Analysis of PFAS Compounds in Indoor Air using Thermal Desorption GC-MS Part 3:

Improvements for High Volume Sampling and Preconcentration of Volatile PFAS Species

Kurt Thaxton, GERSTEL GmbH
John Stuff, and Jackie A. Whitecavage, GERSTEL Inc
Jesse Miller, CAMSCO

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The end, first.

A complete method for known and unknown PFAS species in indoor and other air has been developed and will soon be published

For high volume samples, a robust TD and a GC-QQQ are needed to handle the ‘dirty’ matrix

Like PFAS in water, Teflon/PTFE/”Polymeric PFAS” remain an issue and can blank-limit detection limits

There is a A LOT of work to be done yet in how to collect PFAS onto TD tubes and how to focus them for good gas chromatography

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Indoor Air PFAS Method Goals –
So Where Were We at NEMC 2021?

- ✓ 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
  - Detection limits are often background limited
  - Teflon a.k.a. “polymeric PFAS” could be a contributor
- ✓ Accommodated 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

PFAS Compounds in Indoor Air: Which?

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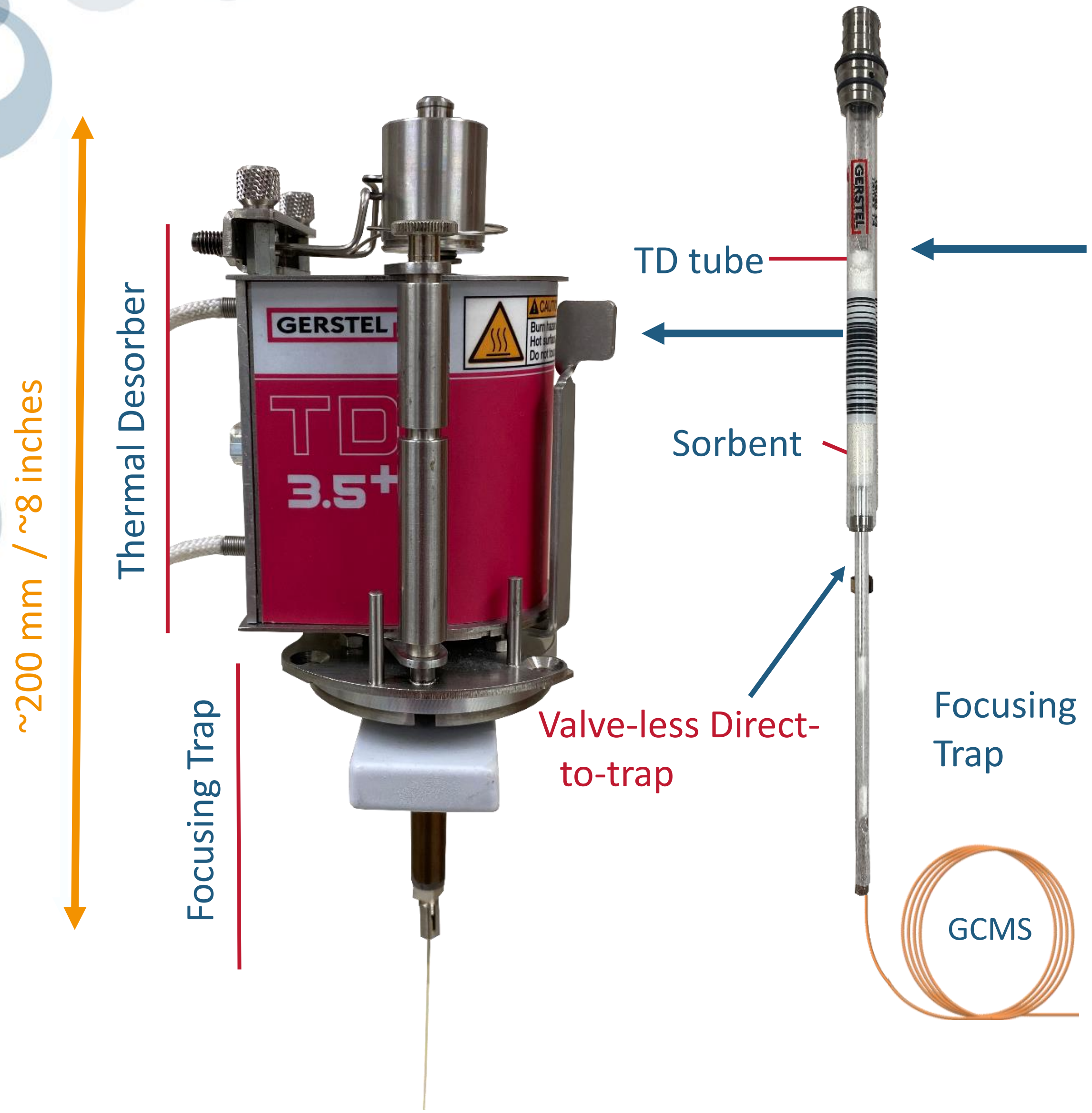
Volatile/Semivolatile Neutral PFAS (four)

- 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 GC-MS~~

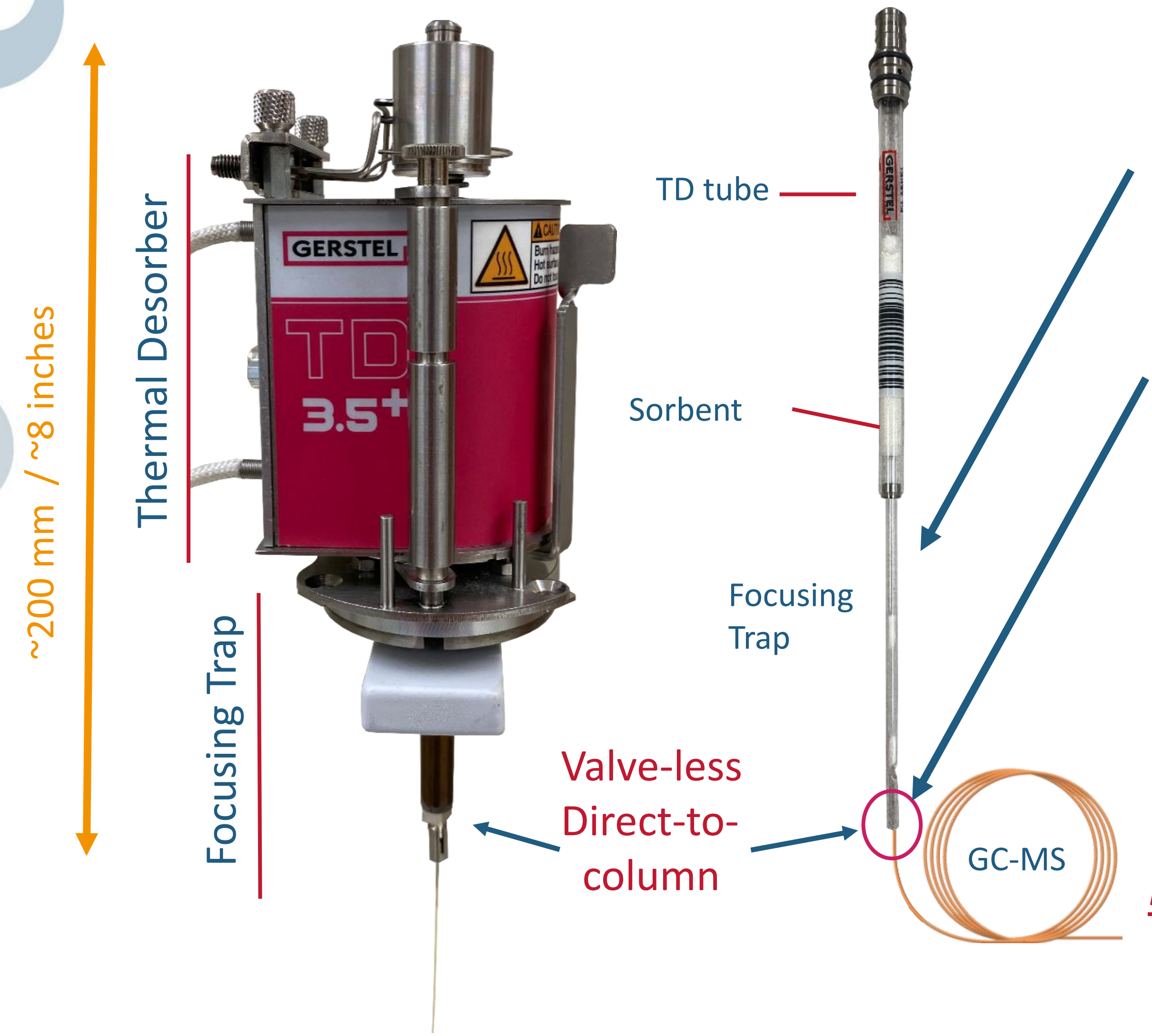
Why TD? How does it work?



Two Stage Thermal Desorption:

- Tubes are easy to use, keep clean, and are relatively inexpensive
- 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)

How does Thermal Desorption Work?



Two Stage Thermal Desorption:

- ○ 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

Thermal Desorption Analysis Conditions

GERSTEL TD 3.5^+ with Autosampler
Agilent 8890 / 7000D Triple
Quadrupole GC-MS/MS

Thermal Desorption (GERSTEL TD 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 (hydrogen possible)
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 & based on “physics”; saves method development time best for non-targeted work

This was also used in the original method to eliminate optimizing the “chemistry” of sorbent-based traps

GC-MS/MS Analysis Conditions

GERSTEL TD 3.5$^+$ with Autosampler
Agilent 8890 / 7000D Triple
Quadrupole GC-MS/MS

Gas Chromatograph

Agilent 8890

Column:	Rxi-624Sil MS, 60m x 0.25 mm ID x 1.4 µm d_f
Mode:	Constant Flow: 1 mL/min
Temp.:	40°C (3 min), 15°C/min; 260°C (6 min)

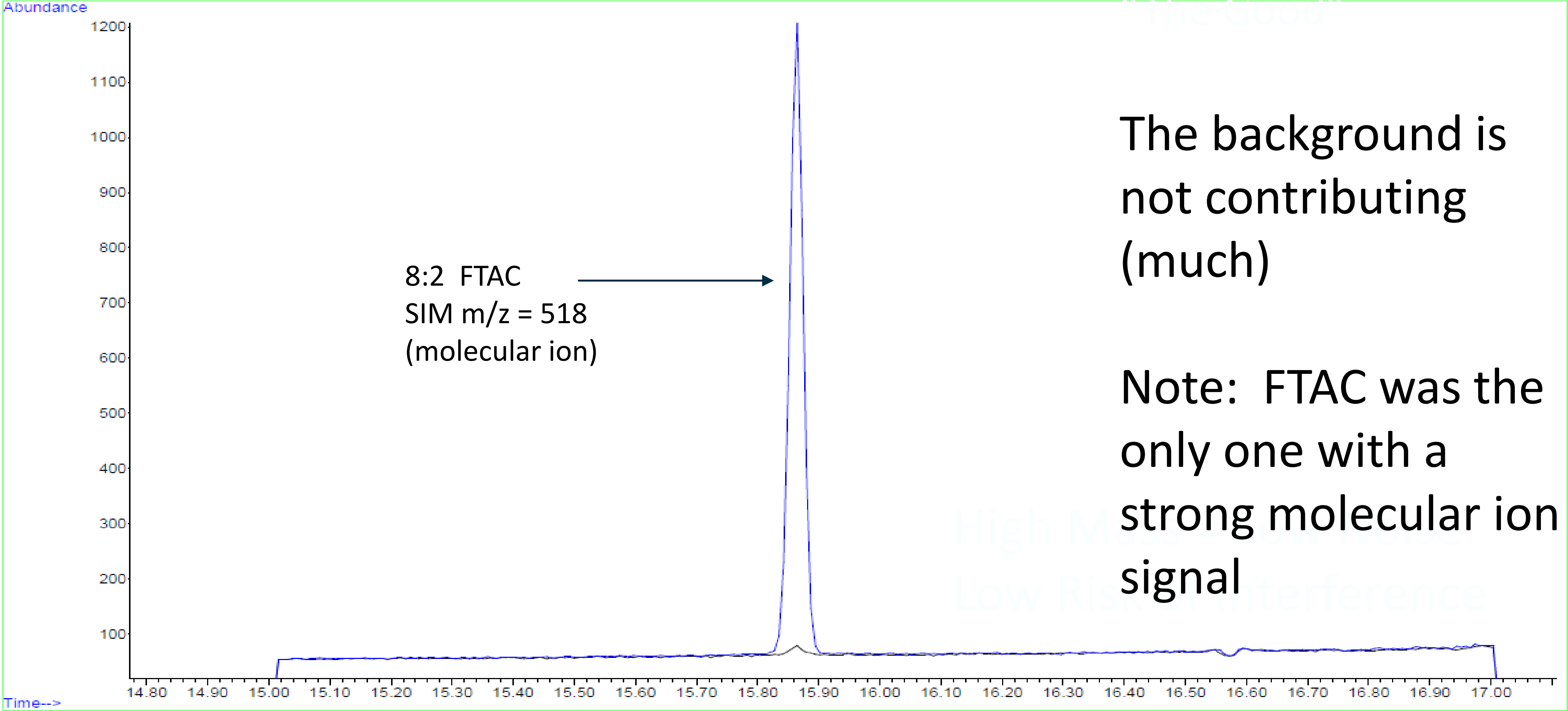
Triple Quadrupole Mass Spectrometer

Agilent 7000D Inert Plus source

EI mode, both SIM and MRM modes used

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

An Example: 8:2 FTAC in Office Air
Spiked Tube (Blue) vs.Unspiked Tube Black (both 57.6 L sampled)



8:2 FTAC
SIM m/z = 518
(molecular ion)

The background is not contributing (much)

Note: FTAC was the only one with a strong molecular ion signal

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Instrument Calibration – Linearity, Precision

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

The use of RRF’s assumes “linear through zero” – *that the blank does not contribute significantly*

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Instrument Calibration – Detection Limits

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C4 PFCA	2.8772	2.2921	2.0194	2.1319	1.7526	1.9321	2.0950	2.1572	16.7
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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
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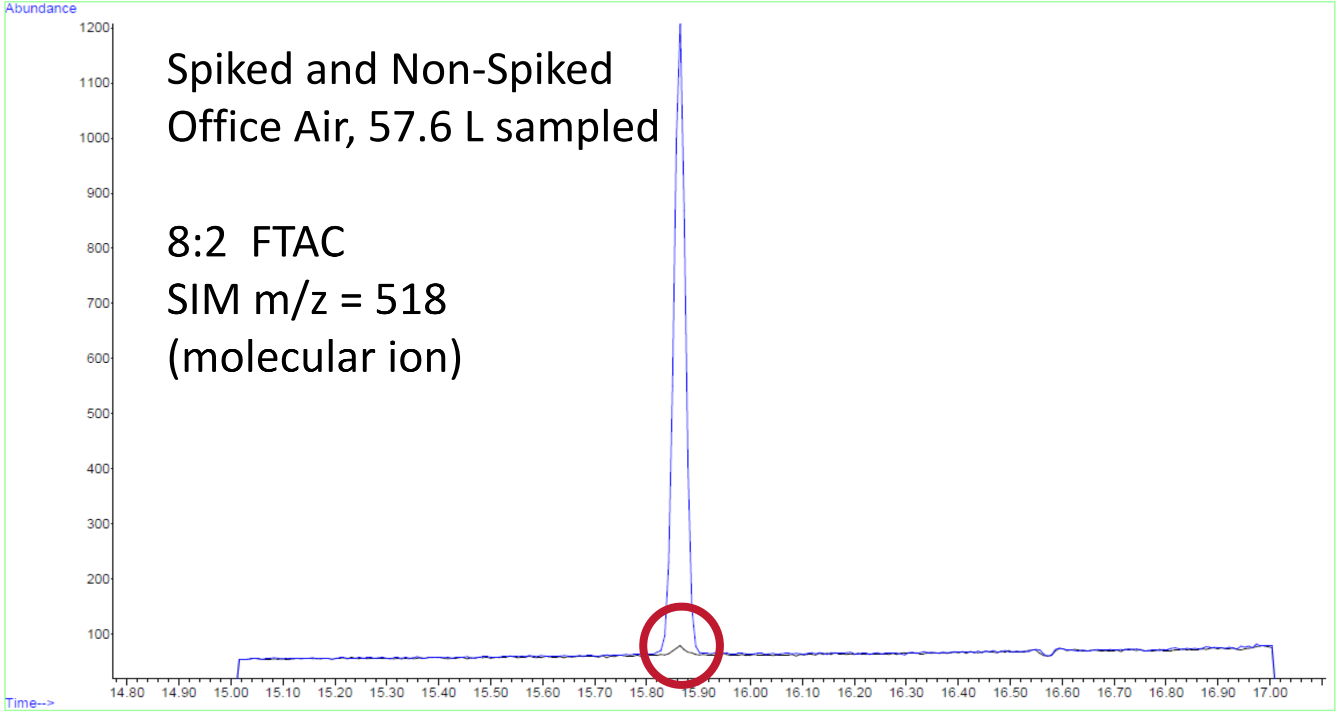
- Except for MeFOSA, 50 pg was the low standard on the curve, so IDL is < 50 pg
- For the rest of the species, based on signal strength alone an 0.005 ng (5 pg) standard would be easily visible, so MDL’s likely less than 0.005 ng, *assuming no blank contribution*
- Consequently, for most species this will equate to sub-part-per-trillion V/V detection limits or less than ~10 ng / m^3 over large volumes of air sampled

The not-so-surprising surprise



Spiked and Non-Spiked
Office Air, 57.6 L sampled

8:2 FTAC
SIM m/z = 518
(molecular ion)

For some species, blank-values of office air are significantly non-zero; that peak is 'real'

Happens when the S/N ratio is high enough to expose it such as here, where the 518 GC-MS/MS blank was baseline flat yet the office air 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*.

Method Development **Complete**

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✓ Targets a wide range of PFAS classes

- Perfluorinated Alkyl Acids AND Precursors using perfluorochemical analysis tubes

✓ Achieves High Sensitivity

- Looking for break-down products at low concentrations
- Detection Limits in the 10 ng / m^3 (low ppt V/V) range

✓ Accommodates 24 hour TWA measurements

- > 50 Liters, assuming a low flow pump at 25 to 50 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 Final Result: a completely developed TD-GC-MS/MS method for Indoor Air that has the best sorbents, column, and MS/MS detection for sensitivity, TWA measurements, and overall strong analytical performance.

A joint GERSTEL/Agilent app note is being written now

The end, in the middle.

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For high volume samples, a robust TD and a GC-QQQ are needed to handle the ‘dirty’ matrix

Like PFAS in water, Teflon/PTFE/”Polymeric PFAS” remain an issue and can blank-limit detection limits

There is a A LOT of work to be done yet in how to collect PFAS onto TD tubes and how to focus them for good gas chromatography

So What's New?

- ~~$\eta = c / \lambda$~~
- Improvements in preconcentration
- Remaining limitations in preconcentration
- Improvements in volumes sampled

Thermal Desorption Analysis Conditions: Optimizing for Targets

GERSTEL TD 3.5$^+$ with A/S
Agilent 8890 / 7000D Triple Quadrupole GC-MS/MS

We started three years ago with glass wool at -120 ˚C via LN_2 cooling

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

But what if you know what you're looking for?

You can optimize trapping substrates and temperatures

Let's use the perfluorinated acids (PFCA's) as an example – they are the earliest eluting and hardest to optimize

Perfluoro acids trapped at -120 °C on quartz wool in focusing trap: current method

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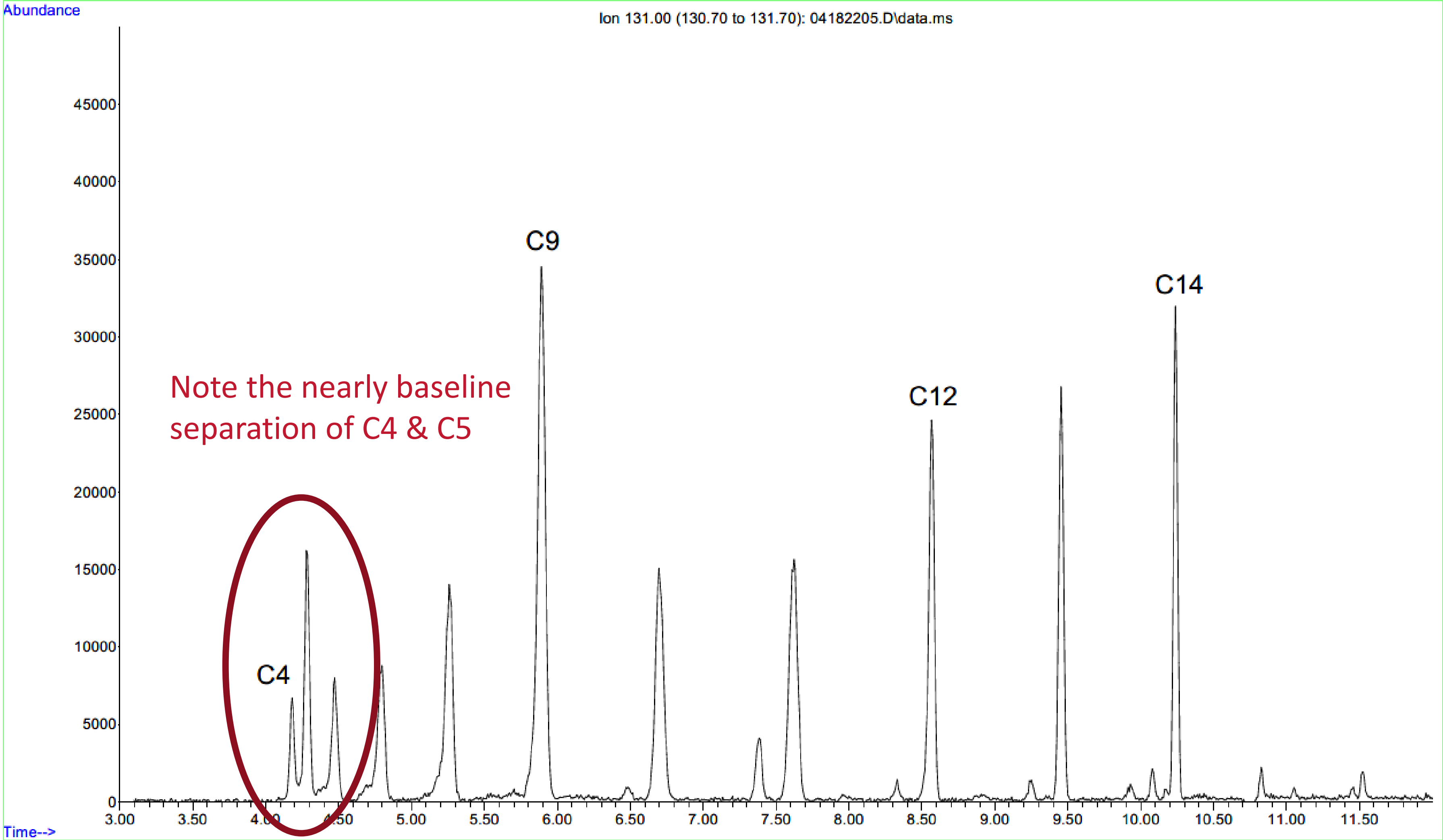

Note the nearly baseline separation of C4 & C5

Perfluoro acids but now trapped at -40 °C with Tenax TA in focusing trap

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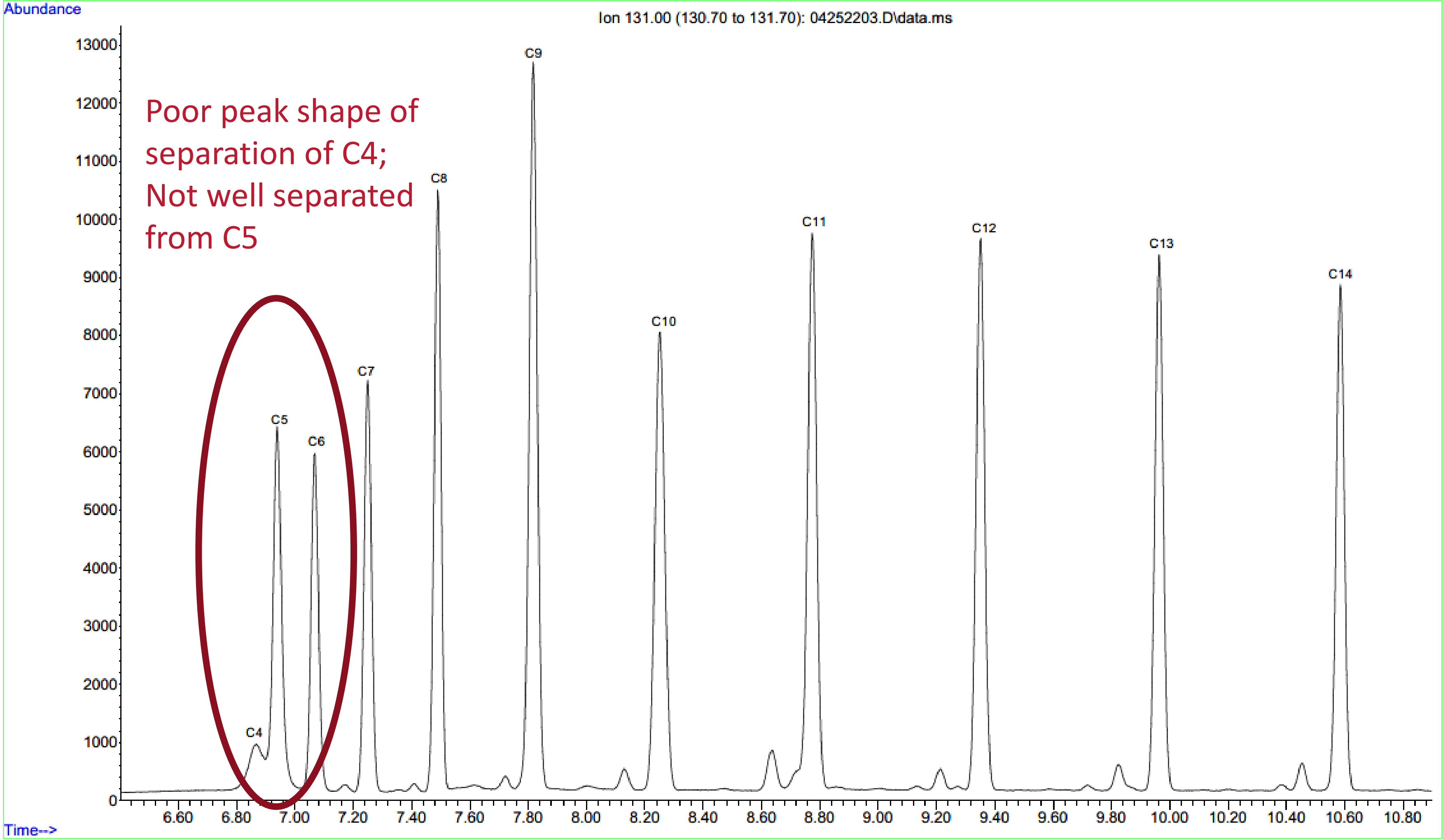

Poor peak shape of separation of C4; Not well separated from C5

Mostly Good News!

At -40 °C on Tenax TA, we are still retaining all the acids (and the later eluters too – data not shown)

The C4 acid peak (pefluorobutanoic acid) is not as well resolved but is workable

At -40 °C Peltier or similar cooling is possible, which are “cryogen free”

However, at that temperature water freezes out. We’d like to trap higher, to have an option for pre-purging the water from the trap. Let’s try it!

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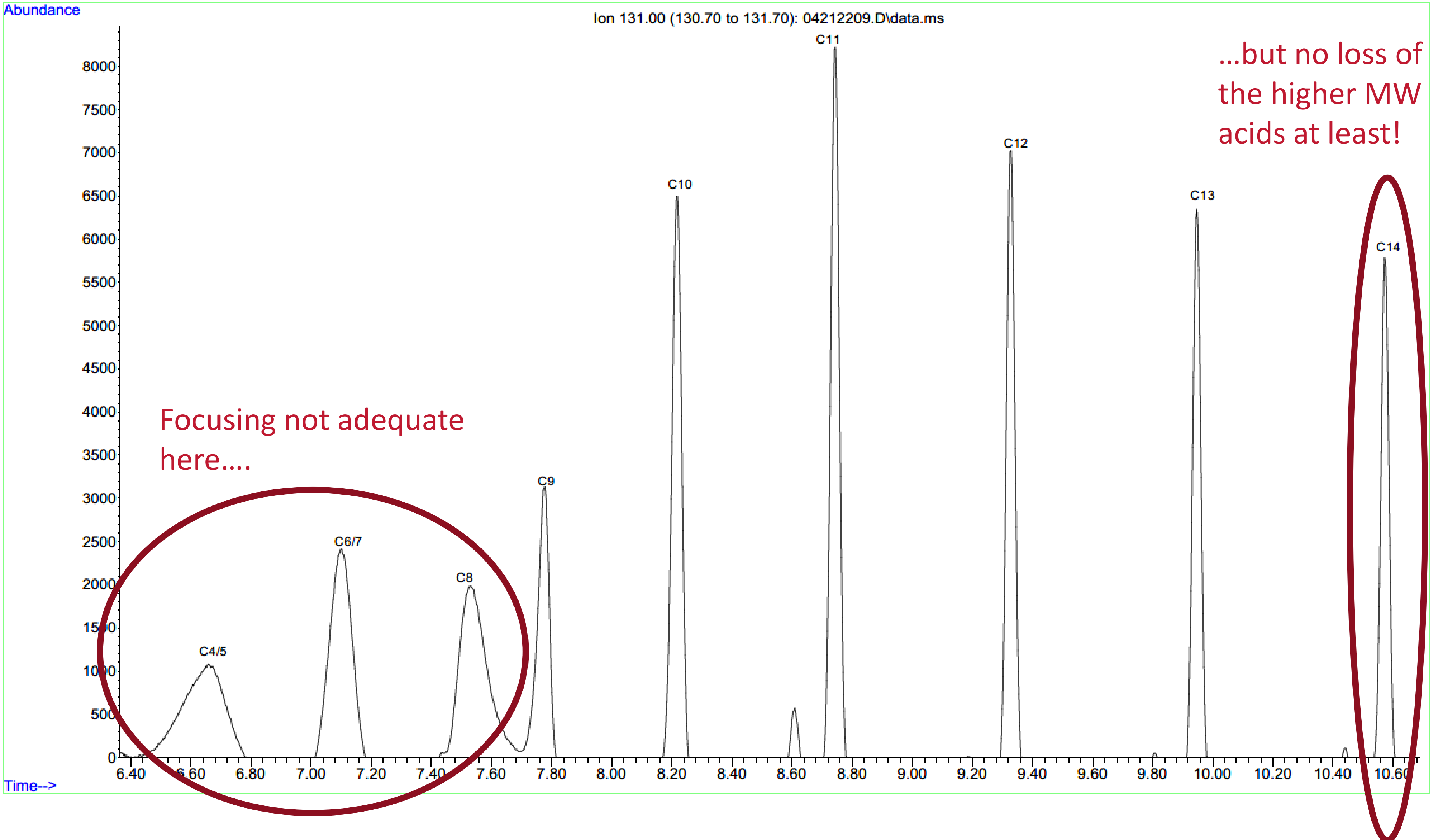
Alkyl perfluoro acids trapped at +10 °C on Tenax



Focusing not adequate here....

…but no loss of the higher MW acids at least!

Not as Good News

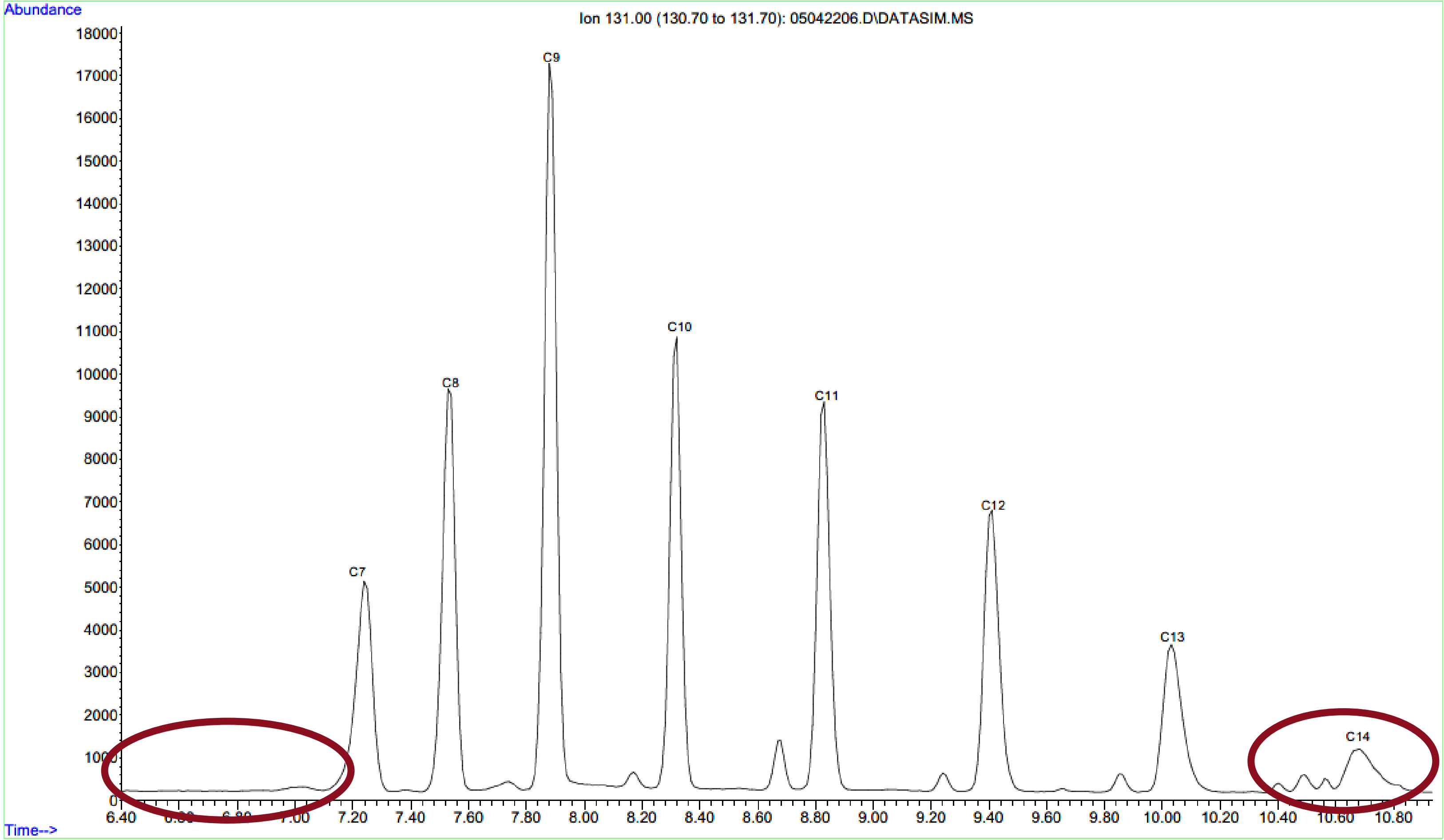
At +10 °C on Tenax TA, we not focusing the C4 to C8 acids well (and C8 – PFOA – *is of critical importance*)

The rest of the acids sill do OK, as do the other PFAS compounds (data not shown)

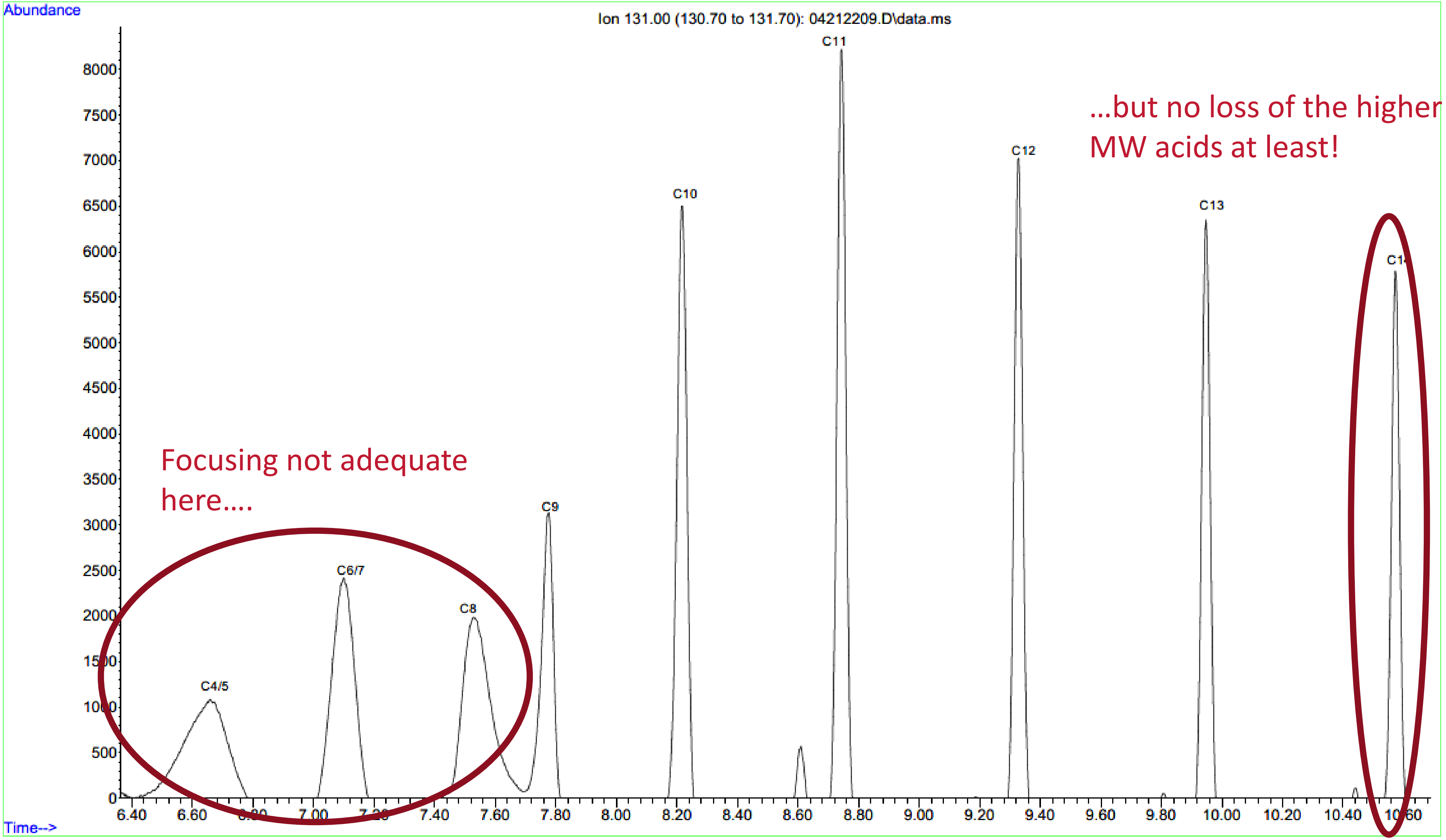
At +10 °C water can be pre-purged out (but wasn't in this example)

Of course, we want to have it all though. What if we switch to a stronger sorbent in the trap?

Perfluoro acids at +10 °C on Carbopack B: Loss on Both Ends!



Reminder: +10 °C on Tenax Worked Well



Focusing not adequate here….

…but no loss of the higher MW acids at least!

So What Gives?

The stronger sorbent is costing us the higher MW species

<u>And yet, the lightest are ALSO lost (and it wasn't pre-purging – not used)</u>

Tenax TA seems to be 'better' for focusing traps, just not at +10 °C: the data at -40 °C seems 'good enough'

This is really odd: **you <u>CAN</u> use single bed Tenax focusing traps** for 'normal' VVOC's (and the full column range, like in EPA's TO-15/17 methods) **and also trap at + 10°C** …

…just why not volatile PFAS?

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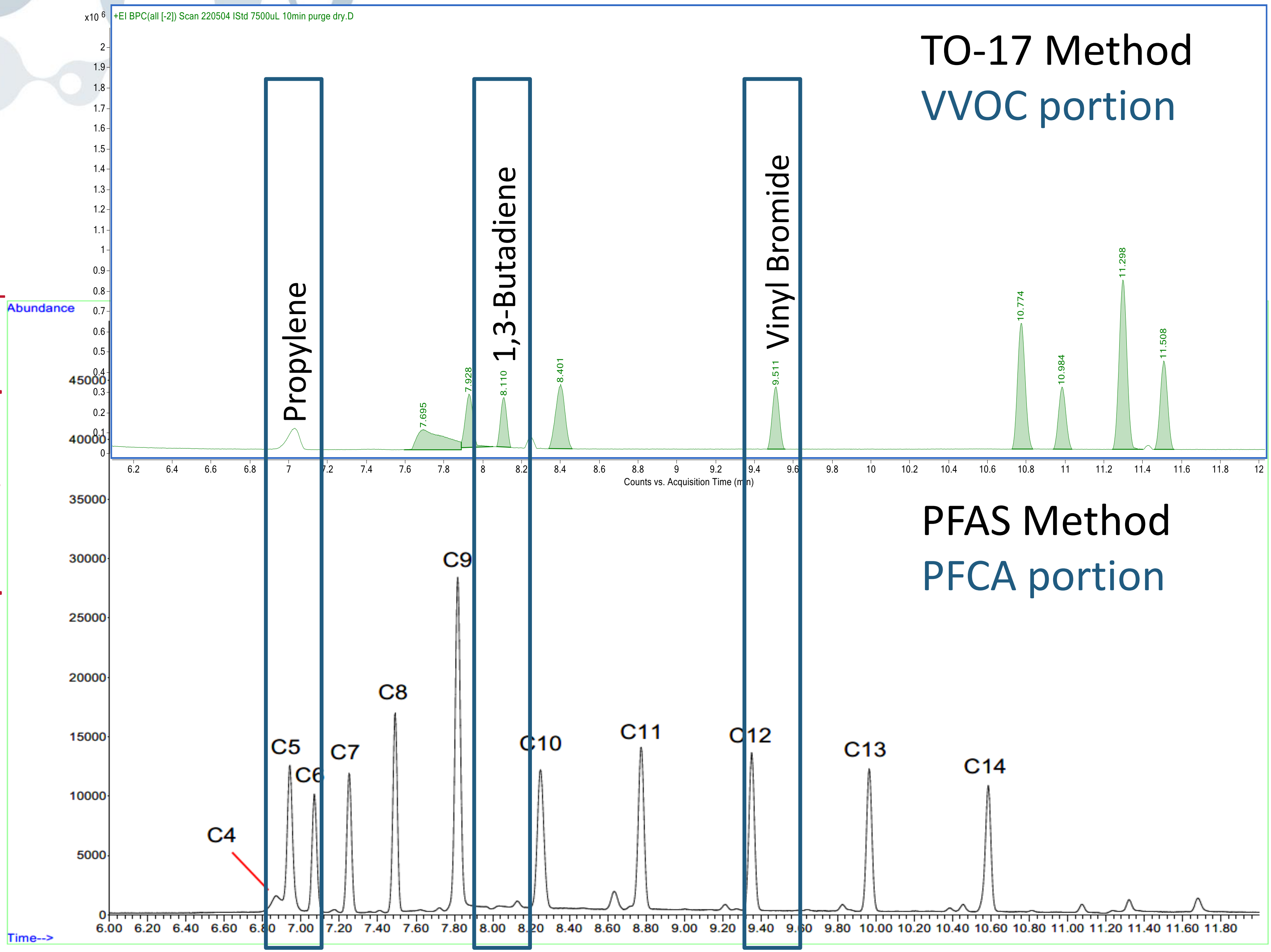
Both Chromatograms:

DB-624 60 m 250 µm ID, 1.4 µm d_f



TO-17 Method

VVOC portion

Tenax TA trap **+10 °C**

PFAS Method

PFCA portion

Tenax TA trap **-40 °C**

Clearly, We Aren't in Kansas Anymore.

PFAS species *are hundreds of amu heavier* than TO-17's VVOC's

C6 PFCA = 314 amu nominal, propylene = 42 amu nominal

PFCA's are also polar acids, yet don't tail at all, and have better peak shape than TO-17 VVOC's, like propylene which is an olefin!

And they all elute in similar times on a DB-624.

So what’s next?

If the light PFCA acids are of interest, more work needs to be done on both the TD tubes used and the material in the focusing trap

It may not be possible to trap OR focus C1-C3 perfluoro-acids at all, at least with the current selection of sorbents

The stronger sorbents may not be winners – there might be something else in play here…

Improvements in High Volume Sampling

New sorbent choices, advances in sampling have driving volumes sampled as high as 300 Liters in total, and possibly more

As before, a valveless, robust TD and a GC-QQQ are needed to manage the matrix

High volume indoor air samples have demonstrated good recoveries in laboratory tests, and the method is supporting field sample collection and analysis.

Please contact Heidi Hayes at Eurofins for additional information.

The end, at last.

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We are VERY grateful for the help of

- 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
- Two Groups at the US EPA
  What to look for, where, and why
- All of You!