

Selection, Optimization, and Validation of Thermal Desorption for analysis of VOCs and PAHs in Combustion Emissions

Caleb Marx, Dena McMartin, Kevin Hayes,
Court Sandau, Gwen O'Sullivan

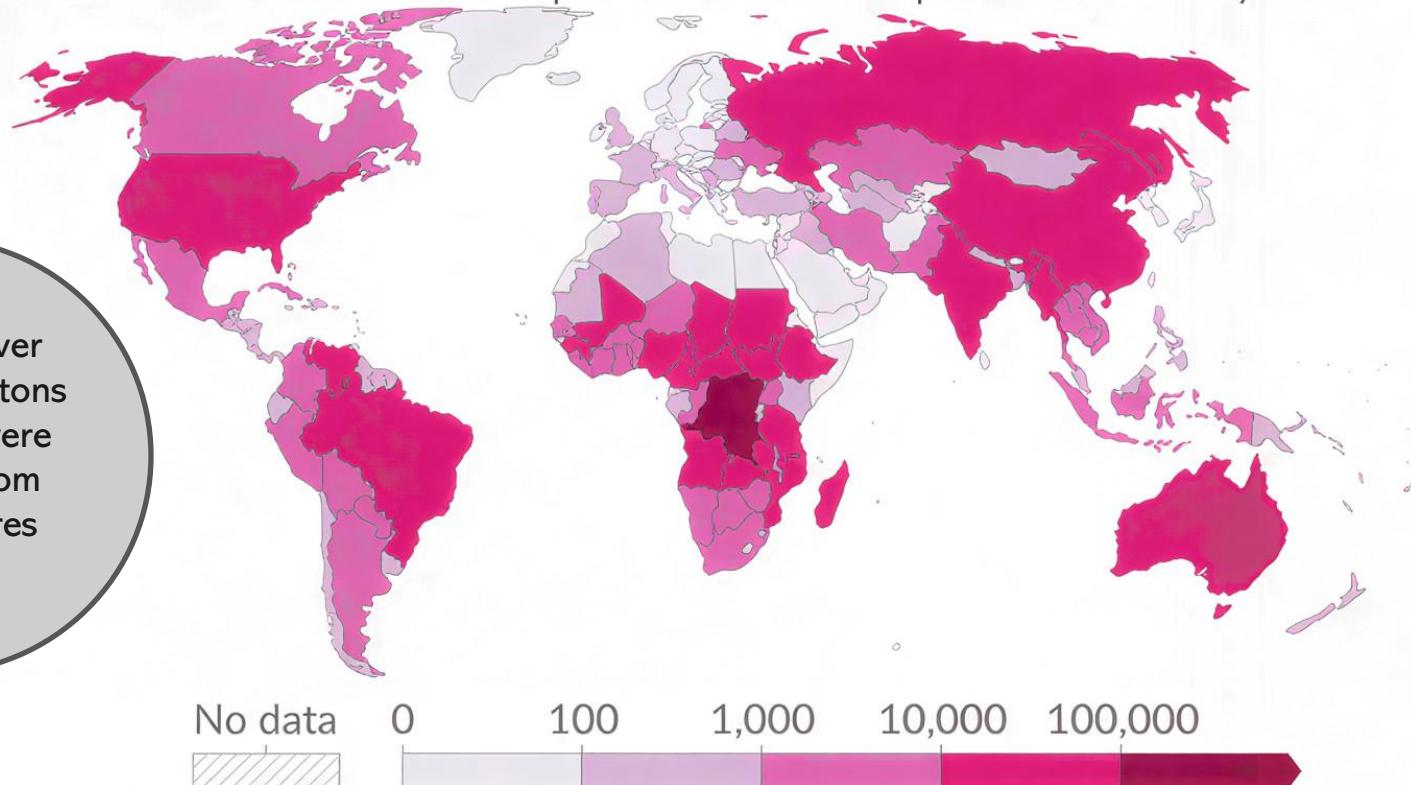
Lethbridge, AB, Canada



Annual number of wildfires, 2025

Number of wildfires. The 2026 data is incomplete and was last updated 09 January 2026.

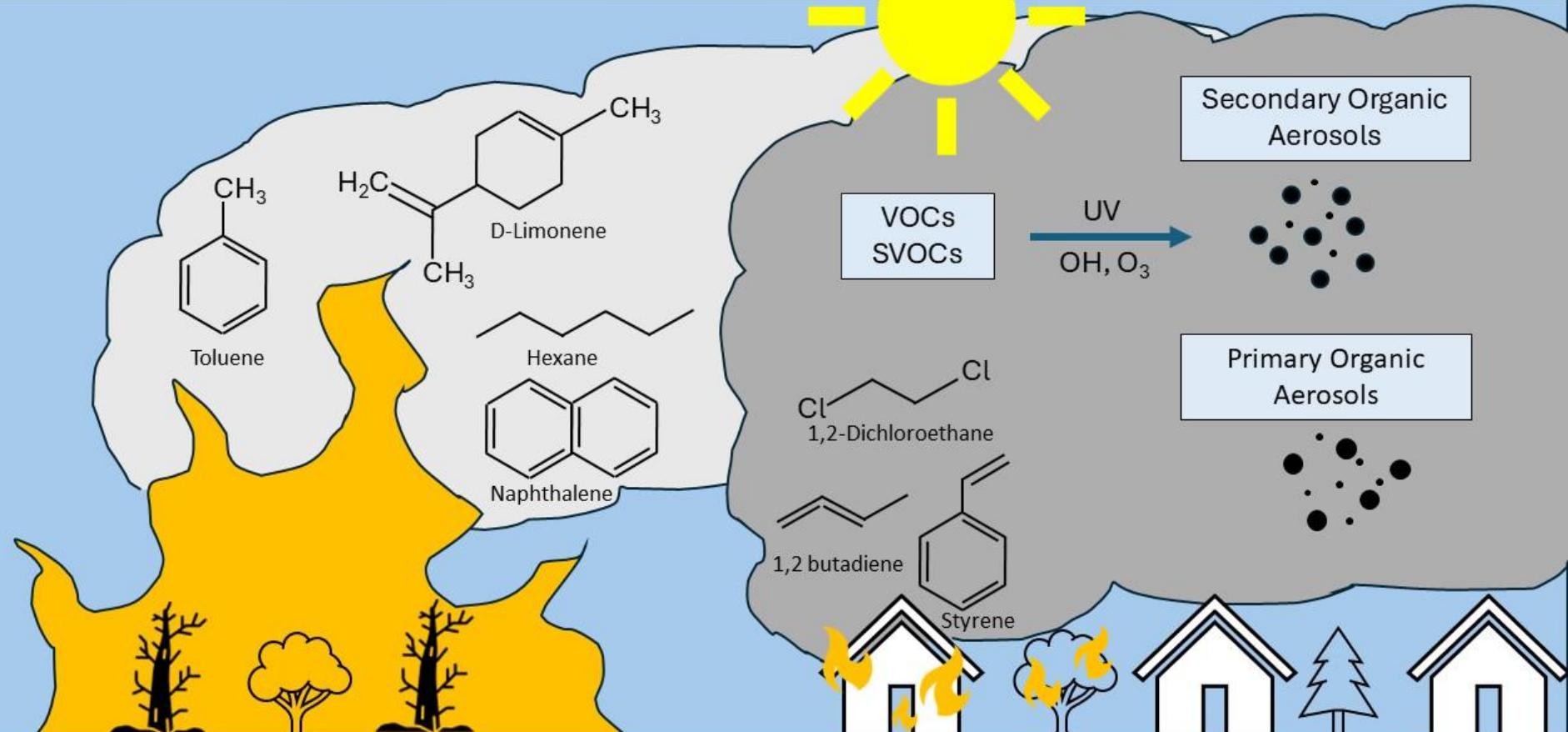
In 2025, over 1400 megatons of carbon were released from wildland fires



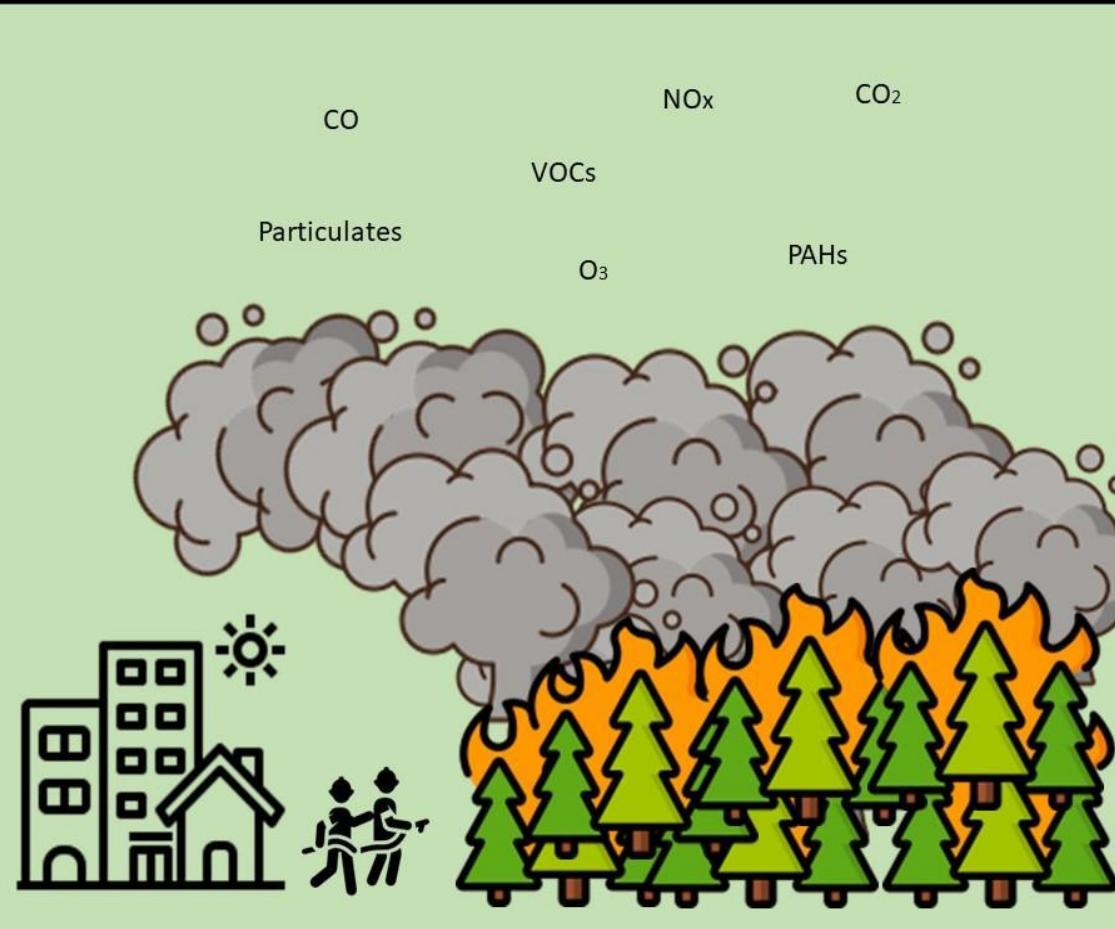
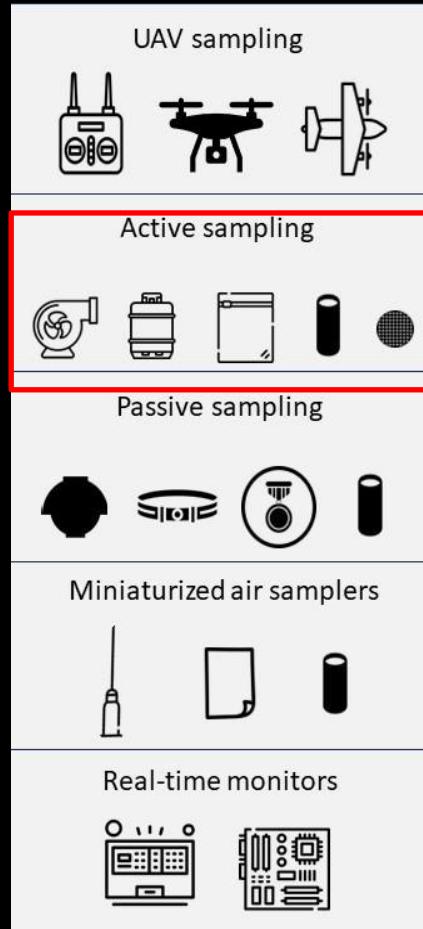
Background: Smoke

Smoke emissions from wildland fires contain harmful products, causing adverse human and environmental impacts. As airborne pollutants, they can also persist in the atmosphere and travel for hundreds of kilometres, causing hazardous air quality across large geographical areas.



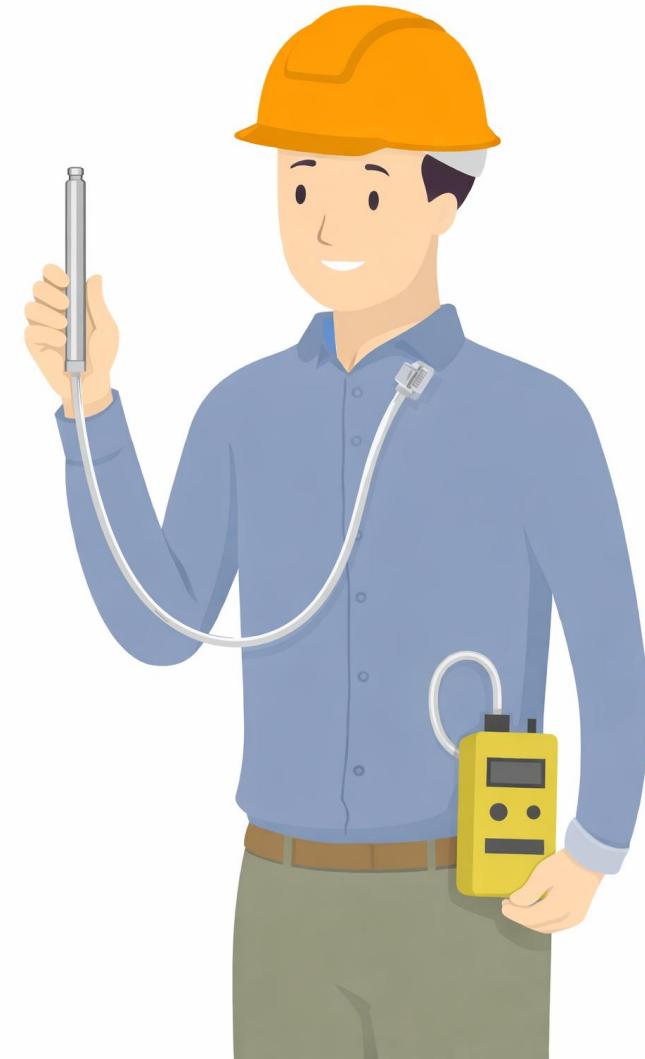


Secondary Organic Aerosol Formation



Limitations of Current Methods

- Smoke emissions are chemically complex, making sampling method selection challenging
- Filters primarily capture particulate-phase constituents
- Gas-phase organics are often underrepresented despite health and SOA relevance
- Thermal desorption enables direct capture of free-phase organic compounds
- Multibed TD applications in smoke characterization remain limited



Thermal Desorption

- Thermal desorption is a modern tool for gas and particle-phase VOC sampling
- “Brita filter for air”
- A wide range of sorbent materials are available
- Sorbents can be combined to form multibed tubes
- Multibed tubes expand analyte retention and compound coverage





Sorbent type:	Porous polymers	Graphitised carbon blacks	Carbonised molecular sieves	Zeolite molecular sieves
The porous polymer sorbent Tenax® TA is the most popular sorbent for TD.				
Sorbent strength: The weaker the sorbent, the better it is at analysing heavier and reactive molecules.				
Water retention: Weaker sorbents are generally more hydrophobic, making them a better choice for sampling humid environments.				

Image from Markes International

1

Sampling

2

Tubes are
moved into
analytical
system

3

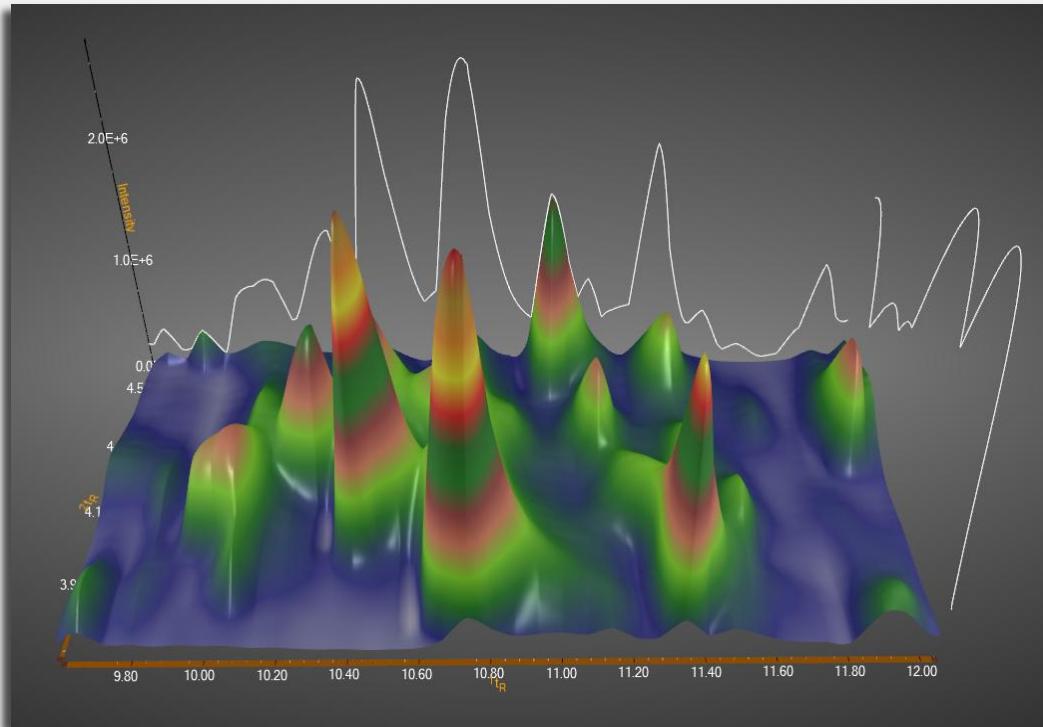
Heat and carrier
gas

4

Analytes are
desorbed

Thermal Desorption / Conditioning

Two-Dimensional Gas Chromatography



- GCxGC offers several advantages over conventional GC-MS
- Primarily, a reduction in peak coelution through second dimension separation
- Though limited work has been done utilizing GCxGC for smoke characterization

1D: 5% non polar phenyl column
(20 m x 180 μ m x 0.18 μ m)
BPX-50 50% diphenyl semi-polar
column (5 m x 250 μ m x 0.25 μ m)
5 °C / min up to 260 °C
SepSolve INSIGHT flow modulator:
4 second modulation



Outline

01

Sorbent Bed Optimization

Six unique sorbent bed combinations were compared using a VOC/PAH standard mixture

02

Conditioning Optimization

Spiked thermal desorption tubes were conditioned at varying method parameters

03

Desorption Optimization

Desorption parameters were manipulated to optimize recovery and peak area

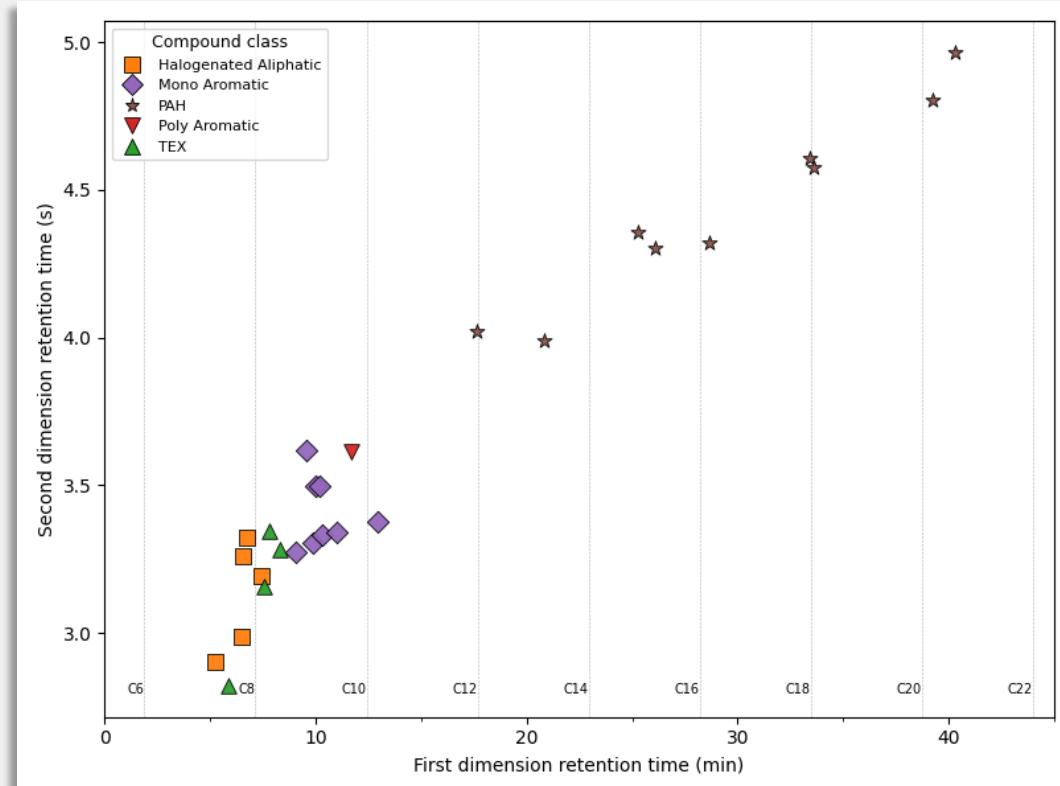
04

Long-Term Storage Test

Spiked Tubes were sealed and stored for set periods to investigate analyte loss over time

Liquid Standard Mixture

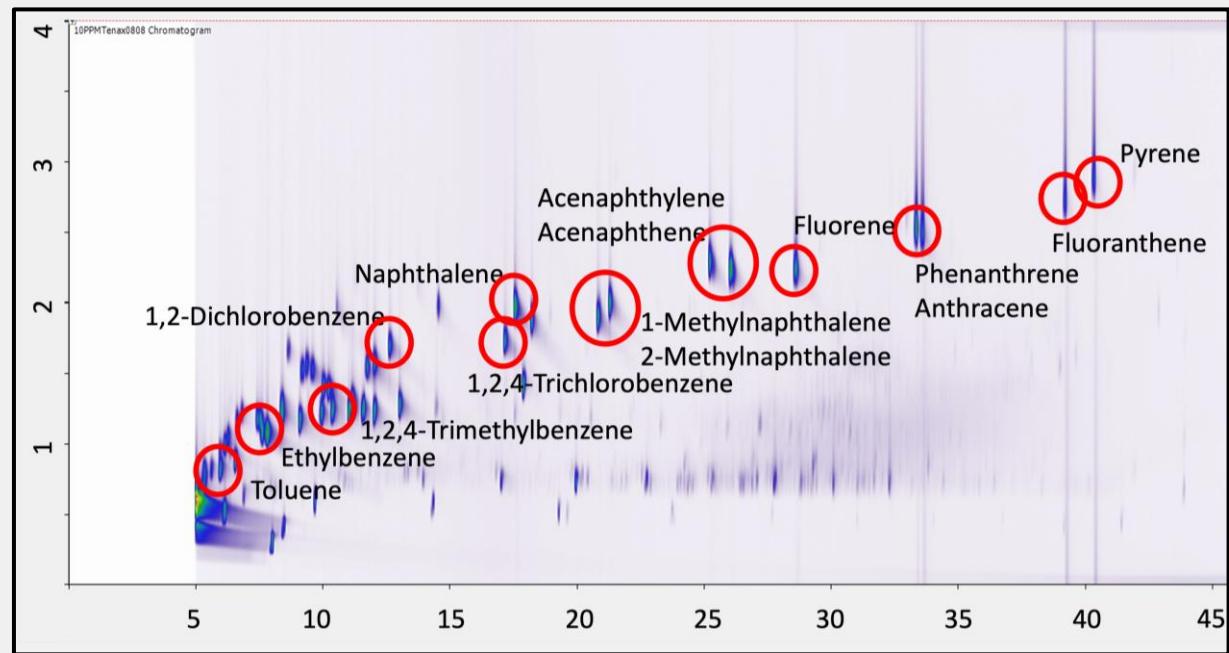
- 41 unique compounds from two standard mixtures a certified reference material PAH mix and an EPA 502/524.2 VOC Mix were combined for this study
- Analytes were separated into five unique compound classes
- RI: 600 – 2100
- log K_{ow}: 1.7 to 5.16
- Henry's Law constants from 9.45×10^{-6} to 0.01177 atm·m³/mol



Tube Spiking



Markes Calibration Solution Loading Rig: CSLR

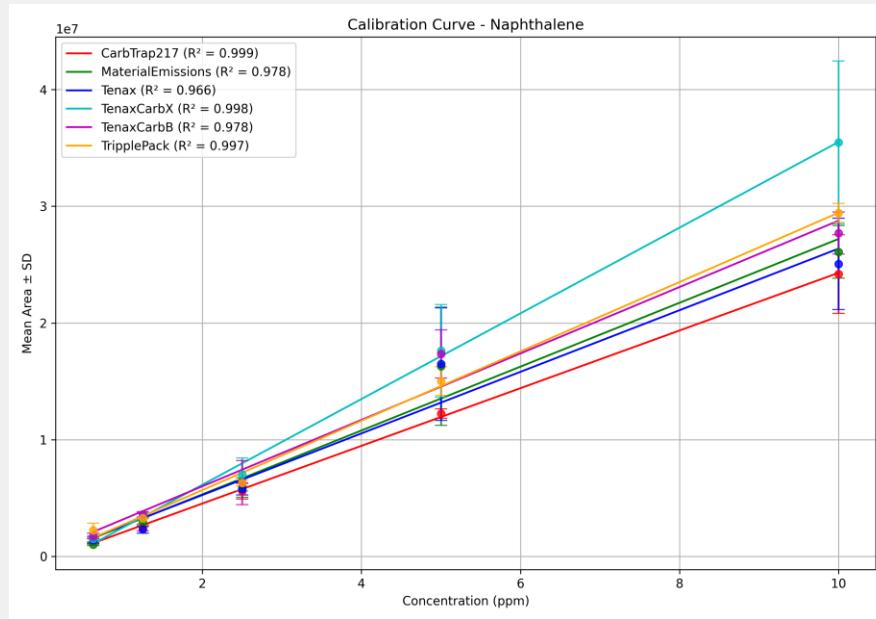
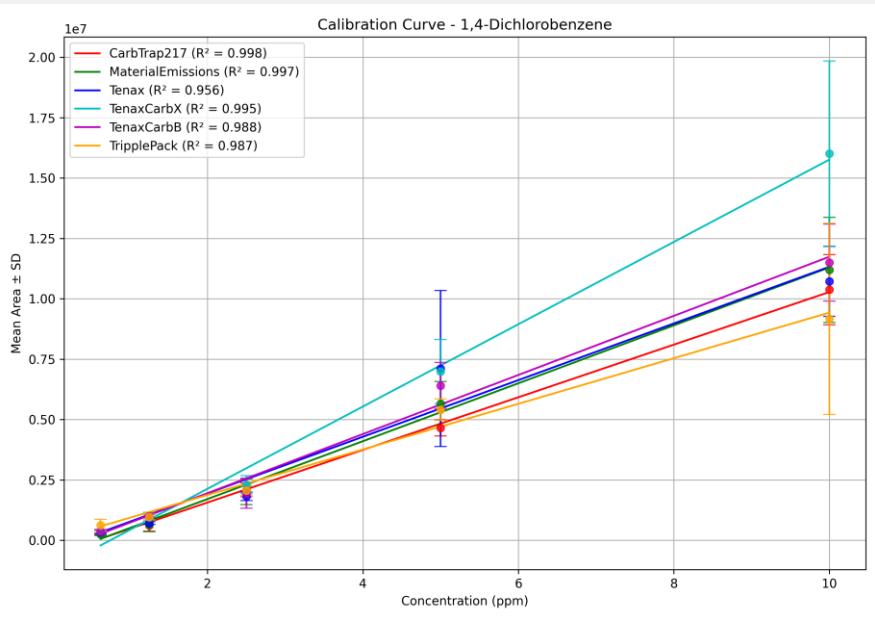


01

Sorbent Tube Optimization

- Six sorbent bed types were compared at five concentration levels:
- (10, 5, 2.5, 1.25, 0.625 µg/mL)
- Tube comparison was based on three metrics:
 1. Recovery
 2. Linearity
 3. Limits of Detection

Tube	Tube Information	Sorbent and packing order (front to back of tube)	Material	Mass of Sorbent (mg)	Sorbent retention strength	Optimum Carbon Range (C_x - C_y)	Maximum Temperature Stability (°C)
A	CarboTrap 217: Commercial	Carbopack B	Graphitised carbon black	-	Medium	C_5 - C_{14}	400
		Carboxen 1000	Carbonised molecular sieve	-	Strong	C_2 - C_5	400
B	Material Emissions: Commercial	Proprietary information	-	-	-	-	-
C	Tenax TA: Commercial	Tenax TA	Porous polymer	200	Weak	C_6 - C_{30}	350
D	In-house	Tenax TA	Porous polymer	150	Weak	C_6 - C_{30}	350
		Carbopack X	Graphitised carbon black	150	Medium	C_3 - C_8	400
E	In-house	Tenax TA	Porous polymer	150	Weak	C_6 - C_{30}	350
		Carbopack B	Graphitised carbon black	150	Medium	C_5 - C_{14}	400
F	In-house	Tenax Ta	Porous polymer	75	Weak	C_6 - C_{30}	350
		Carbopack X	Graphitised carbon black	75	Medium	C_5 - C_{14}	400
		Carbopack B	Graphitised carbon black	75	Medium	C_3 - C_8	400



01 Sorbent Tube Optimization

Sorbent Bed Type 10 (µg/ml)

	A	B	C	D	E	F
1,2-Dichloropropane	61.0%	83.3%	55.9%	100.0%	76.2%	55.4%
Dibromomethane	71.3%	52.0%	78.6%	94.5%	100.0%	69.4%
Bromodichloromethane	64.8%	47.3%	67.0%	100.0%	49.2%	59.8%
cis-1,3-Dichloropropene	54.4%	70.3%	57.3%	100.0%	53.0%	50.4%
Toluene	64.0%	61.7%	71.5%	100.0%	98.5%	74.2%
Tetrachloroethylene	67.2%	76.6%	74.9%	100.0%	80.3%	77.5%
Dibromo-chloromethane	60.9%	62.1%	58.7%	100.0%	73.2%	75.3%
1,2-Dibromoethane	49.0%	68.3%	55.8%	100.0%	80.7%	87.7%
1,1,1,2-Tetrachloroethane	55.1%	55.6%	60.6%	100.0%	79.4%	63.8%
Ethylbenzene	62.5%	84.0%	89.5%	80.3%	100.0%	99.2%
p/m-Xylene	55.3%	90.1%	85.4%	100.0%	70.9%	95.8%
o-Xylene	42.3%	55.5%	73.6%	100.0%	45.1%	45.7%
Cumene	77.6%	70.7%	93.1%	97.2%	100.0%	92.7%
1,1,2,2-Tetrachloroethane	65.7%	73.6%	68.9%	100.0%	73.8%	70.3%
1,2,3-Trichloropropane	64.6%	78.4%	65.6%	100.0%	86.7%	75.9%
Bromobenzene	60.6%	72.6%	69.3%	100.0%	72.1%	83.2%
Propylbenzene	72.9%	76.5%	68.8%	100.0%	68.9%	82.3%
4-Chlorotoluene	76.2%	61.0%	63.8%	100.0%	80.5%	97.0%
2-Chlorotoluene	78.8%	60.1%	67.5%	88.7%	100.0%	86.3%
1,3,5-Trimethylbenzene	72.5%	76.1%	74.4%	100.0%	80.1%	68.2%
tert-Butylbenzene	91.0%	76.8%	80.5%	100.0%	92.2%	75.2%
1,2,4-Trimethylbenzene	36.9%	32.8%	53.3%	100.0%	52.7%	82.6%
sec-Butylbenzene	72.4%	83.9%	92.9%	100.0%	92.7%	76.0%
1,2-Dichlorobenzene	70.8%	72.8%	67.4%	100.0%	75.6%	76.7%
p-Cymene	66.5%	73.3%	73.9%	100.0%	76.6%	82.8%
1,3-Dichlorobenzene	66.7%	68.2%	71.3%	100.0%	74.1%	78.1%
1,4-Dichlorobenzene	64.8%	69.9%	66.9%	100.0%	71.8%	57.3%
Butylbenzene	72.8%	74.6%	69.4%	100.0%	77.2%	60.0%
1,2,4-Trichlorobenzene	73.6%	80.6%	71.8%	100.0%	82.9%	85.5%
Naphthalene	68.2%	73.5%	70.6%	100.0%	78.1%	83.0%
Hexachloro-1,3-butadiene	73.7%	76.7%	80.9%	100.0%	76.3%	83.3%
1,2,3-Trichlorobenzene	66.1%	50.1%	72.3%	100.0%	74.5%	76.6%
1-Methylnaphthalene	60.6%	71.6%	68.4%	100.0%	80.6%	96.0%
2-Methylnaphthalene	64.6%	70.2%	62.5%	100.0%	74.8%	83.2%
Acenaphthylene	59.5%	80.8%	76.2%	100.0%	86.5%	67.1%
Acenaphthene	48.2%	63.7%	72.8%	100.0%	54.4%	89.4%
Fluorene	10.0%	46.8%	54.3%	100.0%	80.5%	99.1%
Phenanthrene	6.1%	60.7%	51.5%	100.0%	97.0%	83.3%
Anthracene	5.8%	59.5%	44.4%	84.8%	100.0%	87.4%
Fluoranthene	6.1%	70.4%	47.8%	92.3%	100.0%	70.5%
Pyrene	5.0%	50.5%	48.2%	83.2%	100.0%	90.2%

Sorbent Bed Type 0.625 (µg/ml)

	A	B	C	D	E	F
	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%
	34.7%	60.3%	72.0%	65.5%	100.0%	40.1%
	50.4%	44.1%	47.0%	74.4%	91.1%	97.1%
	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	33.2%	0.0%	30.4%	0.0%	0.0%	100.0%
	63.1%	41.1%	53.5%	67.4%	81.9%	100.0%
	50.5%	19.9%	52.4%	32.6%	100.0%	48.4%
	70.3%	57.2%	80.8%	87.0%	100.0%	95.1%
	23.8%	21.4%	28.8%	32.2%	32.1%	100.0%
	59.8%	29.8%	60.1%	60.1%	52.9%	100.0%
	48.4%	21.9%	49.4%	46.0%	36.1%	100.0%
	38.7%	0.0%	34.9%	43.7%	23.5%	100.0%
	50.3%	32.9%	40.9%	40.8%	74.0%	100.0%
	52.2%	36.0%	44.8%	68.5%	55.8%	100.0%
	58.3%	36.0%	47.9%	68.9%	55.8%	100.0%
	62.4%	48.8%	73.9%	69.6%	71.9%	100.0%
	59.9%	54.1%	73.1%	87.5%	75.1%	100.0%
	41.1%	29.9%	40.6%	38.3%	100.0%	55.3%
	51.0%	37.2%	50.2%	62.1%	63.5%	100.0%
	49.2%	32.5%	60.9%	58.7%	60.7%	100.0%
	67.4%	45.2%	81.6%	83.6%	74.6%	100.0%
	35.9%	24.3%	42.6%	49.8%	52.4%	100.0%
	48.1%	38.9%	53.2%	58.5%	58.1%	100.0%
	34.1%	37.2%	51.9%	53.3%	40.2%	100.0%
	57.9%	45.1%	63.6%	67.3%	78.2%	100.0%
	63.3%	57.8%	70.7%	62.0%	59.2%	100.0%
	54.8%	43.3%	58.6%	51.2%	54.5%	100.0%
	48.6%	28.4%	49.3%	54.5%	65.1%	100.0%
	48.9%	35.1%	51.1%	50.1%	57.3%	100.0%
	35.9%	33.2%	62.4%	53.4%	54.6%	100.0%
	63.8%	43.5%	73.3%	65.2%	71.0%	100.0%
	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	0.0%	0.0%	47.2%	50.2%	59.2%	100.0%
	0.0%	0.0%	49.4%	33.7%	0.0%	100.0%
	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%
	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%

01

Sorbent Tube

Optimization

02 Conditioning Optimization

- To validate the selection of conditioning parameters (time and temperature), a factorial study design was used
- For each factorial level, four replicates were injected, resulting in a total of 36 samples
- Results demonstrated that decreases in conditioning time and temperature did not improve in artifact removal

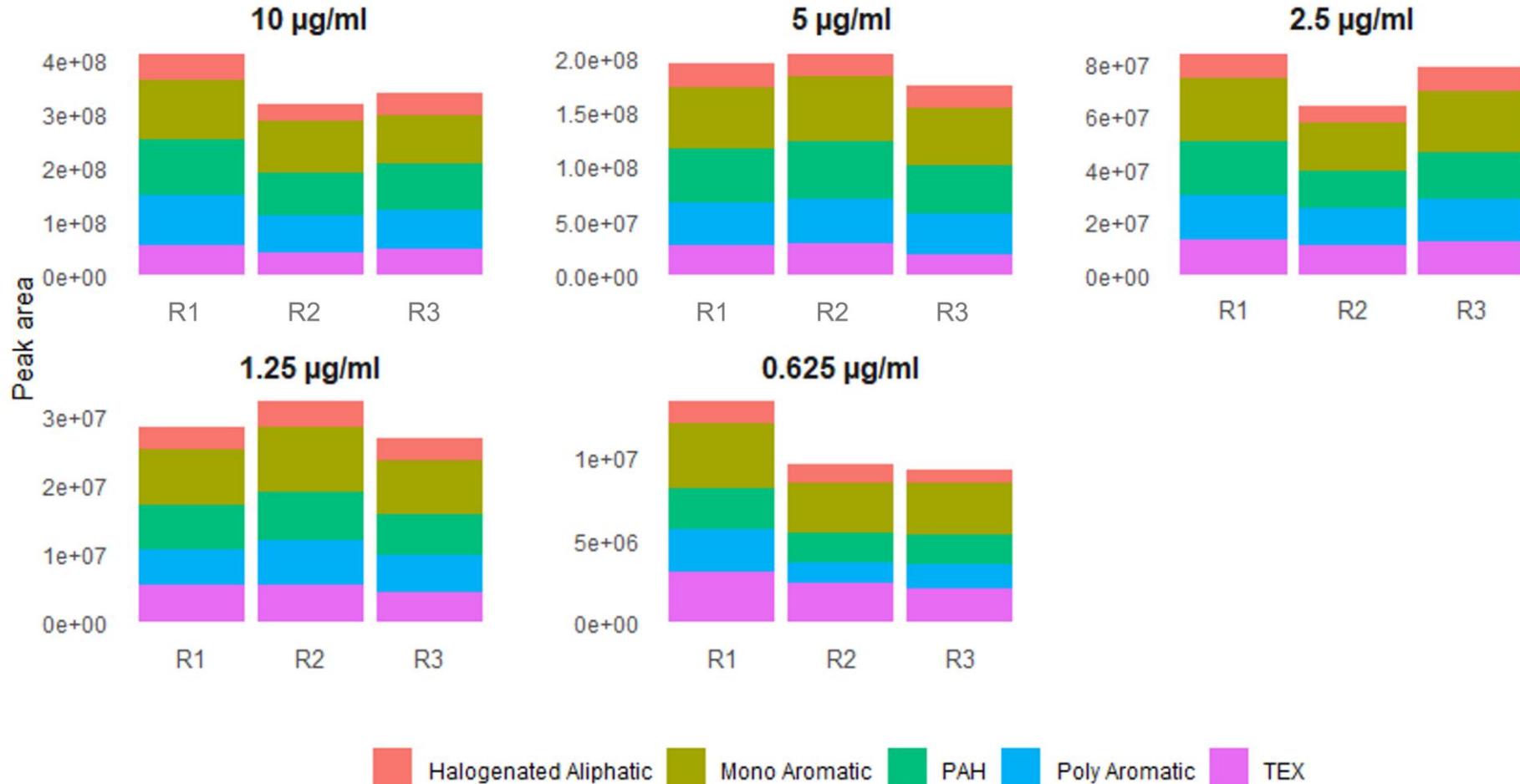
Run	Conditioning Time (Hour)	Conditioning Temp (°C)
1	3 (+)	290 (+)
2	3 (+)	270 (=)
3	3 (+)	250 (-)
4	2 (=)	290 (+)
5	2 (=)	270 (=)
6	2 (=)	250 (-)
7	1 (-)	290 (+)
8	1 (-)	270 (=)
9	1 (-)	250 (-)

03

Desorption Method Optimization

- Modified factorial study design
- Manipulation of desorption parameters had a negligible impact on analyte recovery
- Concentration-dependent variations were observed

Run	Desorb Time (min)	Desorb Temperature (°C)	Trap Flow (mL/min)
1	20 (+)	310 (+)	60 (+)
2	15 (=)	300 (=)	50 (=)
3	10 (-)	290 (-)	40 (-)
4	10 (-)	310 (+)	50 (=)
5	10 (-)	300 (=)	50 (=)
6	10 (-)	310 (+)	60 (+)
7	15 (=)	290 (-)	50 (=)
8	15 (=)	300 (=)	60 (+)
9	15 (=)	310 (+)	40 (-)
10	20 (+)	290 (-)	60 (+)
11	20 (+)	300 (=)	40 (-)
12	20 (+)	310 (+)	50 (=)
13	20 (+)	300 (=)	50 (=)
14	15 (=)	310 (+)	50 (=)

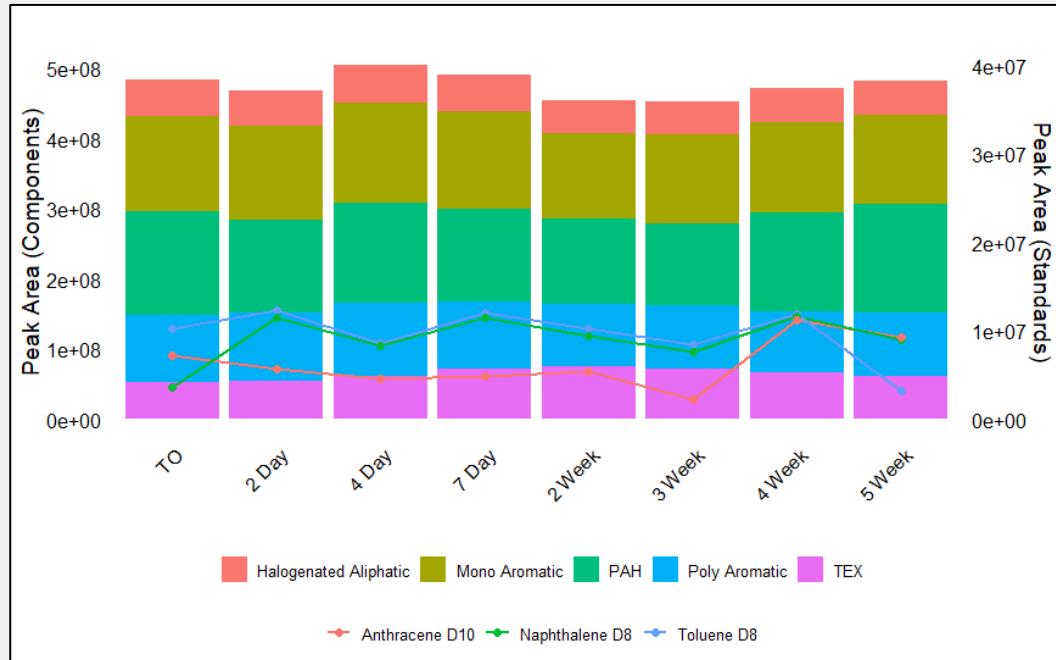


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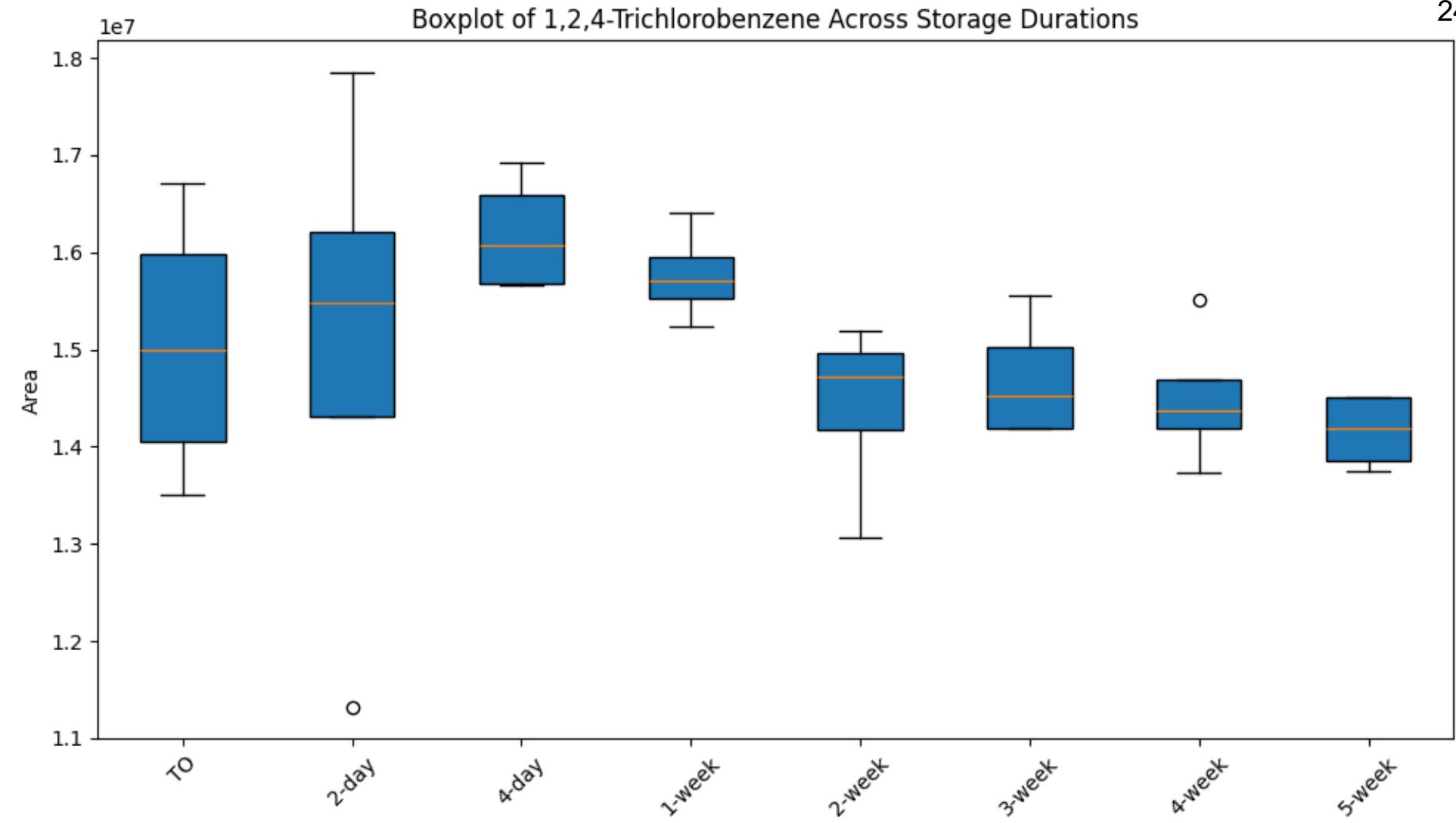
Storage Stability Trial

Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
T0	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31	32	33	34
35	36	37	38	39	40	41

04 STORAGE STABILITY TRIAL

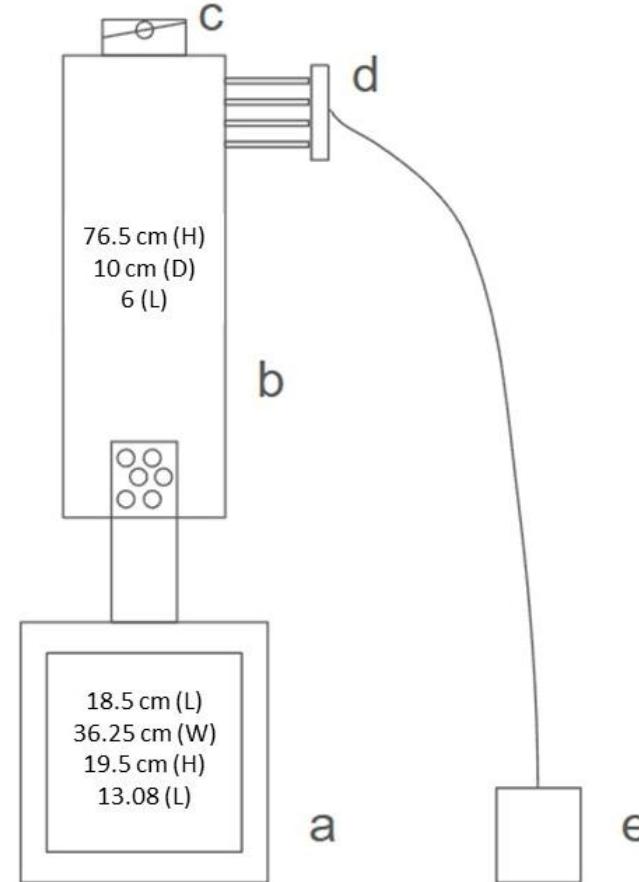


Boxplot of 1,2,4-Trichlorobenzene Across Storage Durations

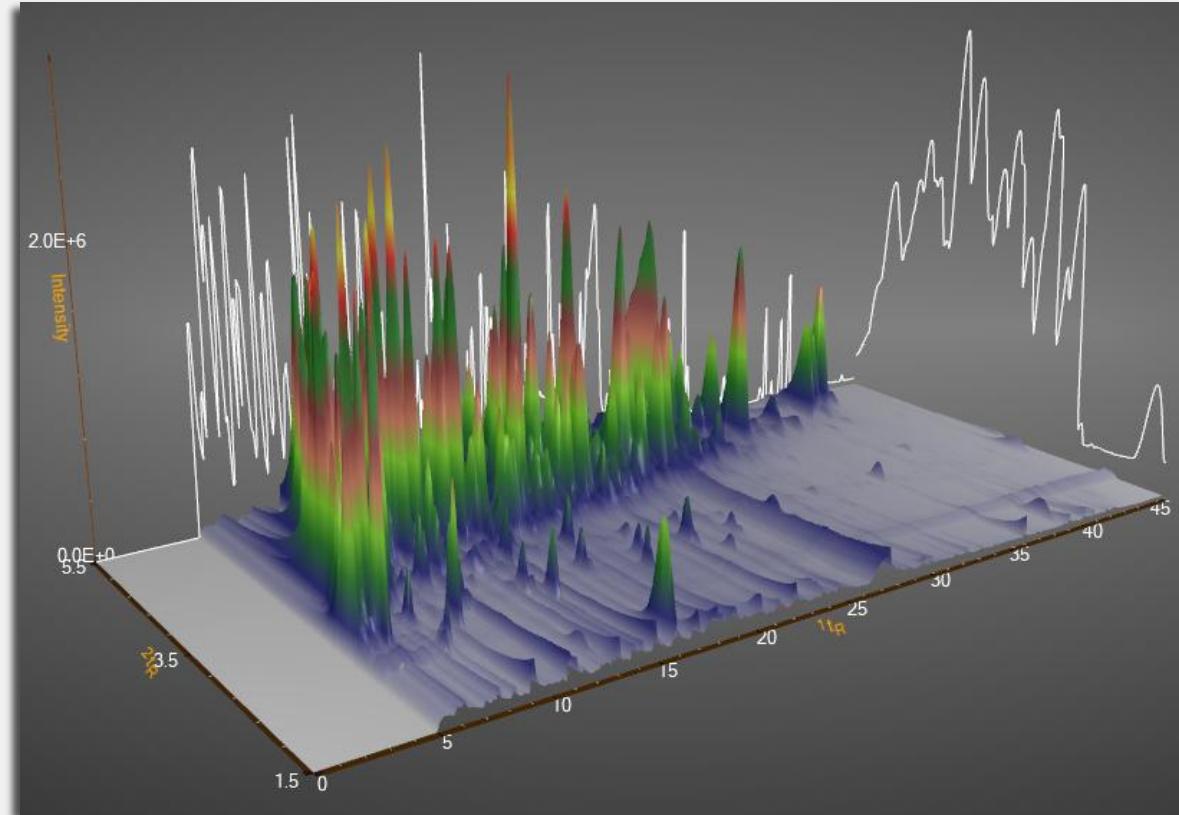


Method Validation

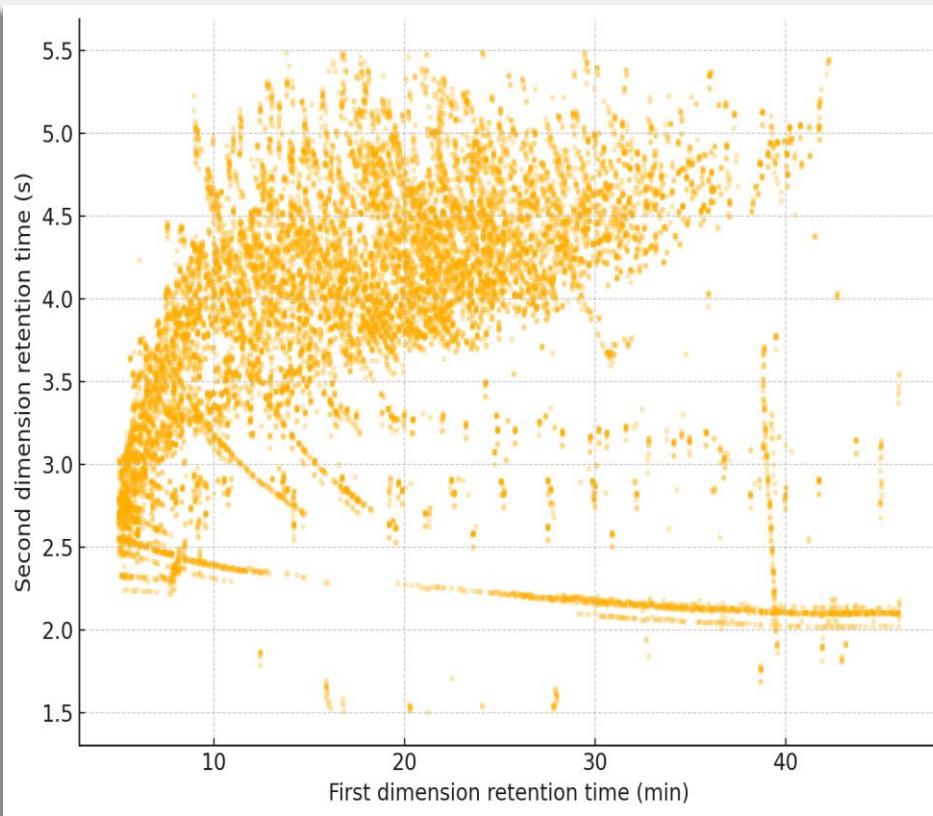
- 150g of white spruce (*Picea glauca*) was combusted
- One litre of emitted smoke was sampled at a flow rate of 100 mL/min
- Samples were analysed on a TD-GCxGC-ToFMS



GCxGC Chromatogram of Smoke Emissions



Smoke Emissions Results



- 1606 peaks per sample
- 78% percent of peaks ranged from C6 to C14, with an average secondary retention time of 4 ± 0.74
- 19 of the 41 standard compounds were identified (all PAHs & BTEX compounds)
- Average concentration of $4.56 \mu\text{g/ml} \pm 3.44$

Summary

- Concentration dependent variations in sorbent tube selection
- Reduction of method parameters
- Stable storage up to 35 days
- Multibed tubes proved very effective at retaining smoke emissions
- Significant advantages from the use of GCxGC



Acknowledgements

- Gwen O'Sullivan / Dena McMartin
- My supervisory committee: Paul Hayes, Court Sandau, Stephanie Schneider
- Special thanks to Kevin Hayes
- Thank you to the organizing committee

16TH Multidimensional
Chromatography
Workshop



Questions?