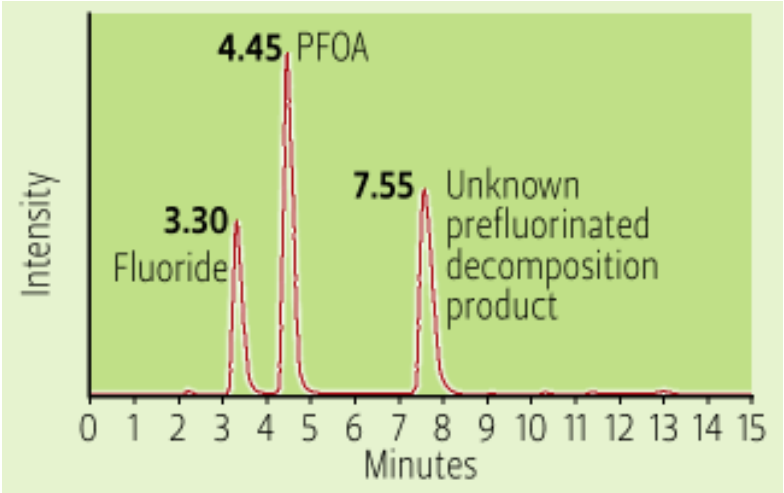
Organofluorine Measurements - Species Specific Peaks

HPLC equipped with autosampler and C18 column achieves automated separation of organofluorine





Approach

- Initially focus on complete combustion of PFASs
- Once we are confident in mass balance, mate to laser spectrometer
- Expectation is to achieve 420 ng/L and 830 pg/g with “out of the box” parameters, then optimize furnace temperature and carrier gas flow
- Early collaboration with Piccaro and Shimadzu Scientific

Validation

50 samples from contaminated DoD sites

Eurofins
- Targeted PFAS by LC/MS/MS EPA 537 or equivalent

Vista Analytical
- Targeted PFAS by LC/MS/MS EPA 537 or equivalent

U of Nevada
- Targeted PFAS by LC/MS/MS EPA 537 or equivalent
- Total Organofluorine by OFC-LS

SNWA
- Targeted PFAS by LC/MS/MS EPA 537 or equivalent
- Total Oxidizable Precursor

U of Nevada
- Comparison and analysis of data
- Weathered/degraded samples may have too many unidentified/non-target PFASs that show up on OFC-LS but not on the LC/MS/MS
- Prepare 25 samples with 2 to 5 LC/MS/MS targeted PFASs and conduct round robin again
- G/NG

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Field Validation

- Transport to Beale and Travis AFBs
- Laser spectrometers are portable and rack-mountable
- Combustion instrument and autosampler are relatively simple
  - Do not foresee complications with the instrument itself
- Safety will be a concern! Generating HF gas in an enclosed space!

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Intentional Inclusion of Potential Interferences

Table 3: Observations made by our team of PFAS co-contamination across hundreds of field sites.[1]

Impacted Media	Source Area Range	Source Area Mean	Comments
Soil (mg/kg)	<0.01 to >30	3 to 5	PFOS>>PFOA, commonly co-contaminated with total petroleum hydrocarbons (TPH), CVOCs, >30% of mass in vadose zone,
Groundwater (µg/L)	<10 to >10,000	1,000 to 2,000	PFOS≈PFOA, large dilute (<10 µg/L) plumes, plumes >1 mile, commonly co-contaminated with TPH, CVOCs

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Summary

- LC/MS/MS not a great hammer for this nail
- Need robust, field deployable tech
  - Ideally cheaper and easier to operate
- Can take advantage of decades of research on combustion of organohalogens to develop robust new instrumentation to advance our knowledge of organofluorine fate

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Acknowledgements

- Rapid Site Profiling of Organofluorine: Quantification of PFASs by Combustion Gas Analysis (ER19-C2-1214)
- Contributors
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  - Bill DiGuiseppi (Jacobs Engineering)
  - Shimadzu Scientific
  - Picarro Instruments