Analysis of PFAS Compounds in Air using Solid Sorbent Tubes with Thermal Desorption Gas Chromatography Mass Spectrometry

Challenges and Solutions for Indoor Air Monitoring

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Progression of “PFAS in Air” Development

Stack Emissions	Ambient Monitoring
• Sampling trains • Extraction • LC/MS/MS • LC/MS/MS less effective for volatile neutrals	• High Volume • PUF/XAD/Filter • LC/MS/MS • LC/MS/MS less effective for volatile neutrals

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• Sampling trains • Extraction • LC/MS/MS • LC/MS/MS less effective for volatile neutrals	• High Volume • PUF/XAD/Filter • LC/MS/MS • LC/MS/MS less effective for volatile neutrals	• Volume? • Sorbent? • Analysis?

Indoor Air PFAS 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 / m^3 (low ppt V/V) range
- Accommodate 24 hour TWA measurements
  - > 50 Liters, assuming a low flow pump at 25 to 50 ml/min

The end goal: a completely developed TD-GCMS 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): 8:2FTAC
  - 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 (PFSAs)~~
    - ~~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 LCMS
  - Wide coverage of VVOC's to SVOC's (neutral AND ionic PFAS)
  - Low flow pumping = long sampling time = large volume TWA sampling

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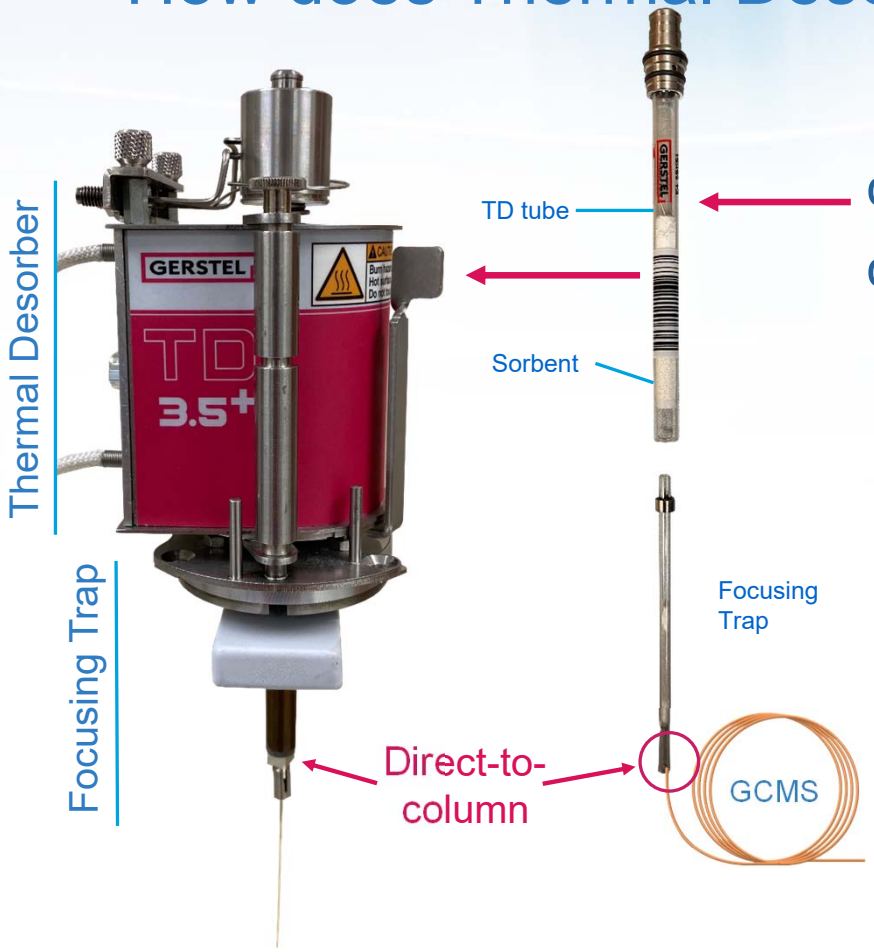
- Risks
  - Difficult or not possible for the most volatile (e.g., CF_4, C_2F_6, …)
  - Large volumes = potentially large water load for GCMS
  - Large volumes = potentially overload, carryover, system clean-out
  - Can't do Sulfonates

How does Thermal Desorption Work?



Two Stage Thermal Desorption:

- Sample is drawn onto a tube containing sorbents
- Tube is placed into the thermal desorber, leak-checked, and heat & flow applied (split or split-less)

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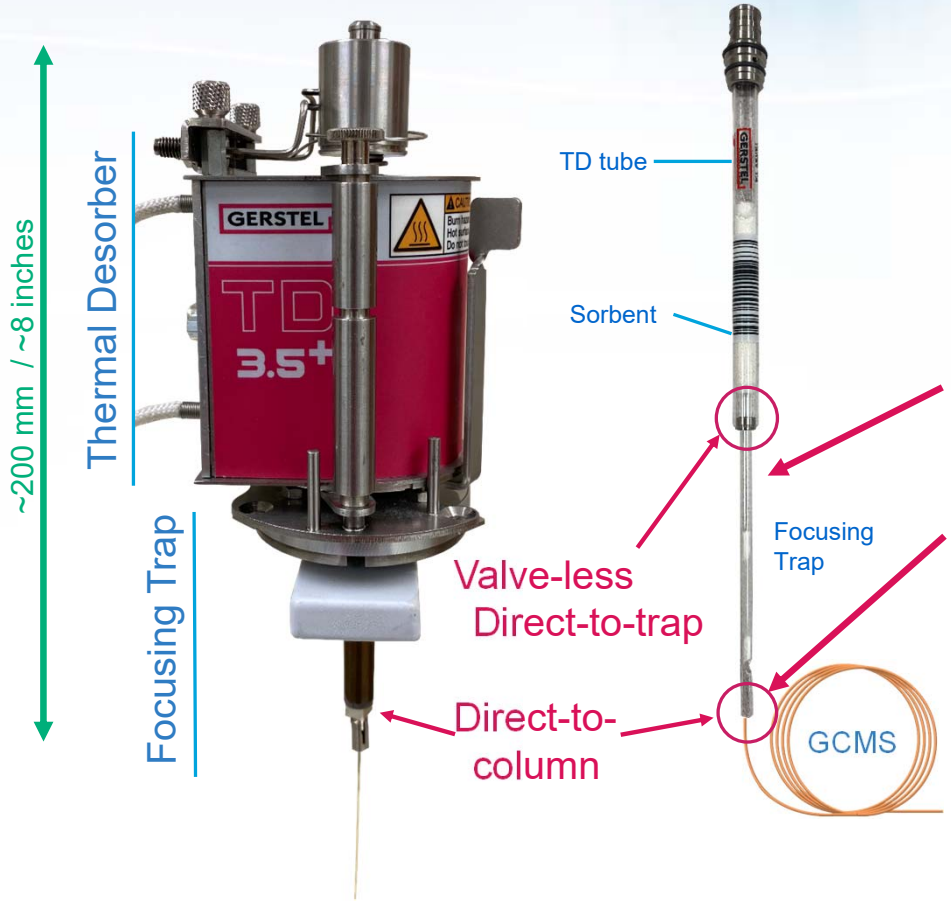

Two Stage Thermal Desorption:

- Sample is drawn onto a tube containing sorbents
- 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 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 compound retention, maintain desorption efficiency, and manage water
  - Determine sampling parameters: flow rates, max sampling volume
- Choose a GC Column that Fits the Range
  - Simulated target mix of PFAS classes
  - Build a GC method around column
- Choose a Mass Spectrometer
  - Single Quad Synchronous SIM/SCAN
  - High res, Tandem MS/MS?
  - Build an MS method around the MS

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
  - They were not the final choice…

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Choosing the Column and GC Parameters

- Method Development - GERSTEL
- Use “starting point” tubes suggested by Eurofins, CAMSCO
  - Start with 30 m DB-5, Single Quad MS detection
  - What are the best column, GC, and MS parameters?
- Once the GC side of GCMS is nailed down, go back to the TD
  - How much can you sample before breaking through?
  - How long can it last in storage?

Thermal Desorption Analysis Conditions

GERSTEL TD 3.5+ with A/S
Agilent 8890 / 5977B MSD

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)

CIS 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

GCMS Analysis Conditions

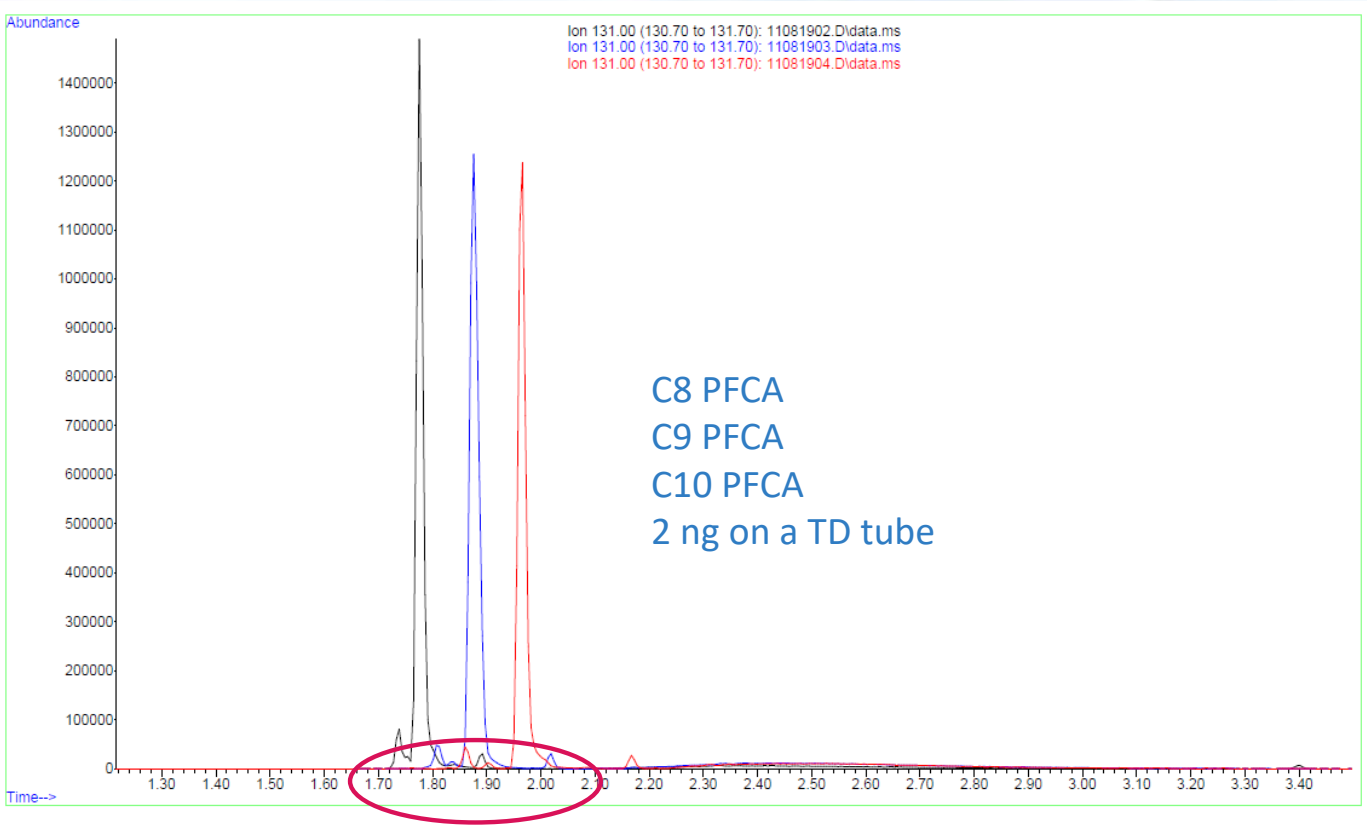
GERSTEL TD 3.5+ with A/S
Agilent 8890 / 5977B MSD

Gas Chromatograph
Agilent 8890
Column: DB-5 (starting point)
Mode: Constant Flow: 1 mL/min
Temp.: 40°C (3 min), 15°C/min; 260°C (2.33 min) (starting point)

Mass Selective Detector
Agilent 5977B
EI, SIM/Scan mode

Transfer line temp.	260°C
Source temp.	230°C
Quad temp.	150°C

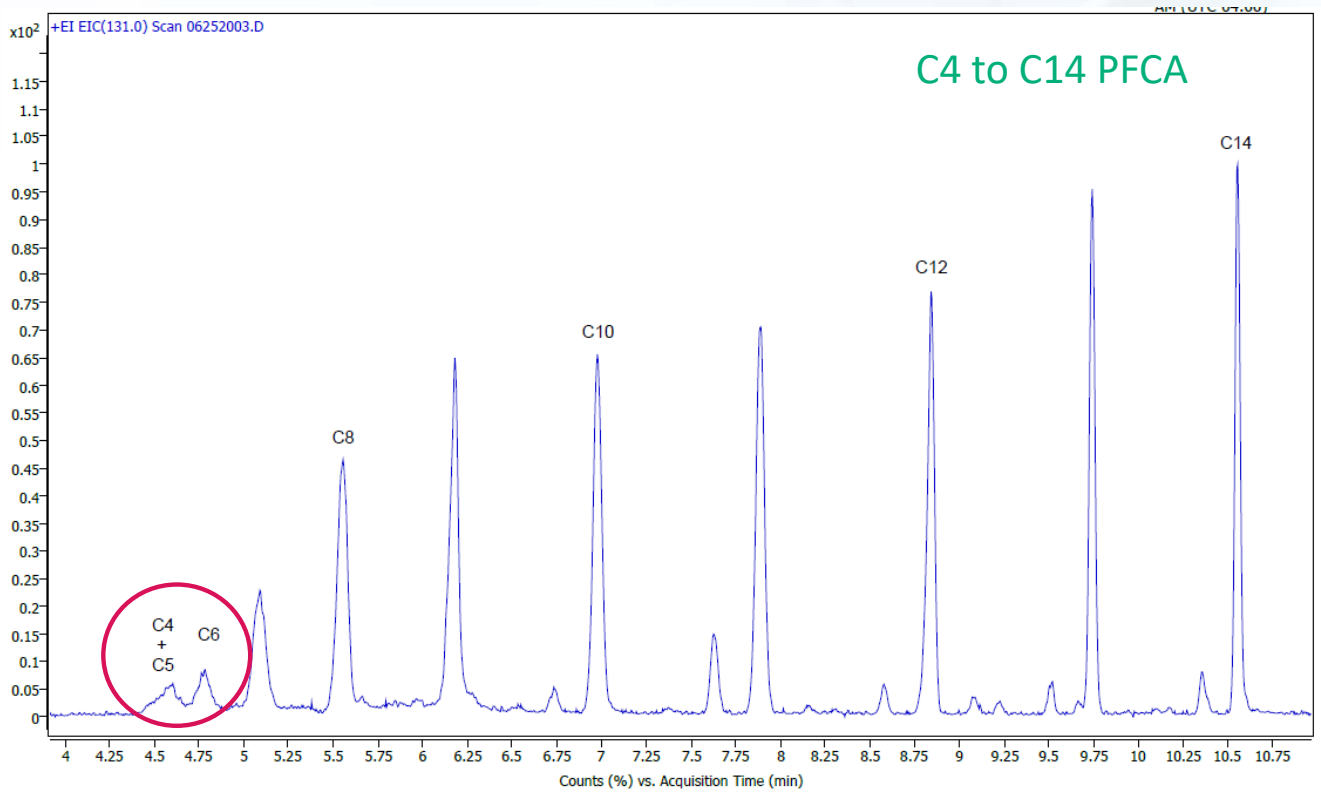
Chromatography – DB-5MS UI; 30 m x 0.25 mm x 0.25 µm



C8 PFCA
C9 PFCA
C10 PFCA
2 ng on a TD tube

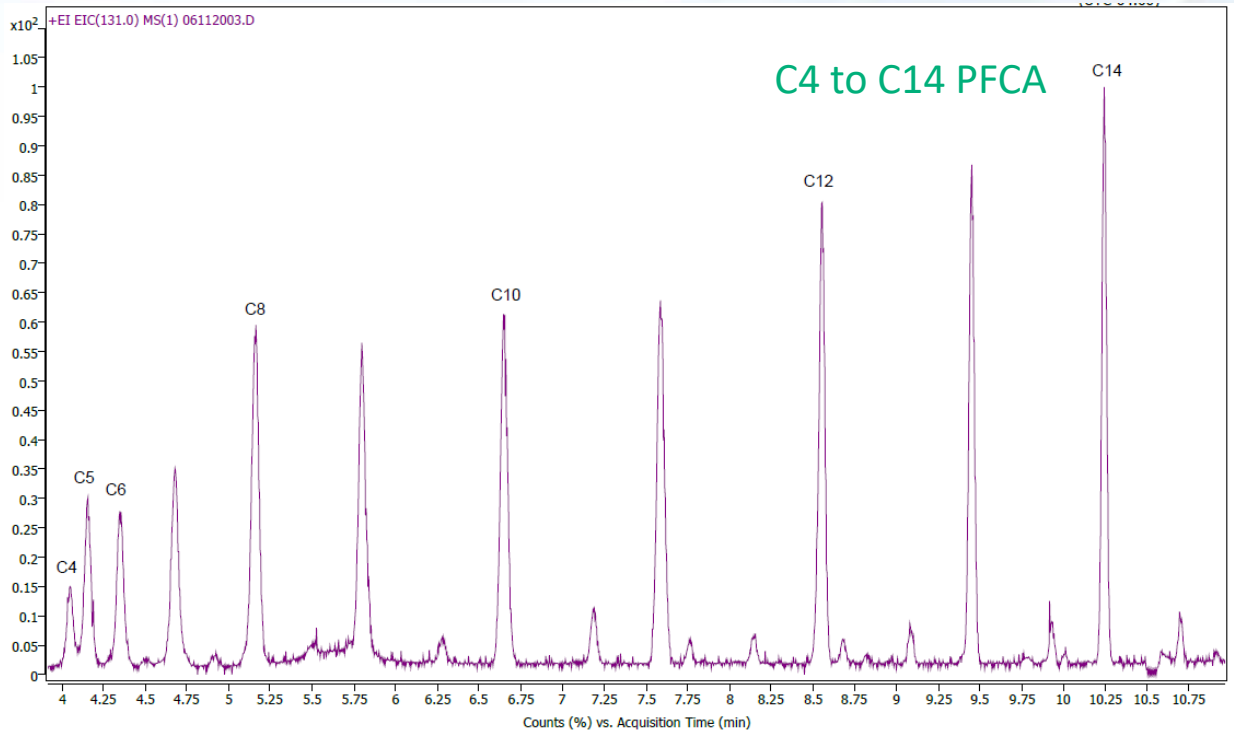
Retention Times Too Short! Need a Stronger Column..

Chromatography – “624 Type”; 60 m x 0.25 mm x 1.40 µm
Upper temperature limit: 300 °C



Better, but poor resolution on the lightest acids

Chromatography – DB-624 UI; 60 m x 0.25 mm x 1.40 µm
Upper temperature limit: 260 °C



We have a winner! Not all “624” columns are the same

Now “match the TD to the column…”

And now back to the TD: Sorbent Optimization

- Tube 1 (Glass) Tenax TA / Carbograph 1TD = starting point
- Tube 2 (SS) Tenax TA / Carbograph 1TD

Then….

- Tube 3 (Glass)
- Tube 4 (Glass)
- Tube 5 (SS)

Overall we evaluated 5 tube types based on recoveries at 20 mL/min for 24 hours (28.8 L total volume), without dry purging.

Tubes 4 and 5 are new Perfluorocarbon Analysis Tubes from CAMSCO.

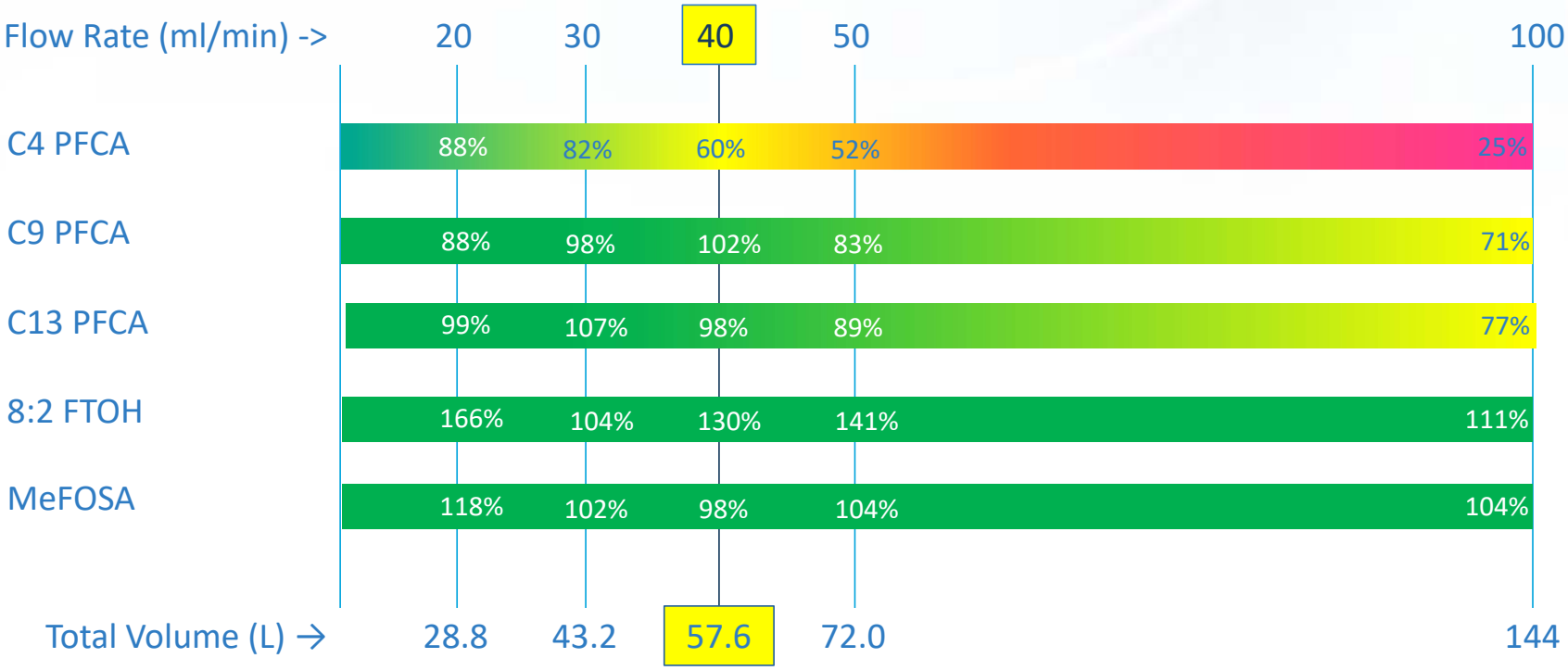
Based on those results, the best performing types (4 & 5) were chosen, both in glass and SS tube formats.

Sampling Volume Determinations Perfluorochemical Analysis Tube

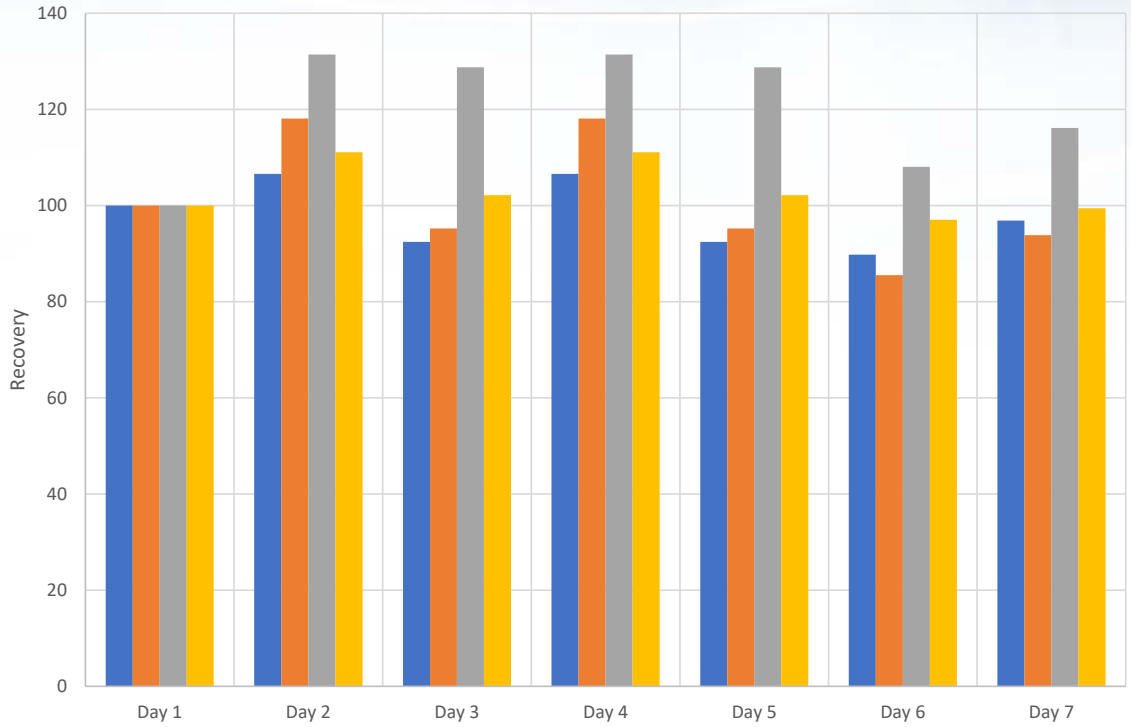
Flow Rate (mL/min)	Total Volume Sampled (L)
20	28.8
30	43.2
40	57.6
50	72.0
100	144

- Spike with 2 µL of Standard in methanol
- Blow onto bed (50 mL/min for 3 min-Dry N_2)
- Sample 24 hours by pulling air through the tube
- Use different flow rates (= different volumes)
- Compare to tube that was spiked, not sampled (no air pulled through)

Recoveries vs. Flow Rate / Volume (24 hour)
40 mL / min = 57.6 L is best compromise



Hold-Time Study: **Neutrals**



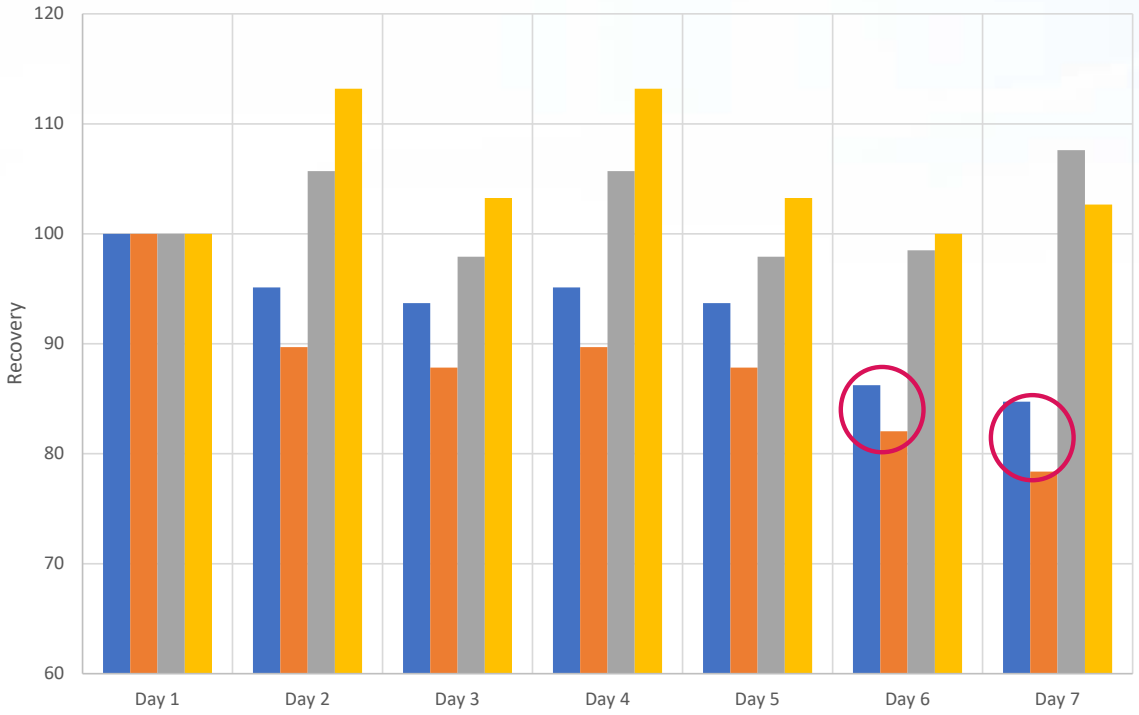
Blue = 8:2 FTOH
Orange = 10:2 FTAC
Gray = MeFOSA
Yellow = EtFOSA

- Spiked Tubes Analyzed over 7 Days
- Stored At Room Temperature with Swagelok sealed endcaps
- Analyzed in duplicate each day

Note that these “heavier” species are fairly stable over seven days

The >100% recoveries are not unheard-of in analytical methods, but need to be studied further, in more detail

Hold-Time Study: **Acids**



Blue = C4 PFCA
Orange C5 PFCA
Gray = C8 PFCA
Yellow = C14 PFCA

The lighter species drop below 90% after five days.

Based on this, the tubes need to be analyzed within five days of sampling.

Refrigeration could also extend storage time.

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More on the MS topic later….for now, let's use a single quad MSD and "take the data"!

Calibration, Precision, MDL's, …
Take "real" data in an indoor environment

Calibration

Compound	0.08 ng	0.16 ng	0.40 ng	0.80 ng	1.2 ng	r^2
C4 PFCA	6423	11004	32550.00	76105	103649	0.9934
C5 PFCA	14147	26469	78189.00	179245	257493	0.9977
C6 PFCA	11303	18366	50144.00	113513	166517	0.9981
C7 PFCA	14069	23493	67279.00	155591	243682	0.9973
C8 PFCA (PFOA)	19198	32284	93101.00	208033	327833	0.9987
C9 PFCA	28471	48435	127187.00	275266	428227	0.9984
C10 PFCA	28178	49074	136534.00	293984	453288	0.9990
C11 PFCA	30935	55415	155721.00	336029	504189	0.9994
C12 PFCA	33065	60013	164484.00	360086	539375	0.9992
C13 PFCA	34188	61589	165476.00	357783	542069	0.9993
C14 PFCA	36497	64352	166521.00	361909	544487	0.9992
	0.40 ng	0.80 ng	2.0 ng	4.0 ng	6.0 ng	r^2
8:2 FTOH	103226	179513	420061.00	877877	1332102	0.9993
10:2 FTAC	7643	12263	30591.00	63789	90918	0.9986
MeFOSA	187350	351209	868603.00	1791395	2549414	0.9987
EtFOSA	127429	231463	588043.00	1208013	1730188	0.9989

- The focus for indoor air was low concentrations, so we kept to the low end
- Calibration was performed by spiking tubes and removing methanol with dry N_2 (50 mL/min for three minutes)
- SIM/Scan was used, 3- or 4-ion SIM
- Note that for PFCA's, the signal increases with carbon chain length

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- Linearity was good across the range
- Despite the low concentrations (80 pg in some cases) there was still adequate signal in SIM mode on single quad MSD
- IDL's should be in the low pg range

“Real Data”: Simulated Indoor Air Analysis

Office Environment, steady temp, RH
Perfluorochemical Analysis Tubes
40 mL/min flow, 24 hours
57.6 Liters samples
Triplicate Spiked Tubes + Unspiked Tube

Assume no latent concentrations in room
Spike tubes to simulate exposure
Run un-spiked tubes as well

SKC AirChek Touch (5-5000 mL/min)
SKC Pocket Pump Touch (20-500 mL/min)
SKC Chek-Mate (20-500 mL/min)

NO TEFLON IN SAMPLING TRAIN
NO TEFLON IN SAMPLE PATHWAY

Spike Levels in Detail

Compound	MW	Mass on Tube (ng)	ng / m^3 (57.6 L sample)	ppt V/V
C4 PFCA	214	0.4	6.9	0.79
C5 PFCA	264	0.4	6.9	0.64
C6 PFCA	314	0.4	6.9	0.54
C7 PFCA	364	0.4	6.9	0.46
C8 PFCA	414	0.4	6.9	0.41
C9 PFCA	464	0.4	6.9	0.36
C10 PFCA	514	0.4	6.9	0.33
C11 PFCA	564	0.4	6.9	0.30
C12 PFCA	614	0.4	6.9	0.27
C13 PFCA	664	0.4	6.9	0.25
C14 PFCA	714	0.4	6.9	0.24
8:2 FTOH	464	2.0	35	1.84
10:2 FTAC	518	2.0	35	1.65
MeFOSA	513	2.0	35	1.67
EtFOSA	527	2.0	35	1.62

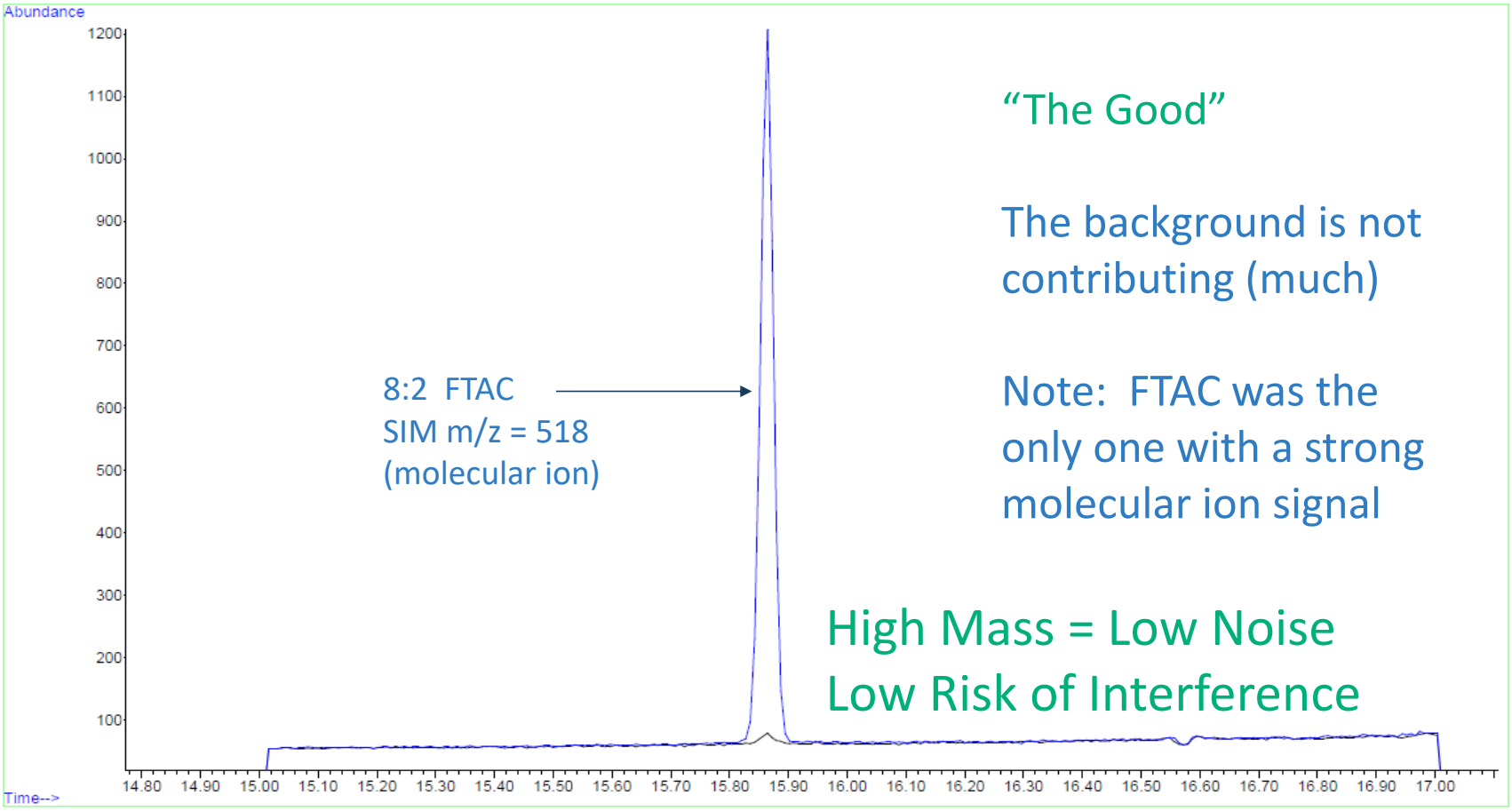
- Spikes were either 0.4 or 2.0 ng on tube
- Because 57.6 L of air was sampled in each tube, this is equivalent to an indoor air concentration of either 6.9 or 35 ng / m^3
- In terms of ppt V/V, this equates to single digit or less part-per-trillion air concentrations

Analysis Summary, "Office Air"

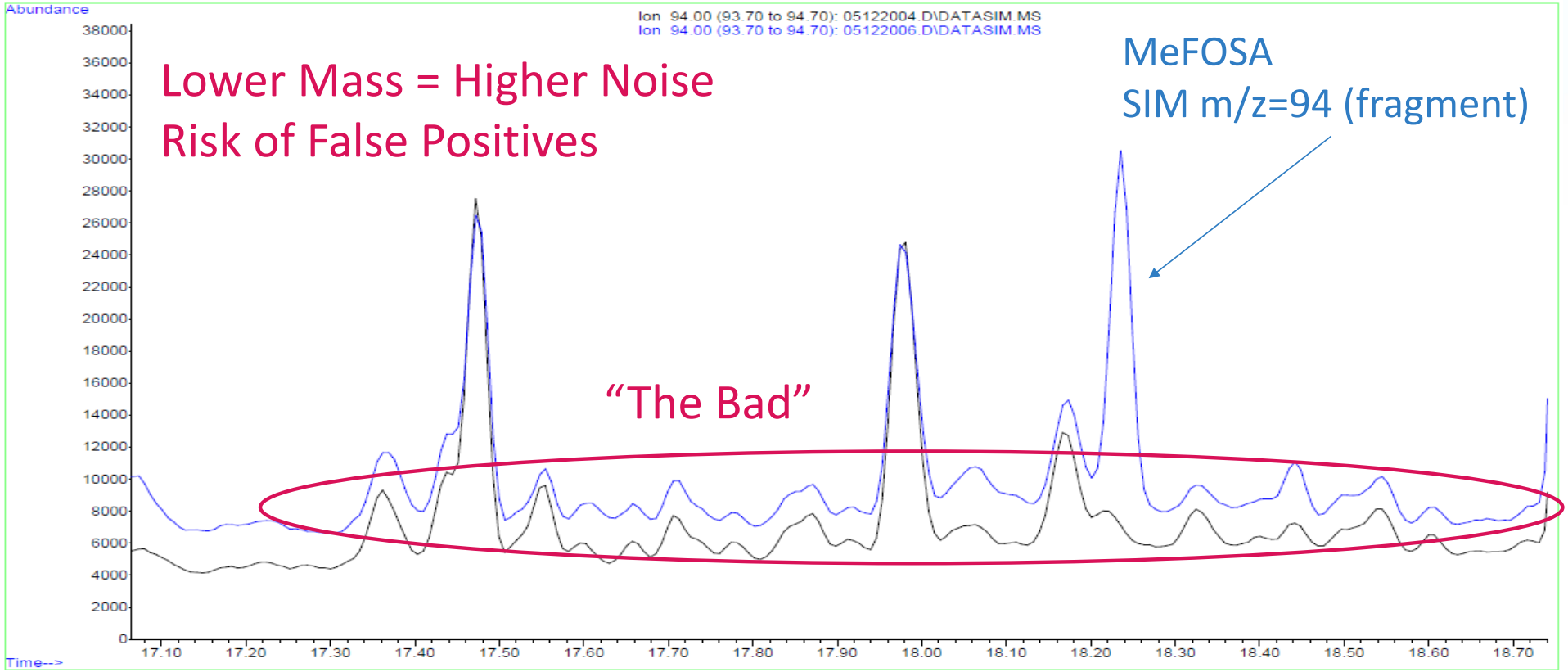
Compound	RT	Rep 1	Rep 2	Rep 3	Average Recovery	RSD
C4 PFCA	4.06	62	96	63	**74**	22
C5 PFCA	4.26	92	71	94	**86**	12
C6 PFCA	4.47	130	106	129	**122**	9
C7 PFCA	4.8	97	99	100	**99**	1
C8 PFCA	5.29	145	109	138	**131**	12
C9 PFCA	5.94	176	147	189	**171**	10
C10 PFCA	6.76	110	99	109	**106**	5
C11 PFCA	7.67	122	99	121	**114**	10
C12 PFCA	8.61	113	98	113	**108**	6
C13 PFCA	9.5	116	101	113	**110**	6
C14 PFCA	10.32	181	98	173	**151**	25
PF Octylethanol	14.45	134	144	133	**137**	4
PF Decylacrylate	15.95	187	120	189	**165**	19
N-Me PF octanesulfonamide	18.33	83	77	97	**86**	10
N-Et PF octanesulfonamide	18.56	99	92	108	**100**	6

- Recoveries on spiked tubes were generally good, with C4 PFCA a bit low (expected)
- The "average of the average recoveries" was 117%
- Precision is generally good as well (average 11%); replicate 2 is a bit lower than 1 and 3, so an ISTD may improve precision
- Recovery of the ionic PFCA's are overall very good and comparable to non-TD results
- Recovery of the four neutral PFAS species was generally better than what has been reported for non-TD results
- High recoveries (>125%) may indicate either presence of an analyte in the air sampled, change in instrument response (ISTD's were not used this round), or possibly matrix interference

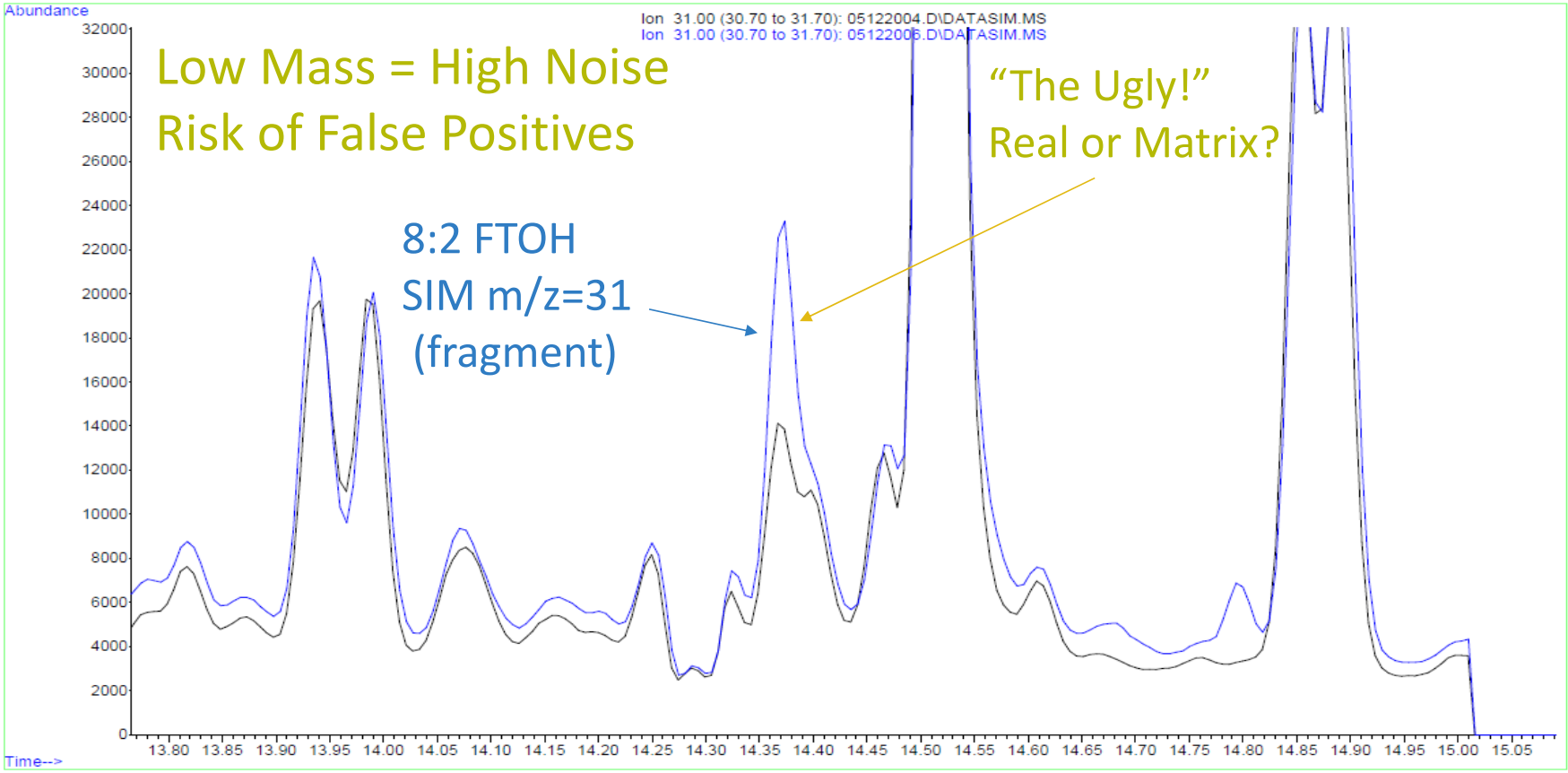
8:2 FTAC: Spiked Tube (Blue) vs. Unspiked Tube Black (both 57.6 L sampled)



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)



The Limitations of SIM for PFAS in Indoor Air

- The m/z 31 fragment was most abundant for 8:2 FTOH
- There are other ions, but not as large in abundance
- Although better than 31 m/z, the other ions are also ‘low’ in mass
- Alcohols never give molecular ions in EI-based MS
- Nearly all the PFAS families we looked at had ‘predominantly low mass ions’

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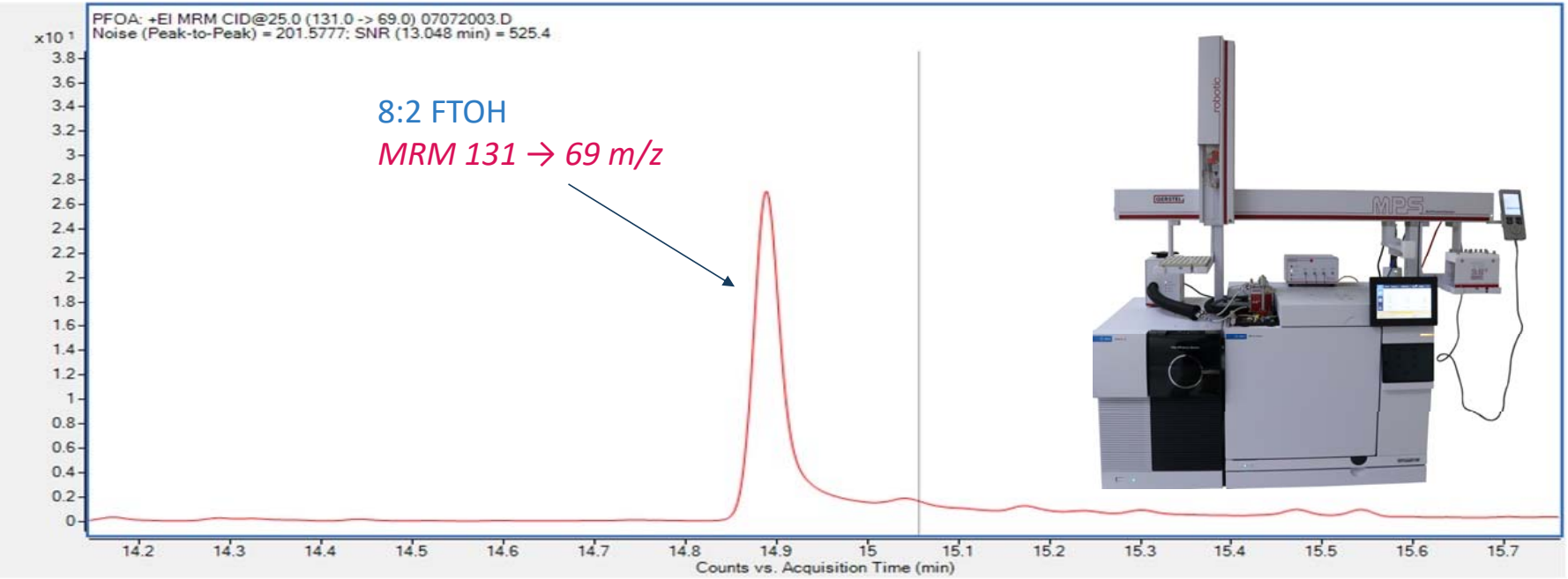
Add to that a near-continuum low-mass ion background from a large volume of air sampled (57 L) for Indoor Air, and you have a recipe for matrix interference.

Spoiler Alert #1: GC-MS/MS is better

Same 400 pg spike, now with MS/MS



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, and lower MDL's as well (Spoiler Alert #2: single digit ppq's in some cases)

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 ~10 ng / m^3
  - Formal MDL’s likely 10x less on MSD, 100x less QQQ
- ✓ 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 likely best choice

The “End of the Beginning”

- Sorbent choice has been worked out
- Sampling conditions have been optimized
- The column and GC method have been determined
- MS-SIM method in place (MS/MS coming soon)

The “roots” of an Indoor Air method for PFAS compounds are there

A lot more work needs to be done….

Next Steps

- Incorporate ISTD and surrogates
  - Bromofluorobenzene or d_5-Chlorobenzene as ISTD
  - ^{13}C labelled perfluorohexyl ethanol (6:2 FTOH) as field surrogate
- GC/QQQ Method Optimization
  - Finish off MRM optimization
  - Figures of Merit
- Method Validation
  - Effect of %RH, recoveries, etc
  - Distributed pair sampling
  - “Real” samples for precision, recovery, etc.
- Expand
  - More telomer alcohols, ultra-short chain acids, other species

Beyond Indoor Air – 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?
  - Spoiler Alert #3: we may have a partial solution…

We are VERY grateful for the help from

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