

Analysis of PFAS Compounds in Indoor Air using Thermal Desorption GC-MS Part 2:

Using Tandem Mass Spectrometry to Improve Detectability and Improve Reliability

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Progression of “PFAS in Air” Development

Stack Emissions

- Sampling trains
- Extraction
- LC-MS/MS
- LC-MS/MS less effective for volatile neutrals

Ambient Monitoring

- High Volume
- PUF/XAD/Filter
- LC-MS/MS
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Indoor Air

- Volume?
- Sorbent?
- Analysis?

Beyond Indoor Air Sampling: Vapor Intrusion

Soil Gas Measurement Challenges

- Target List
 - ▷ Which PFAS have VI potential?
- Risk-based screening level
 - ▷ What reporting limits will be needed?
- Wide range of concentrations (targets & non-targets) possible in subsurface
 - ▷ How to manage sample volumes vs. overloading tubes?



PFAS in Air Method Goals

- ▷ Target wide range of PFAS classes
 - Perfluorinated Alkyl Acids AND Precursors

- ▷ High Sensitivity
 - Looking for break-down products at low concentrations
 - Detection Limits in the ng / m³ (low ppt V/V) range

- ▷ Accommodate 24 hour TWA measurements
 - > 50 Liters air sampled, assuming a low flow pump at 25 to 50 ml/min

The end goal: a completely developed TD GC-MS method for Indoor Air that has the best sorbents, column, and MS detection for sensitivity, TWA measurements, and overall strong analytical performance.

PFAS Compounds in Indoor Air: Which?

- ▷ Volatile/Semivolatile Neutral PFAS (four)
 - Fluorotelomer alcohols (FTOHs): 8:2 FTOH
 - Fluorotelomer acrylates (FTACs): 8:2 FTAC
 - Perfluorooctane sulfonamides (FOSAs) : MeFOSA, EtFOSA
- ▷ Ionic PFAS (vapor, particulate-associated; eleven)
 - Perfluoroalkyl carboxylic acids (PFCAs)
 - ▷ Short Chain (Perfluorobutanoic acid: PFBA = C4, up to C7)
 - ▷ Long Chain (Perfluorooctanoic acid: PFOA = C8 PFCA, up to C14)
 - Perfluoroalkane sulfonates (PFASs)
 - ▷ Perfluorooctane sulfonate (PFOS)
 - ▷ Not amenable to GCMS

Why Thermal Desorption GCMS for Indoor Air?

▶ Advantages

- Concentration! 100 L or more air reduced to a single GC run
- Access to *small/volatile PF degradants* hard to see by LC-MS
- Wide coverage of VVOC's to SVOC's (neutral AND ionic PFAS)
- Low flow pumping = long sampling time = large volume TWA sampling

Why Thermal Desorption GCMS for Indoor Air?

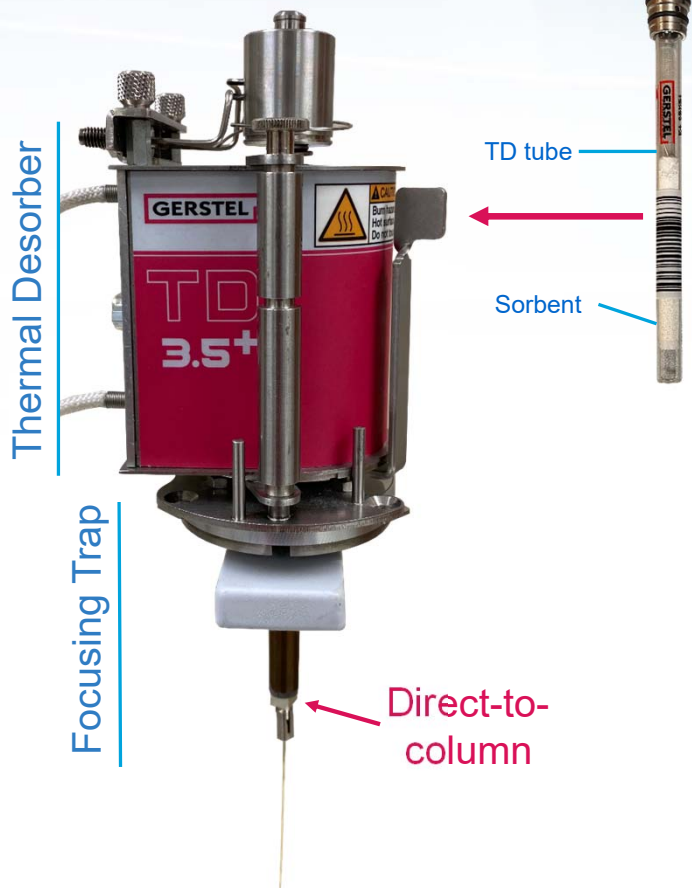
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▷ Risks

- Difficult or not possible for the most volatile (e.g., CF_4 , C_2F_6 , ...)
- Large volumes = potentially large water load for GC-MS
- Large volumes = potentially overload, carryover, system clean-out
- Can't do Sulfonates

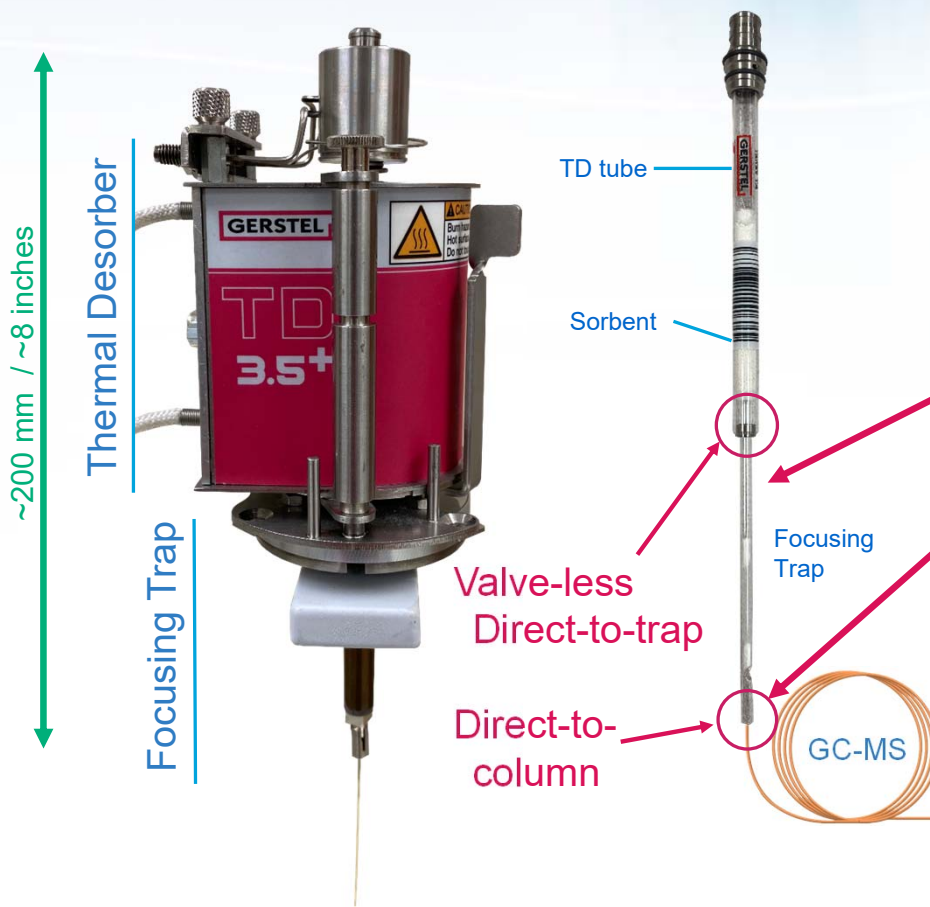
How does Thermal Desorption Work?



Two Stage Thermal Desorption:

- Sample is drawn onto a tube containing sorbents
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- Tube is placed into the thermal desorber, leak-checked, and heat & flow applied (split or split-less)
- Analytes flow directly to a trap where they are focused
- Trap is then heated rapidly with flow, analytes pass directly onto the head of the column (split or split-less)
- Always true, but not seen as important (until lately...): *Teflon Free Sample Pathway; no gain or loss of perfluorinated analytes*

How to Build a TD-GCMS Method in Three “Easy” Steps

- ▶ Choose a Sorbent for Sampling, Optimize Parameters
 - Optimize compound retention, maintain desorption efficiency, and manage water
 - Determine sampling parameters: flow rates, max sampling volume
- ▶ Choose a GC Column, Optimize GC Parameters
 - Simulated target mix of PFAS classes
 - Build a GC method around column
- ▶ Choose a Mass Spectrometer
 - Single Quad Synchronous SIM/SCAN
 - Tandem MS/MS
 - Build an MS method around the MS



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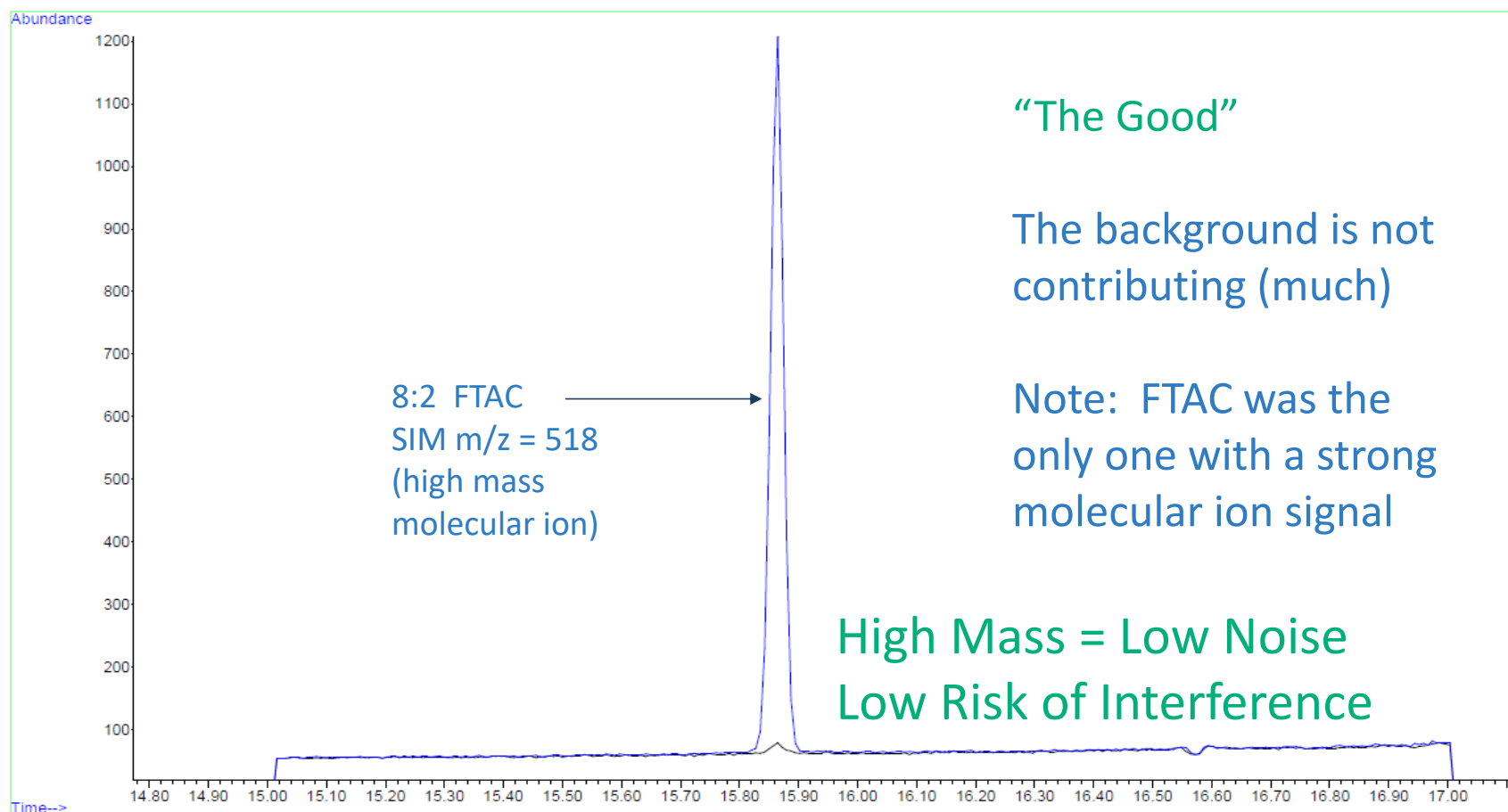
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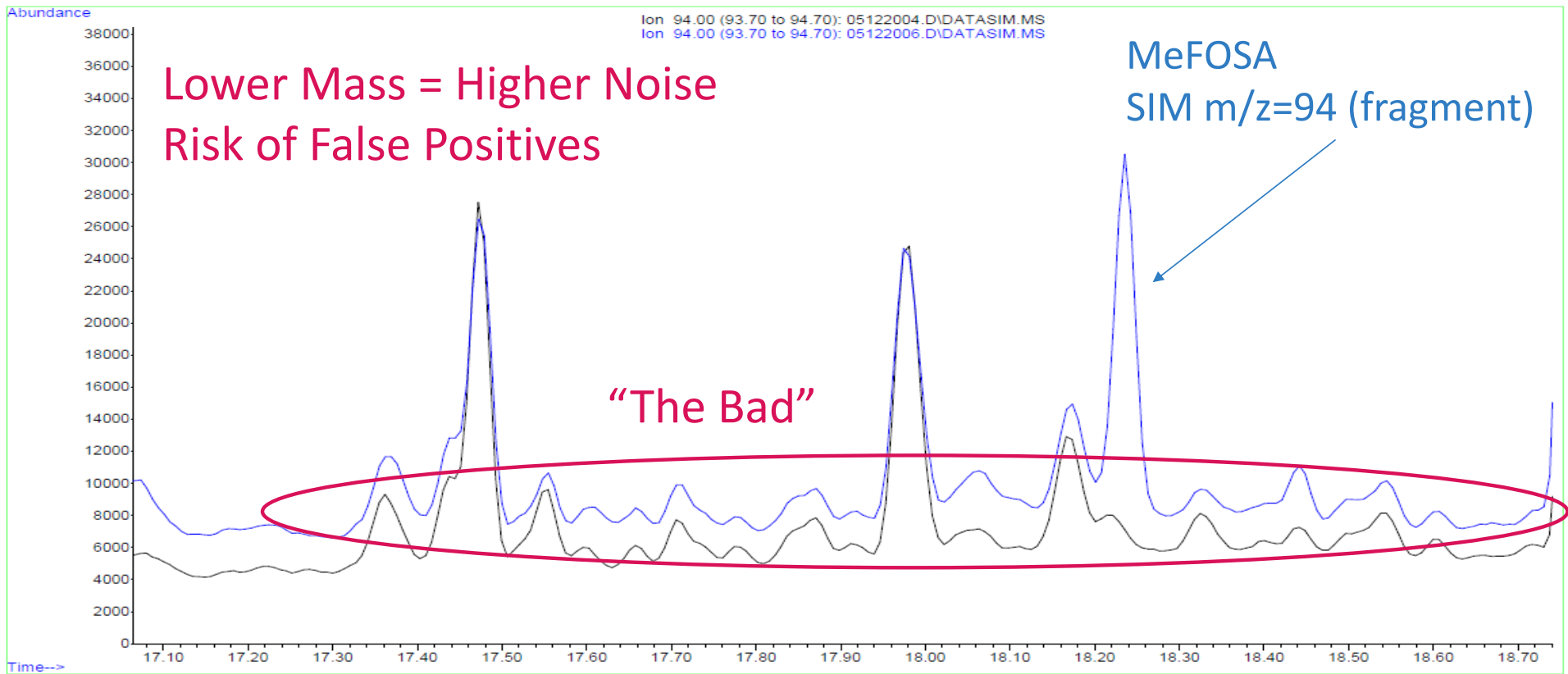
Why Tandem MS? Issues w SIM on 'Real Samples'

Office Air: 57.6 Liters of Air Sampled

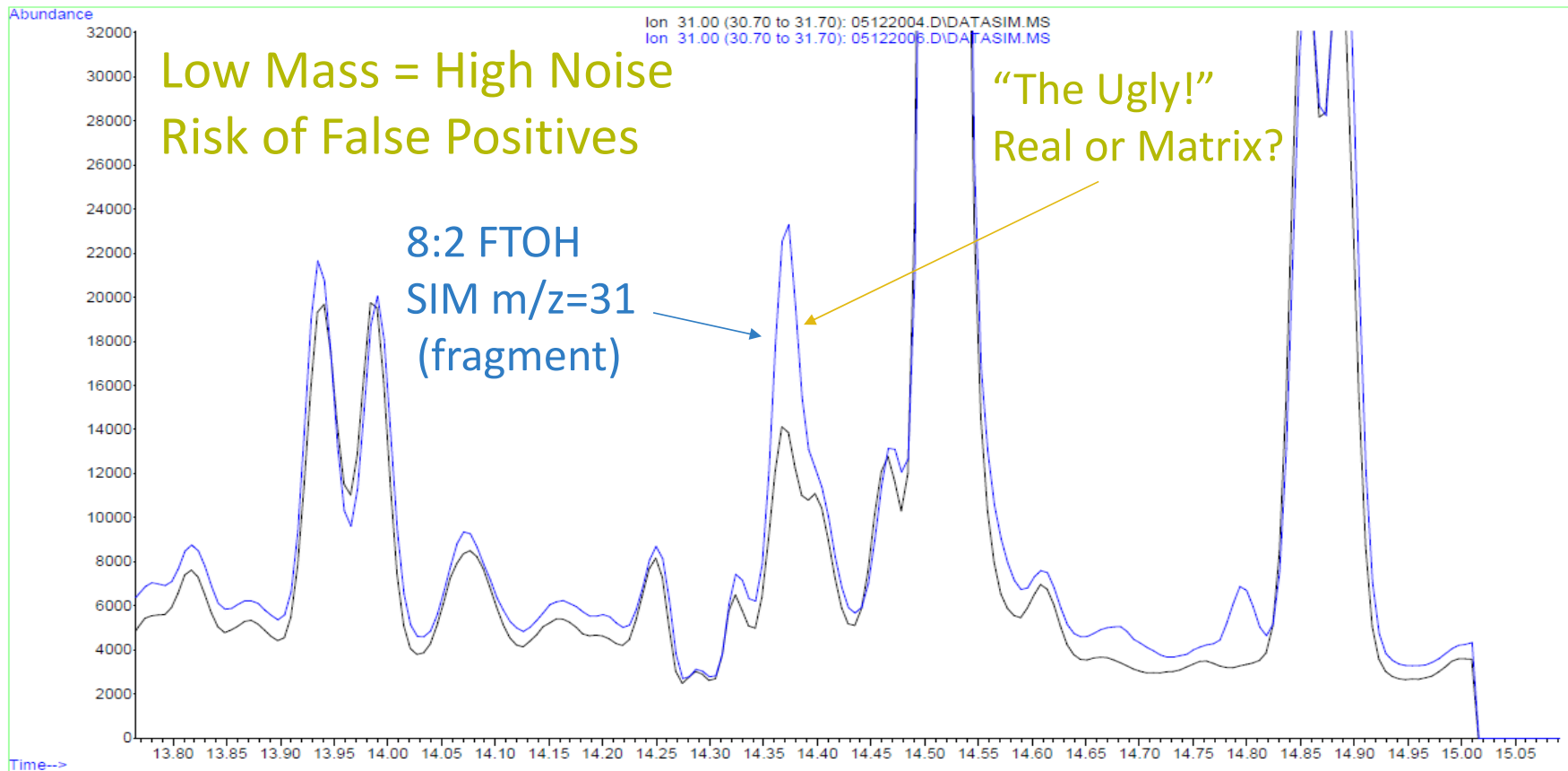
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MeFOSA: Spiked Tube (Blue) vs. Un-spiked Tube Black (both 57.6 L sampled)



8:2 FTOH: Spiked Tube (Blue) vs. Un-spiked Tube Black (both 57.6 L sampled)



Sorbent Selection

▷ Literature Review - Eurofins

- Researchers evaluated Tenax TA and Tenax/Carbograph 1TD (TC1) tubes
 - ▷ Cited TC1 Breakthrough volumes > 50L
 - ▷ Target list generally limited to neutral precursors
- PFCA's not included in previous works
 - ▷ Short chain PFCA's may require specialized sorbent configuration

▷ Choose Tubes, Determine Performance

- Tubes provided by CAMSCO
- Tenax TA / Carbograph 1TD (TC1) were chosen as the starting point
- After method development, a custom "PFCA Tube" was created for this work



Thermal Desorption Analysis Conditions



GERSTEL TD 3.5+ with Autosampler
Agilent 8890 / 7010B Triple
Quadrupole GC-MS/MS

Thermal Desorption (3.5+)

Pneumatics mode:	splitless
Sample mode:	remove tube – no standby cooling
Temperature:	40°C; ramp 400°C/min; 300°C (3.0 min)
Transfer Heater temp.:	300°C
Dry Purge:	Not Used (best for low boilers)

Focusing Trap

Carrier gas:	helium
Pneumatics mode:	solvent venting
Vent flow:	50 ml/min
Vent pressure:	16.6 psi until 0.00 min
Split flow:	10 ml/min @ 0.01 min
Trap type:	quartz wool
Temperature:	-120°C (0.0 min); 12°C/sec; 275°C (5 min)

Quartz wool at -120 °C is non-selective; saves method development time, and is best for non-targeted work ('everything trap')

Sorbent based trapping at ambient (cryogen free) temperatures is also possible for targeted analysis (PFAS included) when trap is 'matched' to targets

GC/MS Analysis Conditions



GERSTEL TD 3.5+ with Autosampler
Agilent 8890 / 7010B Triple
Quadrupole GC-MS/MS

Gas Chromatograph

Agilent 8890

Column: Rxi-624Sil MS, 60m x 0.25 mm ID x 1.4 μ m d_f

Mode: Constant Flow: 1 mL/min

Temp.: 40°C (3 min), 15°C/min; 260°C (6 min)

Triple Quadrupole Mass Spectrometer

Agilent 7010B HES source (GERSTEL – Baltimore MD) or
Agilent 7000D Inert Plus source (Eurofins – Folsom CA)

EI mode, both SIM and MRM modes used

Transfer line temp. 260°C

Source temp. 230°C

Quad temp. 150°C

Transitions for Selected PFAS by GC-MS/MS

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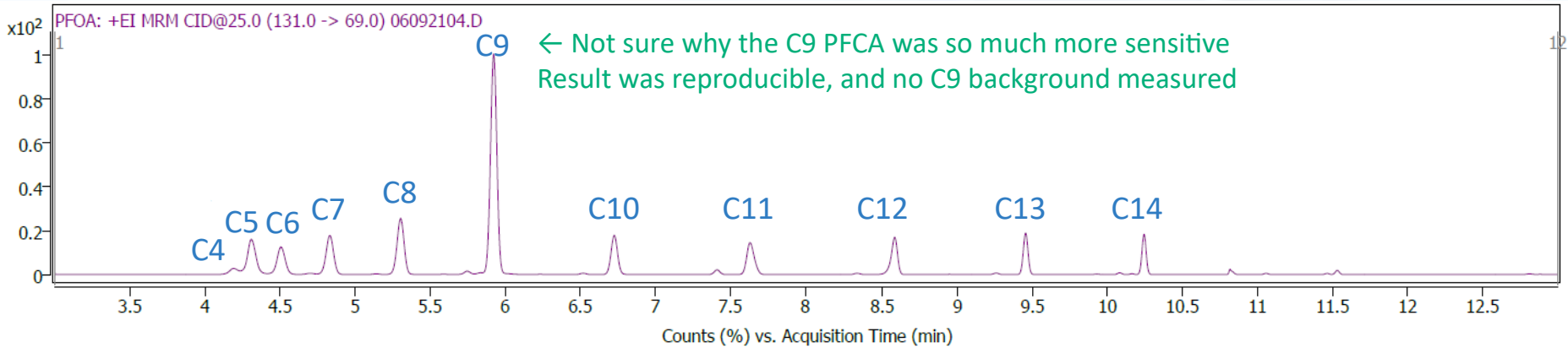
Compound	Precursor	Product
C4 PFCA	131	69
C5 PFCA	131	69
C6 PFCA	131	69
C7 PFCA	131	69
C8 PFCA (PFOA)	131	69
C9 PFCA	131	69
C10 PFCA	131	69
C11 PFCA	131	69
C12 PFCA	131	69
C13 PFCA	131	69
C14 PFCA	131	69
8:2 FTOH	95	69
10:2 FTAC	518	99
MeFOSA	SIM 94	-
EtFOSA	SIM 94	-

- ▷ None of the acids had molecular ions
- ▷ Not surprising – many PFAS molecules don't
- ▷ Consequently, had to use 131 → 69 transition for all the acids
- ▷ Not ideal (e.g., not unique to each species) but still removed noise successfully
- ▷ MRM isn't always the best; The FOSA's have strong SIM signal that seems to be relatively low noise (for SIM)
- ▷ Internal Standards were also used, but were different between the two labs (Eurofins and GERSTEL) and are not listed here

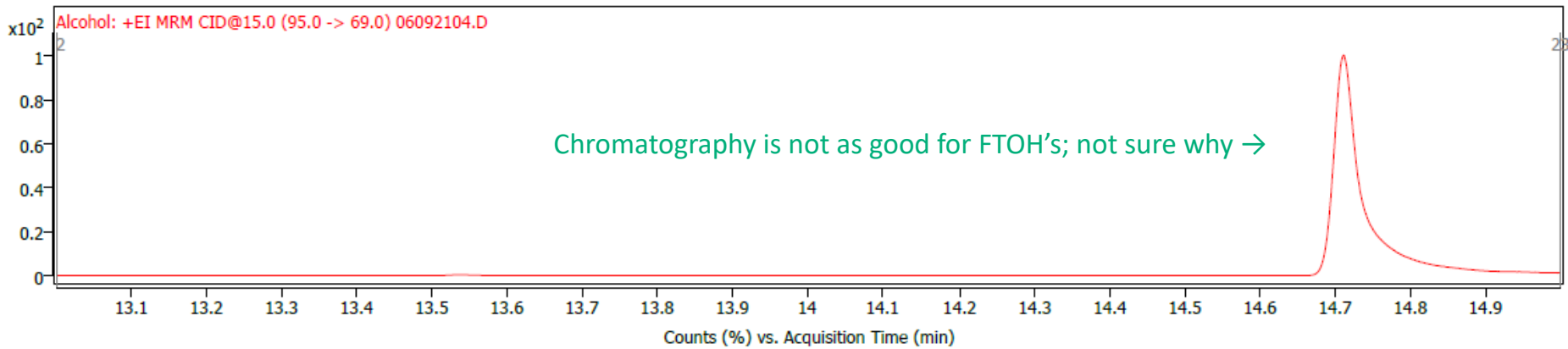
Example Chromatograms



PFCA's



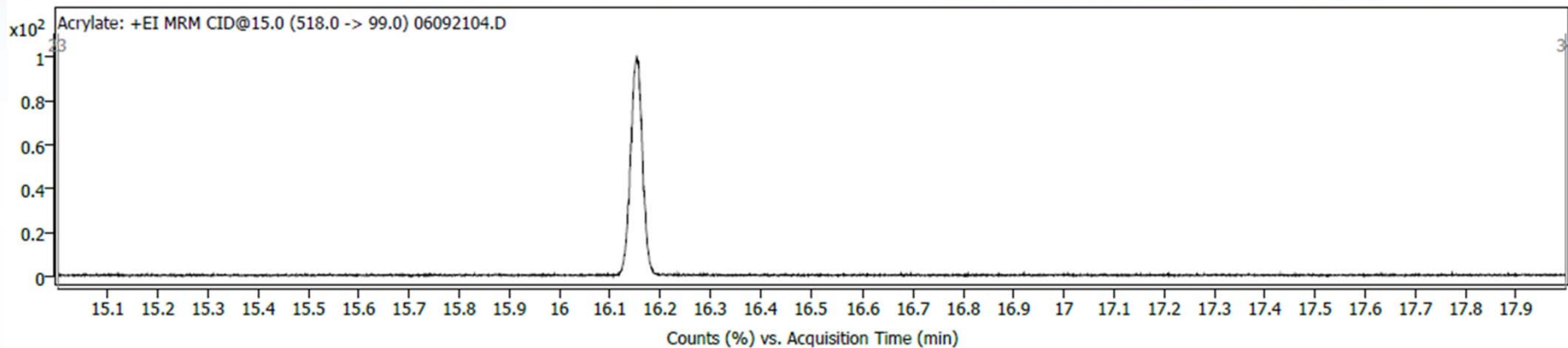
8:2 FTOH



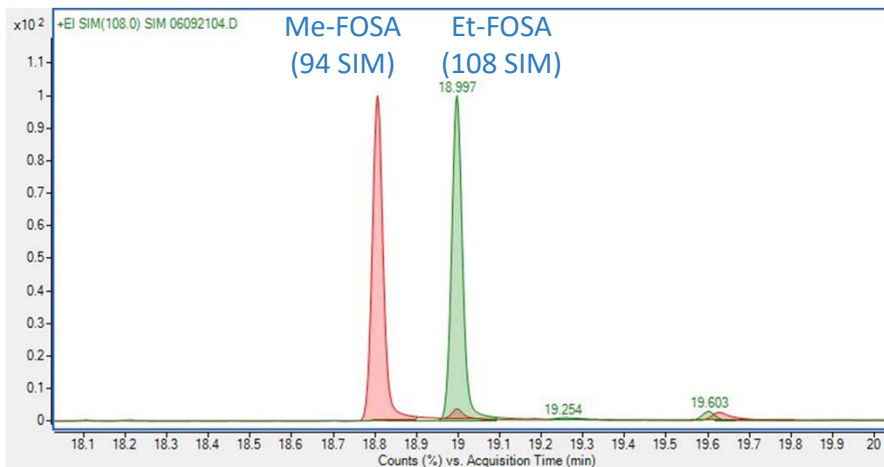
Example Chromatograms

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8:2 FTAC



FOSA's



- ▷ Other than the FTOH's, overall good chromatography and a clean baseline
- ▷ Due to perfluorination, these large molecules behave like low MW VOC molecules (e.g., like hexane, etc.)
- ▷ "Unexpected Volatility" is possible

Instrument Calibration – Nanograms on Tube



Compound	0.050	0.10	0.20	0.40	1.0	2.0	5.0	Avg RRF	%RSD
C4 PFCA	2.8772	2.2921	2.0194	2.1319	1.7526	1.9321	2.0950	2.1572	16.7
C5 PFCA	1.1390	1.0744	1.0734	1.1855	0.9366	1.0332	1.1177	1.0800	7.5
C6 PFCA	0.4569	0.5136	0.4782	0.4345	0.3852	0.4158	0.4579	0.4489	9.3
C7 PFCA	1.6250	1.7614	1.8320	1.4994	1.4313	1.5030	1.6528	1.6150	9.1
C8 PFCA	2.4755	2.6920	2.4202	2.5319	1.9345	1.9227	1.8475	2.2606	15.4
8:2 FTOH	0.0282	0.0364	0.0277	0.0293	0.0226	0.0224	0.0210	0.0268	19.9
MeFOSA		0.2036	0.2298	0.2551	0.1900	0.1913	0.1784	0.2081	13.9
EtFOSA	0.5239	0.6944	0.7114	0.7061	0.5396	0.5511	0.5130	0.6056	15.3

- ▷ Internal Standards were used, so relative response factors (RRF's) evaluated
- ▷ All meet < 30% requirement of EPA TO-17
- ▷ Linearity for PFAS is generally good (previous talk w SIM data had great correlation coefficients...)

The use of RRF's assumes "linear through zero" – *that the blank does not contribute significantly*

Instrument Calibration – Detection Limits



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- ▷ A formal MDL study is underway using established US EPA protocols
- ▷ Except for MeFOSA, 50 pg was the low standard on the curve, so LOD is < 50 pg
- ▷ For the rest of the species, based on signal strength alone an 0.005 ng (5 pg) standard would be easily visible, so MDL's likely less than 0.005 ng, *assuming no blank contribution*
- ▷ Consequently, for most species this will equate to sub-part-per-trillion V/V detection limits over large volumes of air sampled

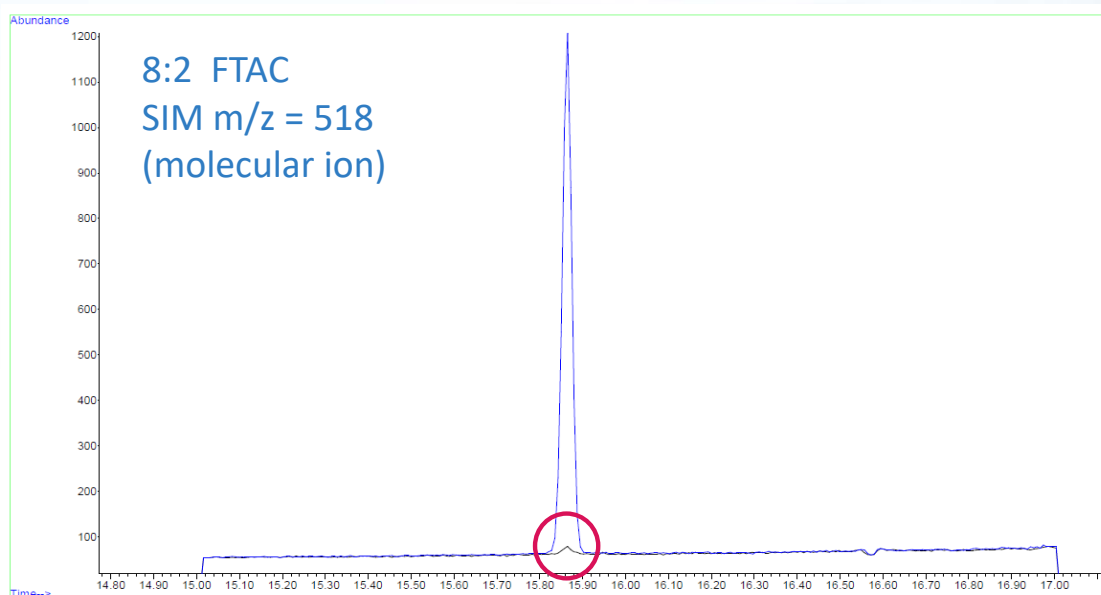
GC-MS/MS Performance “In Matrix”

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- ▶ Data in evaluation as of the date of this presentation
- ▶ Will follow up in October-November with an update via webinar
- ▶ The work is not complete until ‘real’ samples have been run, *but we have learned something important, already*



The not-so-surprising surprise



- ▷ For some species, blank-values are significantly non-zero
- ▷ Happens when the S/N ratio is high enough to expose it (such as here, where the 518 signal is 'clean' yet the blank was non-zero).
- ▷ Consequently, also happens more in MRM mode, and with more volatile or common PFAS
- ▷ Was not obvious until the MRM method was more fully developed

Based on calibration data to this point, for some species there is a significant blank problem due to the presence of PFAS in and around the lab. This was also seen in LC-MS methods.

This contamination means that *detection limits for PFAS are often blank-limited*.

The Limitations of SIM and MRM for PFAS in Air

- ▶ There is no doubt that, even for 'clean' samples like 57 liters of office air, that reliability and detectability can be improved using tandem mass spectrometry
- ▶ The use of Tandem MS in air samples further exposes the depth of the PFAS problem, and builds on what was learned in LC-MS methods
- ▶ Chemical Hygiene will be key: Teflon must be removed from the sample preparation and analysis processes (syringes without Teflon plungers, removal of Teflon in-line filters, etc.)

We Built a TD-GCMS Method in Three “Easy” Steps

▷ Chose a Sorbent for Sampling

- Optimized compound retention, maintained desorption efficiency, and managed water
- Sampling parameters: flow rates, high volume (57 L) TWA sampling

▷ Chose a GC Column that Fits the Range

- Column, Parameters suited for simulated target mix of PFAS classes

▷ Chose a Mass Spectrometer

- Single Quad Synchronous SIM/SCAN is ok, but
- **Tandem MS/MS is better for large sample volumes due to ‘high matrix’**



The use of MS/MS will greatly reduce the background for some of these analytes, although for some species SIM should work well too, if the molecular ion is strong

Indoor Air PFAS Method Goals – ACHIEVED SO FAR

- ✓ Target wide range of PFAS classes
 - Perfluorinated alkyl acids, precursors using perfluorochemical analysis tubes
- ✓ High Sensitivity
 - Can 'see' at or below $\sim 10 \text{ ng / m}^3$
 - Detection limits are often background limited
- ✓ Accommodate 24 hour TWA measurements
 - 57.6 Liters and a low flow pump at 40 ml/min
 - Large volumes, small masses = more chemical noise = MS/MS best choice
 - Vapor Intrusion samples should be even worse in terms of matrix; MS/MS will still be the best choice

The Last Dab

- ▶ Performance in matrix is under evaluation – stay tuned!
- ▶ For more details, please contact Heidi Hayes directly
- ▶ The instrumentation and methodology are now in place in contract and government labs; looking forward to more researcher feedback

By the next NEMC, this method should be complete. It's taken longer than expected, unfortunately for reasons that had also been seen in LC-MS methods.

We are VERY grateful for the help from

- ▶ Heidi Hayes and Diane Benton, Eurofins Air Toxics
 - Vision, Expertise, PFAS Standards, Method Development
- ▶ Jesse Miller, CAMSCO
 - Tubes and Advice
- ▶ Tarun Anumol, Tim Conjelko, and Matt Curtis, Agilent Technologies
 - Encouragement, QQQ Support
- ▶ Colleagues at the US EPA
 - What to look for, where, and why
- ▶ All of You!